Benefits from the Rigorous Mass Transfer Rate Approach to Modelling Acid Gas Absorption Using Mixed Amines

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Abstract

The solution of absorption and distillation problems has traditionally used the equilibrium stage concept, in which the bulk vapor and liquid phases are assumed to be in equilibrium. Tray efficiency is the empirical parameter used to relate this model to the actual equipment.

In recent years, interest has grown in a more fundamental and rigorous method - the "Mass Transfer Rate" approach in which mechanical, chemical and thermodynamic equilibrium are assumed to exist only at the fluid interface. Rates of heat transfer and component mass transfer are determined taking into account the mass and thermal diffusion resistances as well as any chemical reactions taking place in the liquid and vapor phases. Clearly, the increased rigor of the Mass Transfer Rate method is only achieved at the expense of providing or predicting additional physical and transport properties as well as heat and mass transfer coefficients. However, there has been hitherto relatively little published on the practical benefits of applying this more fundamental approach to separation modelling.

Amine treating of natural gas to remove acid species CO_2 and H_2S is an important industrial application of absorption technology. Unfortunately, significant differences in both the equilibrium and the kinetic effects for H_2S and CO_2 can make accurate design and modelling by traditional methods difficult. Furthermore, the magnitude of these effects varies substantially from primary to secondary to tertiary amines. One positive consequence of these effects is the potential to use a blend of amines (usually two), which is tailored to obtain the degree of separation while maintaining minimum regeneration energy needs. Such an optimization of both the amine blend and the detailed equipment configuration can only be realistically performed with the help of a rigorous Mass Transfer Rate approach to the calculations. This paper describes the technical issues involved in using the Mass Transfer Rate method for distillation and absorption design and modelling and compares performance predictions using this method with actual gas sweetening plant operating data.

Introduction

Design and specification of absorption and distillation processes almost always involves application of commercial or proprietary models of separation process equipment. Using today's technology, that separation model is generally based upon the equilibrium stage model. In the equilibrium stage model, vapor and liquid are assumed to enter a tray or cross section of packing in a column, exchange matter and energy and leave in equilibrium with each other. However, columns rarely, if ever, operate at equilibrium. In fact, distillation and absorption are, by their nature, non-equilibrium processes: mass and energy are transferred across the fluid interface at rates which depend upon the extent to which the phases are **NOT** in equilibrium with each other. Historically, this departure from equilibrium conditions has led to the use of efficiencies. Efficiencies are meant to compensate for the deviation of actual column operation from the equilibrium assumed in the column model.

It is possible to look at the processes occurring in trayed and packed columns with a higher degree of rigor. Consider a stage model where vapor and liquid enter a tray and material and energy transfer between the two fluids through the interface between those fluids. Each phase provides resistance to that transfer which can be modelled using a Fickian type rate expression. In this "Mass Transfer Rate" model, it will be assumed that equilibrium exists only at the fluid interface. This interface is a singular surface which provides no resistance to mass or heat transfer and does not accumulate energy or matter. The resistance to mass transfer is limited to a thin film on each side of the fluid interface. Mass and heat transfer through this region can be modelled using the film theory of heat and mass transfer. Chemical reaction may occur in either or both of the two fluid phases.

Using the nomenclature of Krishnamurthy and Taylor [], the equations describing this model of separation processes are termed the **MERQ** equations. That is

> ° **M**aterial balance equations
> ° **E**nergy balance equations
> ° **R**ate equations
> ° e**Q**uilibrium relations

The model uses detailed information about the column construction and characteristics along with fluid composition, flow and physical property information determined during the simulation of the separation process to calculate mass transfer coefficients for each component in each fluid phase, heat transfer coefficients, interfacial area available for material and energy transfer, phase equilibrium ratios at the interface and column hydrodynamic parameters such as degree of flooding and pressure drop. When chemical reactions are occurring, the model is capable of describing the effect the reactions have on mass and heat transfer rates. Complete descriptions of the "Mass Transfer Rate" or "Non-equilibrium Stage" Model can be found in Krishnamurthy et al. [] and Sivasubramanian [].

Amine Based Gas Treating

Removal of H2S and CO2 from natural gas streams is an important application of chemically reactive solvents in absorption practice. There are often limits placed upon the levels of H2S and CO2 which may be in gas streams. These restrictions may be due to economic considerations such as reducing the level of corrosion of gas pipelines, to environmental regulations such as limiting the amount of sulfur released during combustion of the gas or to consumer requirements such as

minimum gas heating values. Unfortunately, both H2S and CO2 tend to have low physical solubilities in most acceptable (physical) solvents. To compensate for this, two general approaches are available. The first approach is to operate under conditions where physical solubility is enhanced - e.g. high pressure and low temperature, the second is to use a solvent which enhances the acid gas solubility by reacting with it - providing a sink for the acid gases.

Among the chemically reactive solvents is the commercially important family of alkanolamines. These solvents can be thought of as substituted ammonia molecules. The type of alkanolamine is determined by the number of substitutions on the nitrogen atom. For example, if one hydrogen atom on the nitrogen is replaced with a functional group, the molecule is termed a primary amine. If two hydrogens are replaced the molecule is a secondary amine, and if all three hydrogens are replaced, it is a tertiary amine. Example of primary amines are monoethanolamine (MEA) and di-glycolamine (DGA); diethanolamine (DEA) and di-iospropanolamine (DIPA) are examples of secondary amines, while methyl-diethanolamine (MDEA) and triethanolamine (TEA) are examples of tertiary amines.

The most important single difference between primary or secondary amines and tertiary amines is that tertiary amines do not directly react with CO2 to form carbamates. At most, they catalyze the hydrolysis of CO2 to bicarbonate. This fact leads to varied applications of the classes of amines. When deep removal of CO2 is required, primary or secondary amines such as MEA and DEA are typically applied. On the other hand, when CO2 concentrations are already within or near tolerance, tertiary amines can selectively remove H2S while picking up a minimum of CO2.

This selectivity arises from two sources. First, MDEA is **thermodynamically selective** for H2S removal. That is if we allow a mixture of equal moles of H2S and CO2 to sit over an aqueous solution of MDEA for a very long period of time, more of the H2S will be absorbed than CO2. This can be seen by examining the data of Lal, Otto and Mather []. Furthermore, MDEA is **kinetically selective** for the removal of H2S. That is if we plot the amount of H2S and CO2 in the liquid phases of the system described above, we will see that initially far more H2S will be absorbed than CO2. In fact, the amount of H2S absorbed at a given intermediate time may be greater than the final equilibrium concentration it achieves. As the CO2 is absorbed, it may replace some of the H2S and cause its desorption. Thus a competition between kinetic and thermodynamic effects can arise.

To a degree, the competition between chemical kinetics and thermodynamics allows one to exercise some control over the selectivity of MDEA towards hydrogen sulfide over carbon dioxide by adjusting the gas-liquid contact time. This can be done through appropriate choice of tower hydraulics including liquid depths on trays, solvent circulation rates, packing versus trays and so on. In fact, the very short liquid residence times in packed towers recommends the use of packed equipment for increased selectivity when these packed columns are designed using reliable methods. Higee promises to give degrees of selectivity well beyond what can be reached using conventional technology (Bucklin et al.[]). However, in many applications one finds that MDEA is too selective, i.e., it allows too much carbon dioxide to slip through the absorber, while diethanolamine (DEA) and monoethanolamine (MEA) are not selective enough. Lack of sufficient selectivity causes too much carbon dioxide to be removed and pushes up solvent regeneration costs. The best solvent is one with exactly the right selectivity. This can be produced by blending a primary or secondary amine with a tertiary amine such as MDEA in just the right proportions.

Another advantage of tertiary amines is the relatively weak bonding that occurs with CO2. This means that regeneration to remove CO2 from MDEA is more economical than in the primary and secondary amines.

The Rate Approach to Column Modelling

Traditionally, all tower calculations produce either the number of equilibrium stages needed to perform a specified separation or the separation achieved by a specified number of ideal trays. The translation from real trays to equilibrium stages and back again depends on tray efficiency information.

Material Balance

Equilibrium stage methods apply component and energy balance calculations around each complete ideal stage in a tower. In contrast, Mass Transfer Rate based modles such as GasPlant and GasPlant-Plus consider component and energy balances around each phase present on every real stage of the column (or, in the case of packed towers, in each horizontal slice of the tower). The individual phase balances are linked by the requirements that (i) the mass transfer rate of each chemical component and energy transfer rate from one phase must equal the respective transfer rate into the other and (ii) the phases are in mechanical, thermal and chemical equilibrium at the interface between them. There is no requirement that the bulk phases themselves be in equilibrium; in fact, departures from equilibrium are required for mass transfer (i.e., for a separation) to take place.

Mass and Energy Transfer Rates

Mass and energy are transferred from one phase to another at rates that depend on individual film coefficients for mass and heat transfer and on concentration and temperature driving forces for the transfer. Both the gas and liquid phases are important in determining the overall transfer rates because both phases offer resistance to transfer. This approach is completely analogous to the one used in determining heat transfer rates in heat exchangers. There, one uses correlations for shell-side and tube-side heat transfer coefficients and logarithmic mean temperature differences to calculate heat transfer.

Mass-transfer-coefficient correlations are available for various types of trays; for dumped packing of various sizes, materials and styles; and for certain structured packings. These coefficients depend on physical and transport properties, flow rates, temperature, pressure and type of equipment, including such details as the packing type, size, material and number of redistributors and the tray type and its construction details. These coefficients are then used with the differences in chemical potential in each film to determine the rates of mass transfer in the separation equipment.

Additionally, energy is transferred between the contacting phases. Two phenomena contribute to the energy transfer; conductive transfer due to temperature gradients and convective transfer of energy within the transferring molecules. As was the case with the phase equilibrium, thermal equilibrium is assumed to exist only at the fluid interface. The bulk vapor and liquid may differ significantly in temperature. This is commonly observed at the bottom of absorption towers and on the feed tray of the regenerator. The difference in temperature of the vapor and liquid exiting the bottom tray of an MEA or DGA contactor can be 80°F or more.
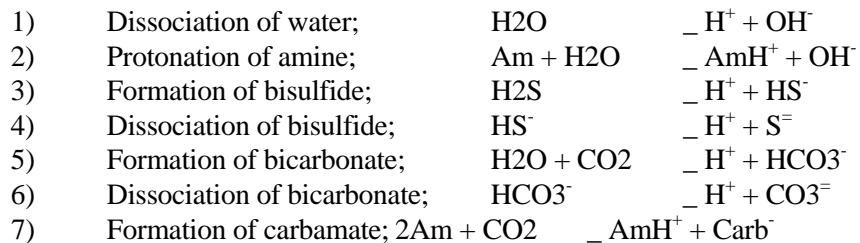
Phase Equilibrium

Phase equilibrium plays an important a role in rate models just as it does in equilibrium stage calculations. In a rate model, phase equilibrium is assumed at the fluid-fluid interface, not between the bulk phases leaving a tray or packed section. Thus, phase equilibrium is one of the key factors in setting driving forces for mass transfer and, therefore, in determining the separation that is actually achieved on a real tray or within an actual cross section of packing. The liquid-phase activity coefficient model used within GasPlant and GasPlant-Plus is based on the extended Debye-Huckel model of Edwards, Newman and Prausnitz (1975) as described by Deshmukh and Mather (1981). Because the model is thermodynamically sound, it has been possible to extend it to mixed amine systems. These extensions have been described in some detail by Chakravarty, Phukan and Weiland (1985) and Vickery and Weiland (1986, 1987). Predictions of the thermodynamic model have been checked against limited experimental data.

Reaction Effects & Enhancement Factors

Liquid-phase chemical reactions always increase mass transfer rates. Reaction effects are usually expressed through enhancement factors. Unlike tray efficiencies and HETPs, enhancement factors are not empirical constants to correct for the effects of chemical reaction. They are very well defined parameters that are calculated from the knowledge of the chemical kinetics, the reaction stoichiometry, liquid composition and a few physical and transport properties of the components in the liquid. Enhancement factors depend, therefore, on such parameters as temperature, amine concentrations, acid gas loadings, kinetic constants and so on. Reaction models that correctly account for the way that two amines interact with each other during the process of absorbing the acid gases are used for blended amines. These models are not empirical; they are based on knowledge of the actual kinetics involved.

The major reactions which occur within the H2S - CO2 - alkanolamine system are:

$$
\begin{array}{llll}
1) & \text{Dissociation of water;} & H2O & \_\ H^+ + OH^- \\
2) & \text{Protonation of amine;} & Am + H2O & \_\ AmH^+ + OH^- \\
3) & \text{Formation of bisulfide;} & H2S & \_\ H^+ + HS^- \\
4) & \text{Dissociation of bisulfide;} & HS^- & \_\ H^+ + S^= \\
5) & \text{Formation of bicarbonate;} & H2O + CO2 & \_\ H^+ + HCO3^- \\
6) & \text{Dissociation of bicarbonate;} & HCO3^- & \_\ H^+ + CO3^= \\
7) & \text{Formation of carbamate;} & 2Am + CO2 & \_\ AmH^+ + Carb^-
\end{array}
$$

It is reaction (7), the formation of carbamate, which occurs only with primary and secondary amines.

Reactions (1), (2), (3), (4) and (6) involve only the transfer of a proton are much faster than reactions (5) and (7). In general, these reactions can be assumed to have achieved equilibrium in the bulk liquid phase. The formation of the carbamate is a fast reaction and also tends to achieve equilibrium in the bulk liquid. Thus in each of these cases, the resistance to mass transfer lies primarily in the vapor film. Absorption under these conditions is said to be vapor phase controlled.

However, reaction (5) is a slow reaction. For tertiary amine systems, it is generally this reaction which determines the transfer rate of the CO2. For this reason, CO2 absorption in tertiary amines is generally liquid phase controlled.

Example 1. - Amoco's Wasson CO2 Recovery Plant

Amoco's Wasson CO2 removal Plant is a part of their gas treating facilities in Wasson, Texas. CO2 is used for tertiary recovery in fields of West Texas. The Gas from the fields is brought to the plant, compressed and H2S is removed using an iron chelate process. The remaining gas is dried by contacting it with a TEG solution. The dry gas then proceeds to a Ryan-Holmes column. The bottoms stream forms an NGL product and the resulting gas which is upwards of 50% CO2 is sent to an MDEA loop for bulk CO2 removal. The recovered CO2 is used for reinjection into the fields.

The bulk CO2 removal system employs MDEA to remove the large amounts of CO2 from the gas stream. The lower regeneration requirements of MDEA as opposed to MEA or DEA means that the typical amine stripper can be replaced with a two stage flash process. The pressure drop within the flashes is sufficient to regenerate the amine solution.

The absorption column is a 60 foot packed tower, 9 feet in diameter. Two redistributors are located in the column, one at 20 feet and one at 40 feet. The packing is a 1.5 inch plastic ring. Inlet pressure of the CO2 rich gas is approximately 800 psi. Typical feed stream conditions to the absorber are given in Table 1.

	Sour Gas	Lean Solvent
Temperature	73' F	133' F
Pressure	814 psia	820 psia
Composition		
Nitrogen	2.28 %	
Carbon Dioxide	51.80 %	0.08 loading
Methane	36.96 %	
Ethane	8.96 %	
MDEA		32 wtpct

Table 1. - Typical Feed Conditions for Wasson MDEA Absorber

The lean solvent is already fairly rich in CO2. Thus the exiting gas is not "sweet" in the traditional sense. Typical sweet gas CO2 content is 5% CO2. The column operates so that it is equilibrium limited at the bottom of the column. The idea is to bring the rich CO2 loading up until it is in equilibrium with the entering sour gas. In order to achieve this, the column must have many equivalents of a theoretical plate. Also, the higher the column operating pressure the greater the CO2 pickup. Thus low pressure drop and a large total liquid holdup are desired. These considerations lend themselves well to packed column operation.

Since the column is equilibrium limited, the major benefits of the rate model for this application are to determine the minimum amount of packing required to achieve equilibrium, the ability to look at column profiles and being able to model a packed column rather than using HETP and/or

efficiencies. An equilibrium stage model will do almost as well predicting rich solvent and sweet gas compositions. However, due to the assumption of equal vapor and liquid temperatures in a cross sectional area of packing, the equilibrium model may miscalculate the exiting temperatures.

If one were to try to optimize this process in some way, there are three variables which strongly influence the CO2 pickup in the absorber. The first is the exit pressure of the second stage flash; the second variable is the temperature of the lean solvent stream and the last is the solvent capacity.

The two flashes act as the "regenerator" for the process. The first flash acts to remove a significant amount of the CO2 but it is the second flash that finally determines the amount of CO2 released. Both flashes yield a flash gas of approximately 93% CO2 so the strongest influence of the solvent loading is the flash pressure. The lower the pressure, the lower the backpressure on CO2 over the solution and, hence, the lower the CO2 load in the solvent. Doubling the flash pressure can significantly increase the solvent loading.

The second factor, the lean solvent temperature, affects the results by shifting the bicarbonate and carbonate equilibrium points and Henry's constant. For example, the following data for the Henry's constant of CO2 in pure water and the reaction dissociation constants for the bicarbonate and carbonate formation reactions are taken from Edwards et al. [].

$$\ln(H_{CO2}) = -6789.04/T - 11.4519*\ln(T) - 0.010454*T + 94.491$$

$$\ln(K_5) = -12092.1/T - 36.7816*\ln(T) + 235.482$$

$$\ln(K_6) = -12431.7/T - 35.4819*\ln(T) + 220.067$$

where T is Kelvin.

This gives $\ln(K_5)$ a maximum at 132°F, $\ln(K_6)$ a maximum at 171°F and $\ln(H_{CO2})$ a maximum at 308°F. These factors interact and it is not immediately obvious how inlet lean solvent temperature will affect equilibrium.

The final factor, the solvent capacity is determined by the circulation rate and the solvent strength. Increasing either will give a greater solvent capacity and allow increased CO2 pickup. Increased circulation rate will also affect the energy balance by increasing the amount capacity of the solvent to accept heat.

The effect of changing each of these paraameters on sweet gas CO2 content for a given circulation rate and sour gas feed is shown in Table 2. Note that contrary to what may have been expected, the CO2 pickup increases as the lean solvent temperature increases. Since the abosrber achieves equilibrium, the increase is not due to faster reaction kinetics but rather to the shift in equilibrium conditions for reactions 5 and 6. This shift is enough to compensate for the reduced solubility of the gases in the solvent. For other operating conditions, this may not be the case.

Solvent Strength (wtpct)	Lean Solvent Temperature (°F)	2nd Stage Flash Pressure (psia)	Sweet Gas CO2 (Mole pct.)
30	133	33	22.8
30	133	20	7.8
31	133	33	21.8
31	133	20	5.9
32	133	33	20.9
32	133	20	3.5
32	128	33	22.5
32	128	20	7.1
32	138	33	18.9
32	138	20	3.3

Table 2. - Effect of Process Operating Parameters on Sweet Gas CO2 Content

Example 2. - Marathon's Cody Wyoming Plant

During the 1987 Laurance Reid Gas conditioning conference, Joseph Harbison of Marathon Oil Company and Glenn Handwerk presented operating data on a gasplant Amoco was operating in Cody, Wyoming. They had a selective gas treating system which normally ran with 25-30% MDEA. Somehow, the system had become contaminated with DEA. While this had an adverse effect on the selectivity of the process, it provided an excellent source of operating data for the mixed amine system.

The detailed contactor balance from June 21, 1986 shows the following sour and sweet gas component mole fractions for the sour and sweet gas streams on a dry basis:

Component	Sour Gas	Sweet Gas
N2	1.145	1.303
CO2	19.202	14.383
H2S	2.078	0.022
C1	58.891	64.489
C2	8.551	9.472
C3	4.938	5.259
i-C4	1.163	1.324
n-C4	2.098	2.408
i-C5	0.765	0.905
n-C5	0.634	0.771
C6+	0.535	0.664

Table 3. - Cody Wyoming Contactor Gas Stream Compositions - 6/21/86

While the corresponding rich and lean amine compositons do not quite close a material balance, they are good enough to show the affect of the column operating parameters on process conditions. Among the parameters which will be examined are the tray active area, weir height, number of functioning trays and solvent composition.

Figure 1 shows the affect of relative DEA and MDEA solvent strength on the sweet gas composition. The simulations were run using a total solvent strength of 26 wtpct. The most obvious feature of the figure is that as DEA strength increases, CO2 content of the sweet gas decreases but H2S content increases. This is due to competion between reaction kinetics and equilibrium as described earlier. The lean solvent entering the column encounters a gas which is fairly low in H2S content (< 1000 ppm) but rich in CO2 (>14%). The fast kinetics of the H2S reactions with both DEA and MDEA allow the H2S to be absorbed just as fast as it can diffuse through the gas side film. On the other hand, the rate at which the CO2 can be absorbed is controlled not only by the gas

phase diffusion, but by a combination of the kinetics of the slower bicarbonate formation reaction and the amount of free DEA available to react with CO2 in the faster carbamate formation reaction. As the DEA strength increases, the capacity for carbamate formation increases and it is possible to remove CO2 at a faster rate.

This increased rate of CO2 removal has a negative impact on the H2S pickup. Since the solvent was able to pickup more of H2S initially, it achieved a relatively high loading of H2S quickly. Then as more CO2 is picked up, there is greater competition between the CO2 and H2S to remain in solution. Eventually, some of the H2S actually desorbs and returns to the vapor phase. This shows up as a maximum in the H2S composition in both the vapor and liquid. In essence, an internal recycle of H2S develops. In the case of the Cody plant, enterring sour gas H2S content is 2.078% on a dry basis or 2.066% on a wet basis. The internal maximum H2S content is 2.18% two trays above the bottom tray. In the same way, the maximum H2S loading in the solvent occurs 3 trays above the bottom tray and is a value of 0.167 mole H2S / mole amine compared to a rich loading of 0.156 mol/mol. This internal recirculation reduces the number of trays available for H2S removal. With no DEA present, the CO2 pickup drops and the internal H2S recirculation is not observed.

Similar affects can be seen if straight MDEA is run through the same column configuration but with a varying number of trays. Figure 2 shows how the number of trays affects the H2S and CO2 content in the sweet gas. With 8 trays, no internal H2S recirculation is noted. However, with 18 trays, the H2S content of the gas reaches a maximum of 3.32 mole percent - a 60 percent increase over the inlet composition. Note that to reach the same H2S content as the 10 tray mixed amine absorber requires 16+ trays. The same level of CO2 removal as seen in the mixed amine example can be achieved with approximately 12 trays.

The amount of CO2 pickup can also be controlled by adjusting the active area of the tray or the weir height. Reducing the active tray area or lowering the weir height has the effect of reducing the "volume" of the tray and, in turn, the residence time of the liquid on the tray. This decreases the degree to which the bicarbonate formation reaction goes to completion and the overall CO2 pickup. Conversely, increasing active area and/or weir height increases residence time and CO2 pickup and reduces H2S pickup. The effect of the weir height and active area on the dry sweet gas content for the mixed amine system are shown in Tables 4 and 5.

Active Area (ft^2)	H2S (ppm)	CO2 (mole %)
4.88	466	14.03
5.135	496	14.00
5.39	535	13.97

Table 4. - Affect of Active Tray Area on Sweet Gas Composition

Weir Height (Inches)	H2S (ppm)	CO2 (mole %)
1.75	364	14.13
2.00	496	14.00
2.25	666	13.89

Table 5. - Affect of Weir Height on Sweet Gas Composition

Conclusions

The use of rate-based technology in the simulation of separation processes such as absorption and distillation has proven itself to be technically superior to the traditional quilibrium stage model. This rate-based technology is employed in the GasPlant and GasPlant-Plus programs for the simulation of alkanolamine based sour gas treating. The programs are useful not only in the design stage of plant operation where they can be used to determine the ability of a given column to meet operating requirements, to evaluate alternate types of equipment for separation and to analyze the effect of process and equipment parameters on plant operating conditions; but also in the maintenance of those plants. Specifications allow the determination of tray diameters based upon desired flooding as well as direct specification of diameter. This sizing ability removes the necessity of iterating between a simulation tool and tower sizing programs.

Plant profiles can be compared to model profiles to locate discrepancies in operation. For example if a tray has lost active area due to a physical obstruction or if a solvent stream has been contaminated by another alkanolamine. The model can also be used to evaluate possible alternatives for correcting the problem.

The ability to evaluate process conditions before actually building the plant appears to be especially important in case where selective treatment is required. Overdesign is not a viable option in these cases. We have shown that for selective gas treating too many trays, too large a tray or too high a weir can all increase CO2 pickup at the cost of lost H2S capacity. The results can be off spec gas products or unacceptably dilute sulfur plant feed.