

CO₂ Capture by Absorption with Potassium Carbonate

Quarterly Progress Report

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Abstract

The objective of this work is to improve the process for CO₂ capture by alkanolamine absorption/stripping by developing an alternative solvent, aqueous K₂CO₃ promoted by piperazine. Stripper modeling suggests the energy requirement with a simple stripper will be about the same for 5 m K⁺/2.5 m PZ and 7 m MEA. Modeling with a generic solvent shows that the optimum heat of CO₂ desorption to minimize heat duty lies between 15 and 25 kcal/gmol. On-line pH and density measurements are effective indicators of loading and total alkalinity for the K⁺/PZ solvent. The baseline pilot plant campaign with 30% MEA has been started.

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Introduction

The objective of this work is to improve the process for CO₂ capture by alkanolamine absorption/stripping by developing an alternative solvent, aqueous K₂CO₃ promoted by piperazine. This work expands on parallel bench-scale work with system modeling and pilot plant measurements to demonstrate and quantify the solvent process concepts.

Gary Rochelle is supervising the bench-scale and modeling work; Frank Seibert is supervising the pilot plant. Four graduate students (Babatunde Oyekan, Ross Dugas, Jennifer Lu, John McLees) have received support during this quarter for direct effort on the scope of this contract. Two students supported by other funding have made contributions this quarter to the scope of this project (Eric Chen – EPA Star Fellowship; Babatunde Oyekan – Trimeric).

Experimental

Subtask 2.1 describes equipment modifications that have been made to the pilot plant.

Subtask 2.5 describes the analytical methods used in the pilot plant for the second campaign.

Subtask 2.7 describes the detailed modifications to prepare for the baseline campaign with MEA.

Results and Discussion

Progress has been made on six subtasks in this quarter:

Subtask 1.1 – Modify Vapor-Liquid Equilibrium (VLE) Model

The M.S. thesis by Marcus Hilliard has been submitted as a separate topical report on this completed work.

Subtask 1.2 – Modify Point Rate Model

The Ph.D. dissertation by Tim Cullinane has been submitted as a separate topical report on this completed work.

Subtask 1.3 – Develop Integrated Absorber/Stripper Model

The ACM (Aspen Custom Modeler) model was extended to mass transfer modeling for the 5m K⁺/2.5m PZ. The reboiler duty was minimized and the equivalent work for stripping calculated for 7m MEA and 5m K⁺/2.5m PZ. Generic solvents were modelled and the optimum heat of desorption that minimizes reboiler duty was found to depend on the rich CO₂ partial pressure.

Using the thermodynamics set developed by Hilliard in the absorber model, the addition of oxygen and nitrogen as Henry's components caused convergence problems, until the PURE-12 databank was added.

A FORTRAN subroutine for modeling the piperazine kinetics was developed for use with the absorber model in Aspen Plus[®].

An interfacial area subroutine was developed for the absorber model to reflect the dependence of wetted area on liquid and vapor flow rates. A simple regression was used for three different packings, CMR #2, IMTP-40, and Flexipac 1Y.

Subtask 2.1 – Pilot Plant Test Plan

A detailed test plan was submitted and approved for the third pilot plant campaign, the MEA base case.

Subtask 2.5 – Pilot Plant – Campaign 2

The data for CO₂ loading were correlated with the online pH measurement. However there are unresolved systematic discrepancies between loading analyses performed on two different instruments. The analytical data for total alkalinity were correlated with on-line solution density for Campaign 1, but there appear to be systematic deviations in this correlation for Campaign 2.

Subtask 2.7 – Pilot Plant – Campaign 3 – MEA Baseline

The baseline pilot plant campaign with 30 wt% MEA started in early March and will run through mid-April.

Conclusions

1. In a simple stripper, if 5 m K⁺/2.5 m PZ is able to achieve a rich equilibrium partial pressure of 5 kPa (because it has faster rates than 7 m MEA), it will have about the same steam requirement as 7 m MEA with a rich equilibrium partial pressure of 2.5 kPa.
2. The heat of CO₂ desorption giving the minimum heat duty for a generic solvent ranged from 15 to 25 kcal/gmol depending on the loading of the rich solution.
3. In the stripper, 23 meters of packing height will be equivalent to 10 stages of contacting with 40% Murphree efficiency.
4. Mass transfer modelling revealed that the stripper could be significantly limited by gas film mass transfer.
5. On-line pH measurements are a reliable indicator of CO₂ loading for the K⁺/PZ solvent.
6. On-line density measurements are a reliable indicator of total alkalinity for the K⁺/PZ solvent.

Future Work

We expect the following accomplishments in the next quarter:

Subtask 1.3 – Develop Integrated Absorber/Stripper Model

The mass transfer model for the stripper will be developed further and applied to simulate pilot plant performance. The ACM model will be incorporated with Aspen Plus® to take advantage of the extensive database of Aspen Plus and the other unit operations available.

The modified absorber model for K_2CO_3/PZ will be debugged.

Subtask 1.5 – Simulate Base Case Pilot

The absorber data from Campaigns 1 and 2 will be simulated with a rigorous differential equation model.

The stripper data from Campaigns 1 and 2 will be analyzed with the model developed in Aspen Custom Modeler.

Subtask 2.2 – Design Modifications, Order Equipment and Packing Materials

The following major pilot plant modifications will be completed before Campaign 4 with K^+/PZ :

- A new stainless-steel reboiler will be installed.
- The solvent preheat system will be upgraded by installing a new absorber feed cooler and converting the existing cooler to a lean/rich cross exchanger.
- The PVC absorber feed gas line will be replaced with stainless steel.

Subtask 2.5 – Pilot Plant – Campaign 2

Concentrated samples from Campaign 2 will be reanalyzed for total CO_2 loading. The samples will be covered with parafilm after they are diluted. The loading data will be reconciled with the on-line density and pH measurements.

The energy measurements for Campaign 2 will be evaluated.

Subtask 2.6 – Pilot Plant Campaign 3, Optimization of System Parameters

The final pilot plant campaign is now scheduled to begin in September 2005. Modifications for this campaign will be designed and installed in the next two quarters.

Subtask 2.7 – MEA Baseline

The third pilot plant campaign, the MEA base case, will be completed in mid-April. The absorber and stripper performance data will be compiled and analyzed.

Task 1 – Modeling Performance of Absorption/Stripping of CO₂ with Aqueous K₂CO₃ Promoted by Piperazine

Subtask 1.3 – Develop Integrated Absorber/Stripper Model – Aspen Custom Modeler for Stripper

by Babatunde Oyekan
(Supported by this contract)

Introduction

We have continued to develop the stripper submodel in Aspen Custom Modeler for the overall model of CO₂ absorption/stripping for 7m monoethanolamine (MEA), 5m K⁺ / 2.5m PZ and some generic solvents. This model divides the stripper into sections with Murphree efficiencies assigned to CO₂, water, and temperature. An expression with six adjustable constants is used to represent the VLE and heat of absorption/desorption for 7m monoethanolamine and 5m K⁺/2.5m PZ while a three-parameter expression approximates the equilibrium behavior of the generic solvents. Two process configurations (a simple stripper and a multipressure stripper) are simulated and the effect of varying the rich and lean [CO₂]_T, at a 5-10°C temperature approach on the equivalent work consumed by the process is calculated by this model. The optimum heat of desorption of the solvents that minimize reboiler duty varies from 26 kcal/gmol CO₂ at low rich partial pressures (0.28 kPa) to 15kcal/gmol CO₂ at rich partial pressures (10 kPa). Under typical operating pressures ~ 3-5 kPa the optimum is ~ 20-22 kcal/gmol CO₂ when the absorber is run at 40°C. Some mass transfer modelling was also done on IMTP #40 packing.

Experimental (Model Formulation)

Aspen Custom Modeler (ACM) Model

A model has been developed in Aspen Custom Modeler to simulate the stripper operation. The model was designed for a wide variety of solvents but has currently been applied to a 7m MEA and the generic solvents.

Modeling Assumptions

- The sections were assumed to be well mixed in the liquid and vapor phases.
- The reboiler was assumed to be in equilibrium.

The CO₂ vapor pressure (kPa) under stripper conditions for 7m monoethanolamine and 5m K⁺/2.5m PZ were are represented by the linear expression

$$\ln P = a + b * [\text{CO}_2]_T + \frac{c}{T} + d \frac{[\text{CO}_2]_T^2}{T^2} + e \frac{[\text{CO}_2]_T}{T^2} + f \frac{[\text{CO}_2]_T}{T} \quad (1)$$

while for the generic solvents, the equilibrium expression is given by

$$\ln P = a + b * [\text{CO}_2]_T + \frac{c}{T} \quad (2)$$

P = the equilibrium partial pressure of CO₂ in kPa

T = temperature in Kelvin

[CO₂]_T = total CO₂ concentration (m)

The adjustable constants (Table 1) were obtained by regressing the points for 7m MEA from equilibrium flashes in Aspen Plus[®] using the rigorous model developed by Freguia (2002) from data of Jou and Mather (1995).

Table 1. Adjustable Constants in VLE Expression for 7m MEA and 5m K⁺/2.5m PZ

	7m MEA	5m K ⁺ /2.5m PZ
A	35.12	-0.26
B	-6.43	0.15
C	-14281	-5306.48
D	-11148.5	-16995.5
E	-485777	-469758
F	4667.14	2808.15

The adjustable constants for the generic solvents are given in Table 2.

Table 2. Adjustable Constants for Generic Solvents at Different Average Heats of Desorption in the Stripper

	Average heat of desorption in stripper (kcal/gmol CO ₂)						
	15	20	22	25	27	35	40
A	8.924	16.477	19.50	24.031	27.052	39.137	46.69
B	3.069	3.069	3.069	3.069	3.069	3.069	3.069
C	-7549.07	-10065.4	-11072	-12581.8	-13588.3	-17614.5	-20130.9

The heat of absorption/desorption for 7m MEA and 5m K⁺/2.5m PZ are calculated by differentiating Equation (1) with respect to 1/T. This is given by the following:

$$-\frac{\Delta H}{R} = c + 2d \frac{[\text{CO}_2]_T^2}{T} + 2e \frac{[\text{CO}_2]_T}{T} + f[\text{CO}_2]_T \quad (3)$$

where ΔH represents the heat of absorption/desorption [=] kcal/gmol CO₂ and R is the Universal gas constant [=] cal/K-mol

The rich [CO₂]_T at specified rich P_{CO₂} (kPa) leaving the absorber at 60°C for MEA and the three generic solvents is shown in Table 2.

Table 3. Rich [CO₂]_T (m) at Absorber Conditions at 40 and 60°C

Solvent	Rich P _{CO₂} (kPa)	[CO ₂] _T (m)	
		60°C	40°C
7m MEA	1.25	2.73	3.43
	2.5	2.99	3.68
	5	3.26	3.94
	10	3.53	4.21
5m K ⁺ /2.5m PZ	1.25	4.49	5.05
	2.5	4.72	5.33
	5	4.97	5.61
	10	5.21	5.91

The heat of vaporisation of water, partial pressure of water, heat capacities of steam, CO₂ and the solvent (essentially water) were calculated from an equation derived from the DIPPR database.

The equilibrium partial pressure of CO₂ and water on each section were calculated from Equation (3)

$$E_{mv} = \frac{P_n - P_{n-1}}{P_n^* - P_{n-1}} \quad (4)$$

where E_{mv} is the Murphree plate efficiency defined in terms of partial pressures

P_n, P_{n-1} is the partial pressures of the component on sections n and $n-1$

P_n^* is the equilibrium partial pressure of the component leaving section n .

An efficiency of 40% and 100% were assigned to CO₂ and water. The model assumed a 100% efficiency with respect to heat transfer.

The equivalent work is a convenient way to quantify the heat requirement of the process. It constitutes the work lost from the turbine upstream of the power plant since the condensing steam used to run the reboiler is no longer available to generate electric power. Assuming the enthalpy difference between the feed and products is negligible compared to the heat input and cooling water at 313 K is used to remove heat in the condenser, the equivalent work, W_{eq} , consumed by the process is given by

$$W \text{ (kcal/gmol CO}_2\text{)} = Q \left[\frac{T_{cond} - T_o}{T_{cond}} \right] + W_{comp} \quad (5)$$

where Q is the reboiler duty in kcal/gmol CO₂, T_{cond} is the temperature of the condensing steam (temperature of reboiler plus 10K) in the shell of the reboiler and T_o is the temperature of the cooling water (313K). W_{comp} constitutes the adiabatic work of compression of the gas exiting the top of the stripper to 1000 kPa (an arbitrary pressure selected). For this analysis isentropic efficiency of the compressor was assumed to be 75%.

Results and Discussion

Predicted Stripper Performance

The stripper performance for a simple stripper operating at 160 kPa with five compression stages to compress the gas to 1000kPa with interfolding to 313K between the stages downstream of the stripper and a multipressure stripper operating at 500/280/160 kPa were simulated using the 7m monoethanolamine and 5m K⁺/2.5m PZ solvents.

Figures 1 and 2 show a comparison of the simple and multipressure stripper results for the 7m MEA and 5m K⁺/2.5m PZ solvents. The results shown are for lean concentrations that minimize the reboiler duty for a rich CO₂ concentration.

The results show that the reboiler duty can be reduced by a factor of 2 when the multipressure configuration is used relative to the simple stripper at the lower rich concentrations. At higher concentrations the reduction is of the order of a factor of 1.5.

At a fixed rich partial pressure is observed that the 7m MEA solution gives a lower reboiler duty than the 5m K⁺/2.5m PZ. The optimum capacity of the solution increased with the multipressure configuration.

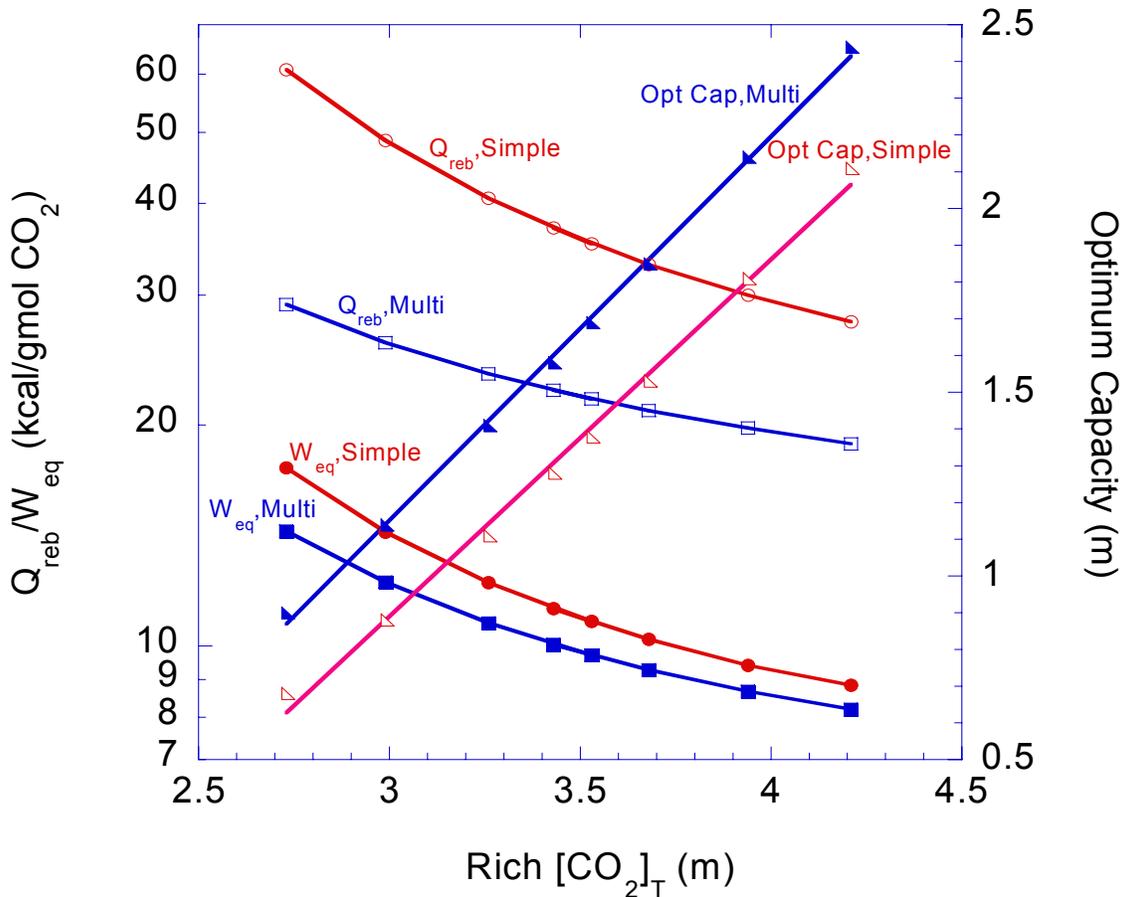


Figure 1. Stripper Performance for Simple and Multipressure Configurations using 7m MEA ($T_{app} = 10^{\circ}\text{C}$, $P_{final} = 1000$ kPa)

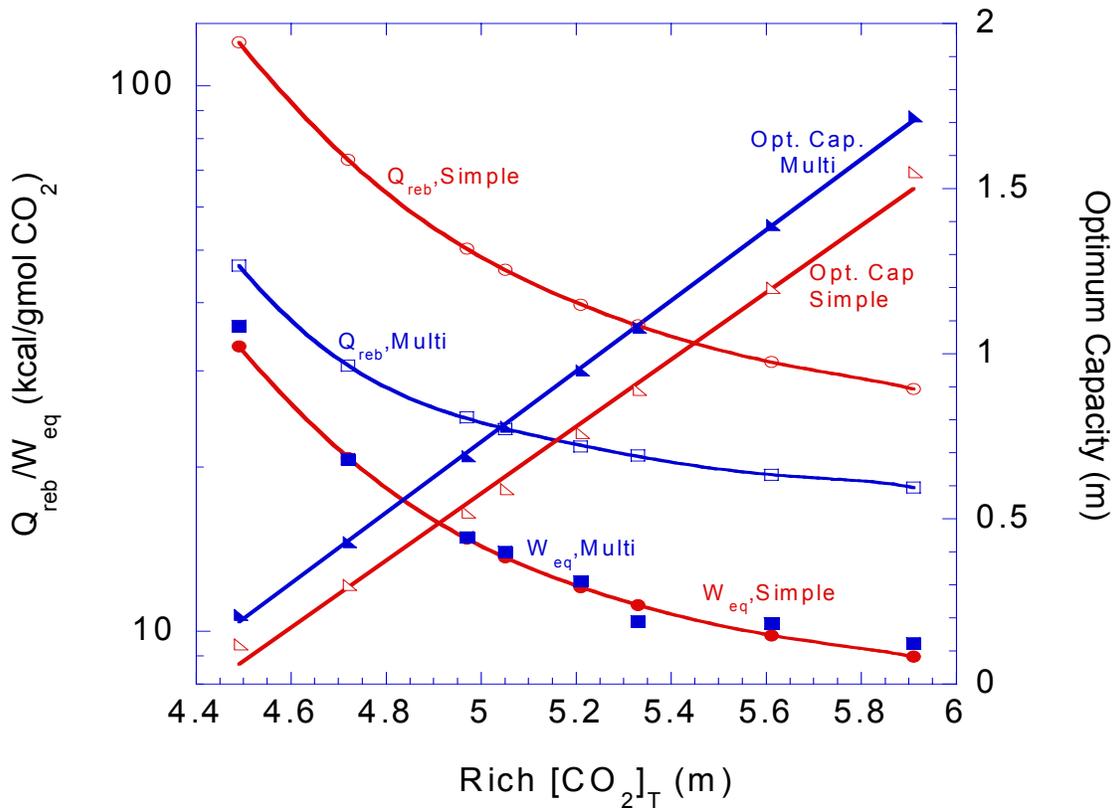


Figure 2. Stripper Performance for Simple and Multipressure Configurations using 5m K⁺/2.5m PZ (T_{app} = 10°C, P_{final} = 1000 kPa)

In Figure 2, we see that for the 5m K⁺/2.5m PZ solvent, the reboiler duty can be reduced by half but the equivalent work is not all that different from the simple stripper. The comparable equivalent work could be due to large volumes of water vapor being compressed in the integrated compressors.

The dependence of the reboiler duty on the temperature approach for 7m MEA and 5m K⁺/2.5m PZ solvent for rich partial pressures of CO₂ when the absorber is run at 60°C is shown in Figure 3. At lower partial pressure, MEA solvent requires about half of the reboiler duty required by 5m K⁺/2.5m PZ, but at high partial pressures, 5m K⁺/2.5m PZ is quite competitive and, since it has a higher reaction rate and could be run at a closer approach to saturation, could be attractive for high partial pressure CO₂.

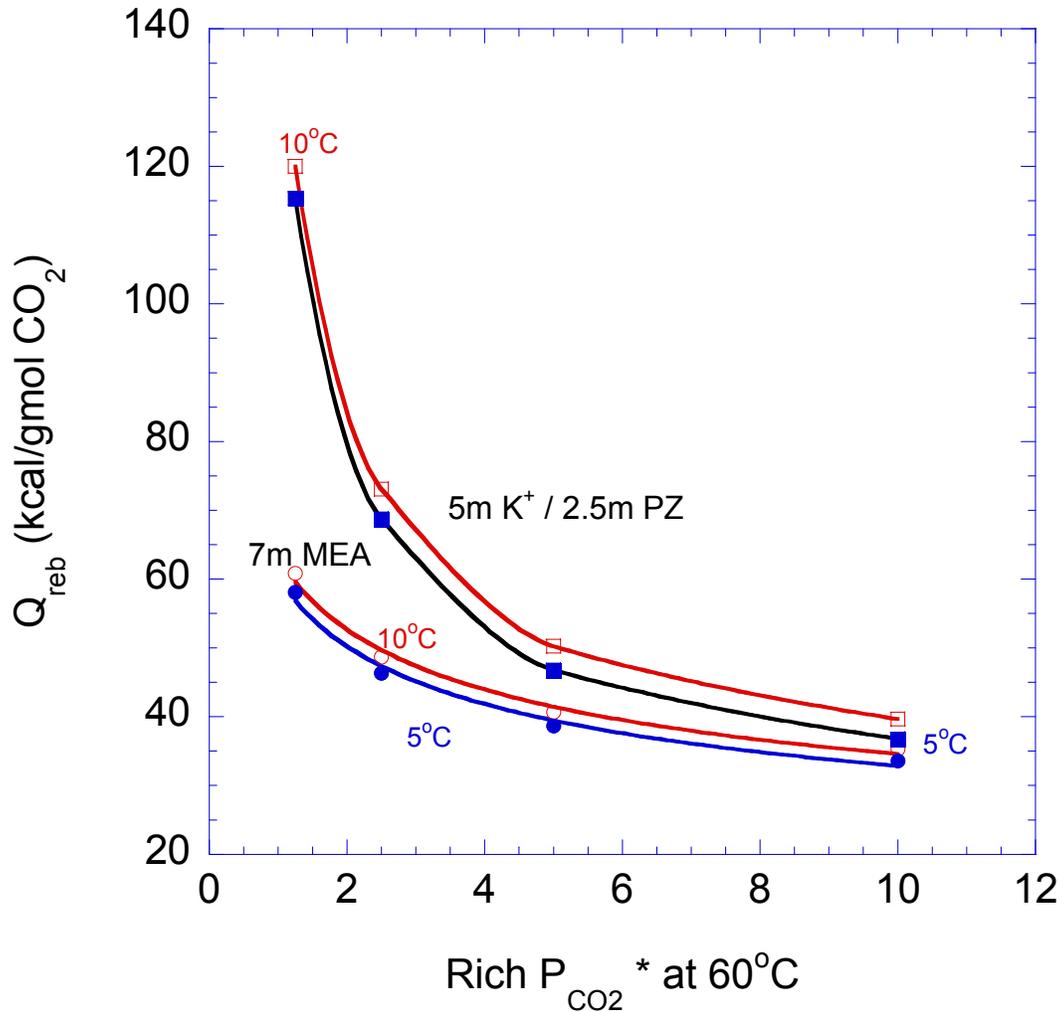


Figure 3. Temperature Effect on Reboiler Duty for Different Solvents

Different generic solvents were simulated to study the effect of using solvents with different properties on the reboiler duty. From the results obtained, the solvent minimum reboiler duty at different rich CO_2 partial pressures when the absorber is run at $40^\circ C$ was identified and is shown in Figure 4. The results show that at lower rich partial pressures, the optimum heat of desorption that minimizes reboiler duty is $26 \text{ kcal/gmol } CO_2$ at lower rich partial pressures and decreases to $22 \text{ kcal/gmol } CO_2$ at 2.5 kPa , $20 \text{ kcal/gmol } CO_2$ at 5 kPa and $15 \text{ kcal/gmol } CO_2$ at 10 kPa . This implies that the optimum heat of desorption of the solvent to minimize reboiler duty depends on the rich partial pressure of the CO_2 achieved in the absorber. At the practical range of rich partial pressures that we could expect from a coal-fired power plant ($2.5 - 5 \text{ kPa}$), the optimum heat of desorption of the solvents required is $20-22 \text{ kcal/gmol } CO_2$. At rich partial pressure representative of a closer approach to saturation, the $5 \text{ m K}^+ / 2.5 \text{ m PZ}$ could a better solvent. The fact that it is a faster solvent is an added advantage.

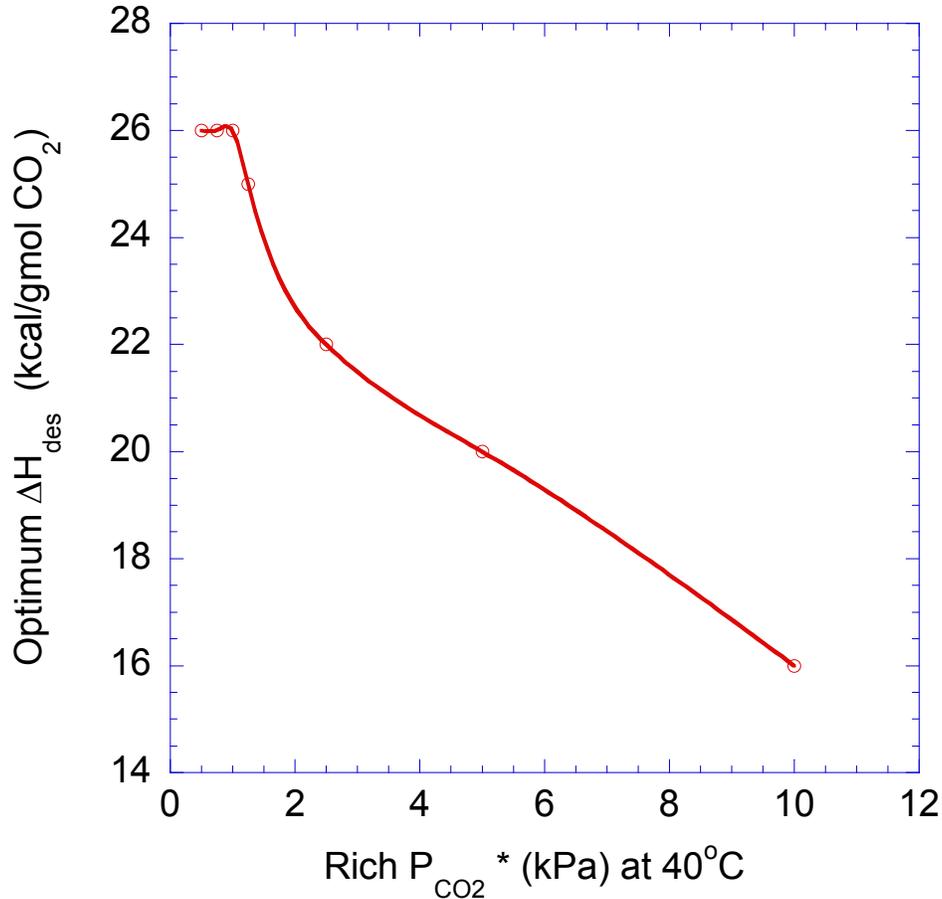


Figure 4. Optimum ΔH_{des} Dependence on Rich $P_{CO_2}^*$ (kPa) at 40°C

Some mass transfer studies were also performed on IMTP #40 packing. Mass transfer studies are essential to determine the height of packing required for a specific separation as well as determination of reaction mechanisms. At 17% flood, the area of the column obtained was 0.147 m², which is quite representative of the diameter of the pilot plant at the UT-SRP pilot plant.

The mass transfer model used was that originally developed by Bishnoi (2000) and modified for potassium carbonate/piperazine solution by Cullinane (2004).

The flux of CO₂ is given by the expression

$$N_{CO_2} = K_G (P_{CO_2}^* - P_{CO_2,b}) \quad (6)$$

where K_G represents the overall mass transfer coefficient based on the gas phase

$P_{CO_2,b}$ is the partial pressure of CO₂ in the gas phase

$P_{CO_2}^*$ is the partial pressure of CO₂ in equilibrium with the liquid phase

The overall mass transfer coefficient is the sum of the gas phase and liquid phase components.

$$\frac{1}{K_G} = \frac{1}{k_g} + \frac{1}{k_g'} \quad (7)$$

k_g is the gas phase mass transfer coefficient while k_g' is the liquid phase mass transfer coefficient based on a gas phase driving force.

k_g is obtained from Onda (1968) and Wilson (2004); k_g' is obtained from Cullinane (2004).

When experiments are performed, the rate of CO₂ is measured. This rate is a product of the flux and the wetted area of contact between the gas and liquid phases. The rate is given as

$$\text{Rate} = K_G A (P_{\text{CO}_2}^* - P_{\text{CO}_2\text{b}}) \quad (8)$$

where A is the wetted area of contact in m². The wetted area of contact depends on the equipment and hydraulics in the column.

Each packing has a specific area (m²/m³). The volume of a segment/section is found by dividing the wetted area of the column by the specific area of the packing.

The height of a segment is found by dividing the volume of the segment by the area of column. The height of packing required for a particular operation is found by summing the heights of all the segments.

Figure 5 shows a typical result of the mass transfer modeling operation for a 5m K⁺/2.5m PZ solvent with a rich P_{CO₂}^{*} = 2.5 kPa (i.e. 5.33m at 40°C) and a lean P_{CO₂}^{*} = 0.24 kPa (i.e. 4.44m at 40°C). The result shows that the fractional resistance in the gas phase varies from 61% at the rich end to 91% at the lean end. The k_g' is an indication of the reaction term. It varies from 3.12e-9 kmol/Pa·m²-s at the rich end to 2.59e-8 kmol/Pa·m²-s at the lean end. This factor-of-ten increase in k_g' is as a result of the increase in free amine in the solution as the liquid goes from the rich end to the lean end.

Conclusions and Future Work

In a simple stripper, if 5 m K⁺/2.5 m PZ is able to achieve a rich equilibrium partial pressure of 5 kPa (because it has faster rates than 7 m MEA), it will have about the same steam requirement as 7 m MEA with a rich equilibrium partial pressure of 2.5 kPa.

In this quarter, the ACM model was extended to mass transfer modeling for the 5m K⁺/2.5m PZ. Mass transfer modelling revealed that the stripper could be significantly gas phase controlled. In the stripper, 23 meters of packing height will be equivalent to 10 stages of contacting with 40% Murphree efficiency.

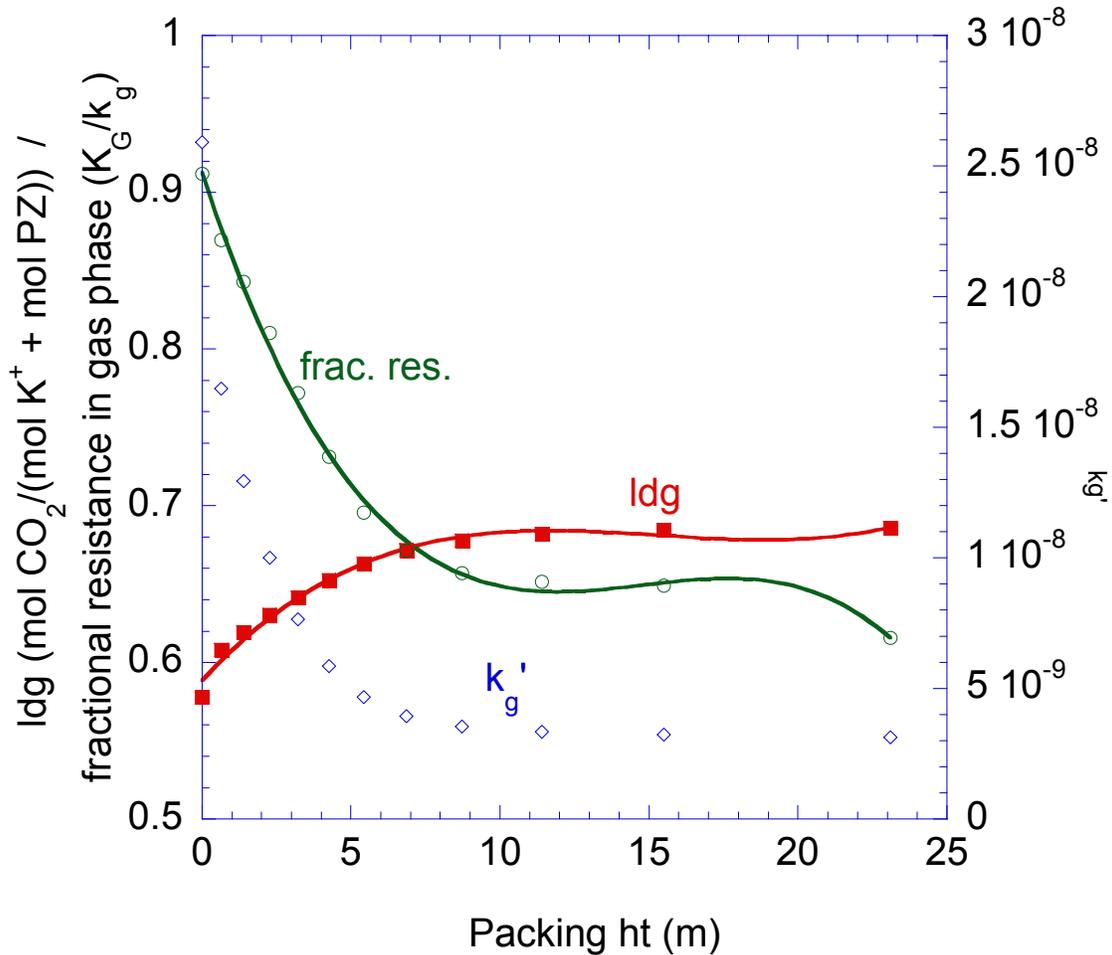


Figure 5. Rate in Stripper for 5m K⁺/2.5m PZ at Rich P_{CO₂*} = 2.5kPa, Lean P_{CO₂*} = 0.24 kPa

The reboiler duty was minimized and the equivalent work for stripping calculated for 7m MEA and 5m K⁺/2.5m PZ. Generic solvents were modelled and the optimum heat of desorption that minimizes reboiler duty was found to depend on the rich CO₂ partial pressure. This optimum ranged from 26 kcal/gmol CO₂ at low partial pressures to 15 kcal/gmol CO₂ for rich partial pressures.

In the next quarter, the mass transfer model will be developed further and applied to simulate pilot plant performance. The ACM model will be incorporated with Aspen Plus[®] to take advantage of its database and the other unit operations available in the software.

Subtask 1.3b – Develop Integrated Absorber/Stripper Model – Absorber Model

by Jennifer Lu
(Supported by this contract)

Introduction

This report presents the continuing development of an absorber model in Aspen Plus[®] for use in modeling the pilot plant. A FORTRAN subroutine for modeling the piperazine kinetics was developed for use with the model in Aspen Plus[®]. The subroutine utilizes the IPFO (Interface Pseudo First Order) expression for the CO₂ flux.

Aspen convergence issues have been solved. Using the thermodynamics set developed by Hilliard (2005), the addition of oxygen and nitrogen as Henry's components caused convergence problems, until the PURE-12 databank was added.

An interfacial area subroutine was developed to reflect the dependence of wetted area on liquid and vapor flow rates. A simple regression was used for three different packings, CMR #2, IMTP-40, and Flexipac 1Y.

Experimental

The RATEFRAC block is a rate-based nonequilibrium model for absorbers. The column is divided into segments and all equations are solved using Newton's method. The calculation is done in two steps. First, the initialization step is calculated, where all segments are treated as equilibrium segments. Then the results from the initialization step are used as a "seed" value for the rate-based calculations.

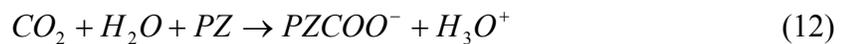
A kinetic subroutine must be written for the absorber. Aspen calculates the flux, N_{CO_2} , in the following manner:

$$R_{tot} = (\sum R_{bulk} + \sum R_{interface})V = (\sum R_{bulk} + \sum R_{interface})A \cdot \delta \quad (9)$$

Here, R represents the reaction rate, with "tot" indicating total reaction rate, "bulk" indicating the reaction rate of bulk reactions, and "interface" indicating the reaction rate of interface reactions. V is the volume of the reaction, or the liquid holdup, A is the interfacial area, and δ is the film thickness. Rearranging Equation (9) gives the flux, given by Equation (10).

$$N_{CO_2} = \frac{R_{tot}}{A} = (\sum R_{bulk} + \sum R_{interface}) \cdot \frac{\delta}{2} \quad (10)$$

We assume that the bulk reactions are negligible, and that there are three kinetic interface reactions:





Knowing how Aspen calculates the flux gives us insight in how to code the kinetics subroutine. The expressions for the three interface reactions must be written such that Aspen will make an accurate calculation for the flux.

Using the IPFO approximation, the CO₂ flux is given by:

$$N_{CO_2} = \sqrt{D_{CO_2} k_{tot}} \left([CO_2]_i - [CO_2]_i^* \right) \quad (14)$$

Here, D_{CO₂} is the diffusion coefficient of CO₂ in a piperazine solvent, k_{tot} is the “total” rate constant, the sum of contributions from all three reactions. These three contributions are given in Equations (15)-(17) below:

$$k_{HCO_3^-} = k_{OH^-} [OH^-] \quad (15)$$

$$k_{PZCOO^-} = k_1 [PZ]^2 + k_2 [PZ][OH^-] + k_3 [PZ] + k_4 [PZ][CO_3^{2-}] \quad (16)$$

$$k_{PZ(COO)_2^{2-}} = k_1 [PZCOO^-]^2 + k_2 [PZCOO^-][OH^-] + k_3 [PZCOO^-] + k_4 [PZCOO^-][CO_3^{2-}] \quad (17)$$

Each term in the carbamate and dicarbamate rate constants, Equations (16) and (17), reflect the four parallel mechanisms (base catalysis) by which the corresponding reactions occur.

Setting Equation (10) equal to Equation (14), we find that the sum of the rate expressions must equal the IPFO approximation, as seen below:

$$\left(R_{HCO_3^-} + R_{PZCOO^-} + R_{PZ(COO)_2^{2-}} \right) = \frac{2}{\delta} \sqrt{D_{CO_2} k_{tot}} \left([CO_2]_i - [CO_2]_i^* \right) \quad (18)$$

The question, then, is how to divide the flux among the three rate expressions. We use the rate constants for each reaction and the k_{tot} rate constant to write the rate expressions as follows, in Equations (19)-(21).

$$R_{HCO_3^-} = \frac{k_{HCO_3^-}}{k_{tot}} \frac{2}{\delta} \sqrt{D_{CO_2} k_{tot}} \left([CO_2]_i - [CO_2]_i^* \right) \quad (19)$$

$$R_{PZCOO^-} = \frac{k_{PZCOO^-}}{k_{tot}} \frac{2}{\delta} \sqrt{D_{CO_2} k_{tot}} \left([CO_2]_i - [CO_2]_i^* \right) \quad (20)$$

$$R_{PZ(COO)_2^{2-}} = \frac{k_{PZ(COO)_2^{2-}}}{k_{tot}} \frac{2}{\delta} \sqrt{D_{CO_2} k_{tot}} \left([CO_2]_i - [CO_2]_i^* \right) \quad (21)$$

Then, the kinetic subroutine must have these three rate expressions coded. In this way, Aspen will calculate the flux to equal the IPFO approximation.

Additionally, each reaction has a different equilibrium CO₂ concentration. A “general” equilibrium CO₂ concentration must be calculated for use in Equations (19)-

(21). We can write rate expressions for the three reactions in the following manner, in Equations (22)-(24):

$$R'_{HCO_3^-} = k_{HCO_3^-} [OH^-] ([CO_2]_i - [CO_2]_{i,HCO_3^-}^*) \quad (22)$$

$$R'_{PZCOO^-} = (k_1 [PZ]^2 + k_2 [PZ] [OH^-] + k_3 [PZ] + k_4 [PZ] [CO_3^{2-}]) ([CO_2]_i - [CO_2]_{i,PZCOO^-}) \quad (23)$$

$$R'_{PZ(COO)_2^{2-}} = (k_1 [PZCOO^-]^2 + k_2 [PZCOO^-] [OH^-] + k_3 [PZCOO^-] + k_4 [PZCOO^-] [CO_3^{2-}]) ([CO_2]_i - [CO_2]_{i,PZ(COO)_2^{2-}}^*) \quad (24)$$

The total reaction rate can be written as:

$$R'_{tot} = k_{tot} ([CO_2]_i - [CO_2]_i^*) = R'_{HCO_3^-} + R'_{PZCOO^-} + R'_{PZ(COO)_2^{2-}} \quad (25)$$

Then, solving for the “general” equilibrium CO₂ concentration, we obtain:

$$[CO_2]_i^* = [CO_2]_i - \frac{1}{k_{tot}} (R'_{HCO_3^-} + R'_{PZCOO^-} + R'_{PZ(COO)_2^{2-}}) \quad (26)$$

The subroutine must also calculate δ , the film thickness. This is easily done by dividing the holdup by the wetted area. Therefore, the subroutine must also calculate wetted area. The Onda correlation used by Aspen for random packings is inadequate; it only applies to older, smaller packings and does not account for dependence on liquid *and* gas rates. Thus, a simple regression, using Ian Wilson’s interfacial area data for CMR #2 and IMTP-40 and pilot plant data for Flexipac 1Y, is used:

$$Area = a + bG^2 + cG + dGL + eL + fL^2 \quad (27)$$

Area is in units of m²/m³, gas flow rate, G, is in units of ACFM, and liquid flow rate, L, is in units of KPPH.

Then, a p-test is performed on each coefficient, to see if any of the coefficients can be set to zero and eliminated. Confidence regions are also examined to see if any other terms can be further eliminated. Holding all but two coefficients constant, the confidence region examines how one coefficient changes in response to another coefficient. If two terms are very correlated, one term may be eliminated.

Results and Discussion

CMR #2

For CMR #2, using the equation in Equation (27), the simple linear regression is:

$$Area = 49.8 - 0.00018 \cdot G^2 + 0.31 \cdot G + 0.0052 \cdot GL + 1.42 \cdot L - 0.0024 \cdot L^2 \quad (28)$$

Additional data, including the p-tests for each coefficient, is given below in Table 4.

Table 4. CMR #2 p-tests, First Regression

Label	Estimate	Std. Error	t-value	p-value
Constant	49.8	17.0	2.921	0.0091
G^2	-0.00018	0.000059	-3.081	0.0064
G	0.31	0.073	4.261	0.0005
GL	0.0052	0.0020	2.668	0.0157
L	1.42	1.16	1.223	0.2371
L^2	-0.0024	0.029	-0.084	0.9337

We will focus on the L^2 term. We hypothesize that the coefficient is actually zero. The t-test gives a t-value of -0.084 and a p-value of 0.9337. That means, there is a 93.37% chance of getting a t-value at least as extreme as -0.084, *if the hypothesis is correct*. That means that there is a lot of evidence for our hypothesis. Or, put another way, there is a 93.37% chance of *incorrectly* rejecting the null hypothesis, if it is true. So, we can be fairly confident in accepting the null hypothesis; then, let's try a fit with the G^2 , G, GL, and L variables.

$$Area = 50.0 - 0.00018 \cdot G^2 + 0.31 \cdot G + 0.0052 \cdot GL + 1.34 \cdot L \quad (29)$$

Data for this regression is given below in Table 5.

Table 5. CMR #2 p-tests, Second Regression

Label	Estimate	Std. Error	t-value	p-value
Constant	50.0	16.2	3.083	0.0061
G^2	-0.00018	0.000058	-3.172	0.0050
G	0.31	0.071	4.380	0.0003
GL	0.0052	0.0019	2.763	0.0124
L	1.34	0.65	2.048	0.0546

We focus on the L term now, hypothesizing that the coefficient for L equals zero. The t-test gives a p-value of 0.0546, which means that there is a 5.46% chance of getting a t-value at least as extreme as 2.048, *if the hypothesis is correct*. That means that there is not a lot of evidence for the null hypothesis. Usually, 5% is the “cutoff” significance level, but we will keep this term. Then, the full model will be the expression given in Equation (21). The correlation coefficient for this regression is $r^2 = 0.96$ with a “sigma-hat”, or standard error of the regression, of $\hat{\sigma} = 10.5$.

Looking at the confidence regions of the coefficients, we find that the G and G^2 coefficients are strongly correlated. If we remove either term, the correlation coefficient

decreases and sigma-hat increases. Thus, we will use Equation (29) for the regression for CMR #2.

Figure 6 below shows how the regression compares to the data.

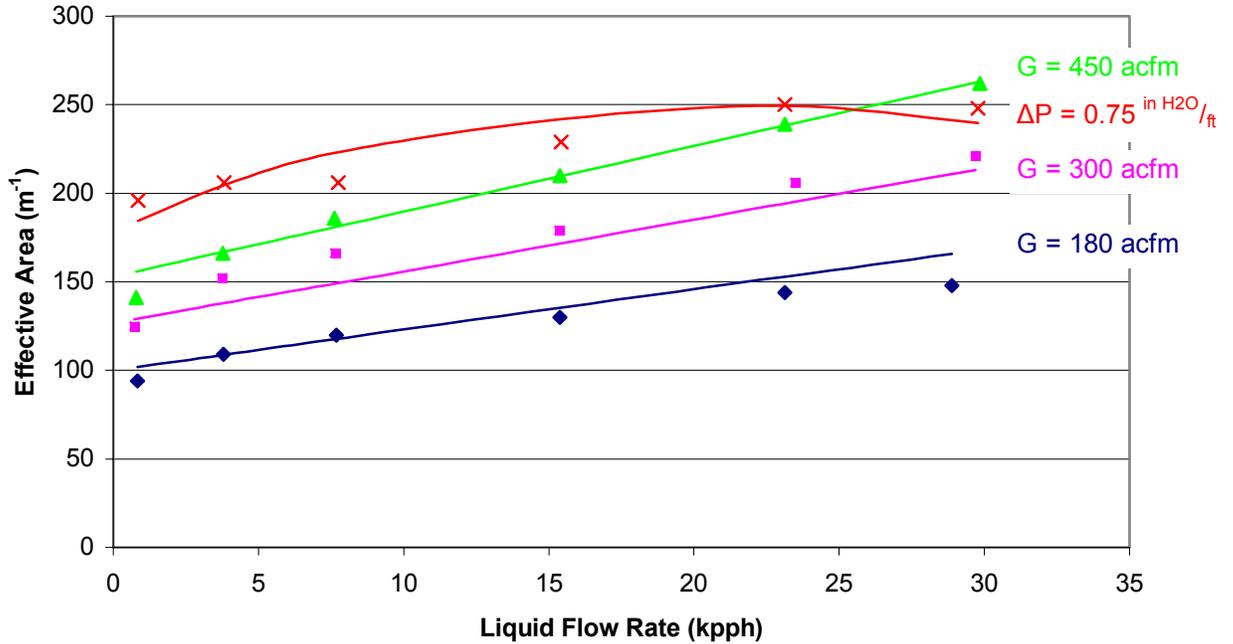


Figure 6. Dependence of Effective Area of CMR #2 on Liquid Rate

The regression is fairly consistent with the data. The constant pressure drop data seems to indicate a straight line, whereas the regression seems to suggest a parabolic function.

IMTP-40

For IMTP-40, using the equation in Equation (27), the simple linear regression is:

$$Area = 42.7 - 0.00021 \cdot G^2 + 0.34 \cdot G + 0.0015 \cdot GL + 3.28 \cdot L - 0.048 \cdot L^2 \quad (30)$$

Table 6 below gives the p-tests for each coefficient:

Table 6. IMTP-40 p-tests, First Regression

Label	Estimate	Std. Error	t-value	p-value
Constant	42.7	14.2	2.998	0.0054
G^2	-0.00021	0.000060	-3.535	0.0013
G	0.34	0.067	5.108	0.0000
GL	0.0015	0.0016	0.927	0.3611
L	3.28	0.91	3.596	0.0011
L^2	-0.048	0.024	-2.030	0.0513

We focus on the GL term first, hypothesizing that this coefficient equals zero. The t-test gives a p-value of 0.3611, which means that there is a 36.11% chance of getting a t-value at least as extreme as 0.927, *if the hypothesis is correct*. That means that there is quite a bit of evidence for the null hypothesis, and we can be somewhat confident in setting this term equal to zero. So, we perform a regression using the G^2 , G , L , and L^2 variables.

$$Area = 32.4 - 0.00025 \cdot G^2 + 0.39 \cdot G + 3.78 \cdot L - 0.050 \cdot L^2 \quad (31)$$

The data for this regression is given below, in Table 7.

Table 7. IMTP-40 p-tests, Second Regression

Label	Estimate	Std. Error	t-value	p-value
Constant	32.4	8.94	3.625	0.0010
G^2	-0.00025	0.000045	-5.551	0.0000
G	0.39	0.044	8.875	0.0000
L	3.78	0.73	5.122	0.0000
L^2	-0.050	0.023	-2.115	0.0426

All p-values are small, so we will keep this regression as the full model. The coefficients for G^2 and G and the coefficients for L^2 and L are highly correlated. Removing the G^2 , G , and L terms reduce r^2 and increase $\hat{\sigma}$. Removing the L^2 term does not change the regression statistics significantly, so this term can be set to zero. The final regression, with $r^2 = 0.92$ and $\hat{\sigma} = 11.7$ is then:

$$Area = 36.8 - 0.00026 \cdot G^2 + 0.40 \cdot G + 2.27 \cdot L \quad (32)$$

Figure 7 below shows how the regression compares to the data. For high gas rates, the regression slightly overestimates the interfacial area. For the midrange gas rates, the regression underestimates the interfacial area. Nevertheless, overall, the regression fits the data.

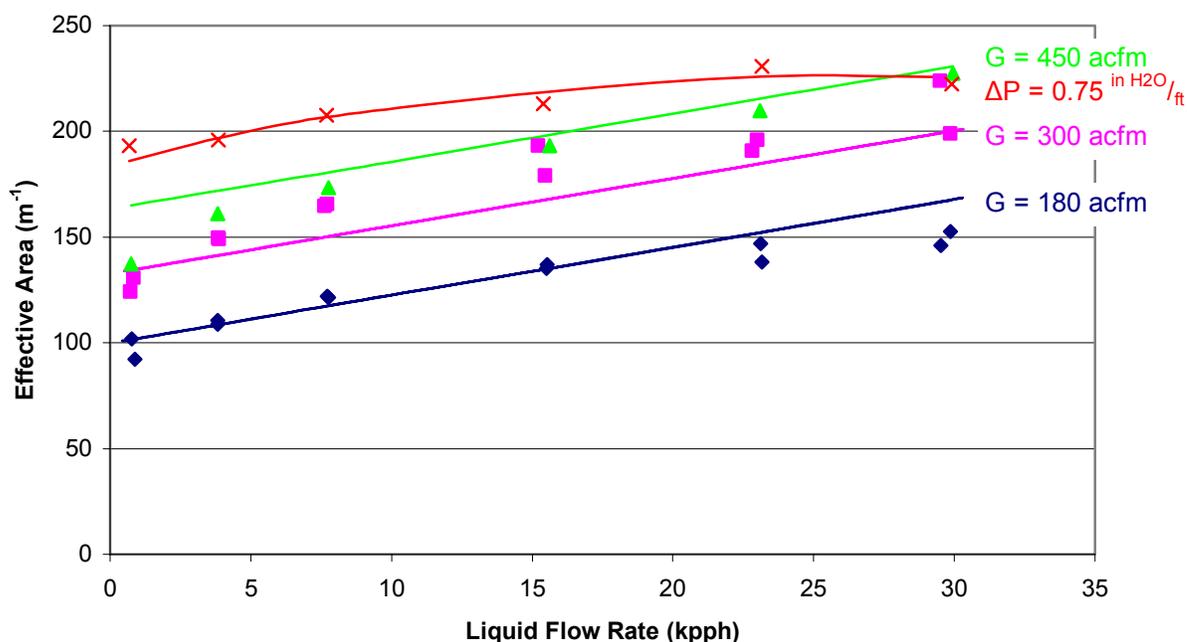


Figure 7. Dependence of Effective Area of IMTP-40 on Liquid Rate

Flexipac 1Y

Using pilot plant data and the regression analysis outlined for CMR #2 and IMTP-40, the regression for interfacial area for Flexipac 1Y is:

$$Area = -0.0012 \cdot G^2 + 0.93 \cdot G + 0.0021 \cdot GL \quad (25)$$

Here, the liquid rate, L , is in units of gpm, rather than kpph.

Figure 8 below shows how the regression compares to the data. The regression underestimates the area for high and midrange gas rates.

Conclusions

The regression for CMR #2 fits the data fairly well. The regression for IMTP-40, however, underestimates area for mid-range gas rates and overestimates area for high gas rates. The regression for Flexipac 1Y underestimates the area for high and mid-range gas rates.

It must be noted that the regressions do not take into account properties of the solvents. The data for CMR #2 and IMTP-40 are based on a 0.1M NaOH solvent and may not be directly applicable to a PZ/K₂CO₃ solvent. A regression that uses units of mass, rather than volume, may be more appropriate.

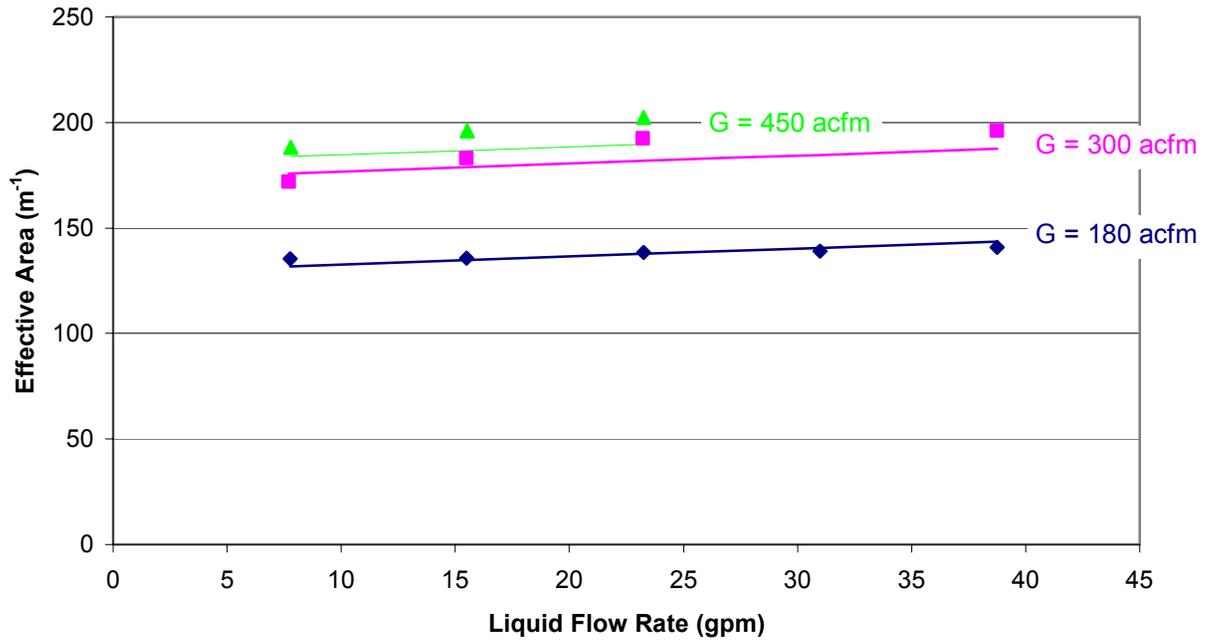


Figure 8. Dependence of Effective Area of Flexipac 1Y on Liquid Rate

Future Work

A working absorber model will be debugged in the next quarter with the kinetics and interfacial area subroutine.

Task 2 – Pilot Plant Testing

Subtask 2.2 – Design Modifications, Order Equipment and Packing Materials

by Eric Chen
(Supported by EPA Star Fellowship)

Introduction

In this quarter, additional modifications were made to the pilot plant before and during the MEA campaign. There were some issues related to CO₂ loading and solution composition analysis and we are still in the process of resolving it.

Experimental – Post-Campaign 2 Modifications

A new extractive CO₂ sampling system was constructed for the additional Horiba analyzer. The sampling system consists of a water knockout, a sampling pump, a filter, a membrane filter, and a rotameter. The gas flows from the sample point to a water knockout and then through the sample pump. Next the gas passes through a filter that removes any condensed water and then through a membrane filter that removes any residual moisture. The gas is then analyzed by the Horiba CO₂ analyzer. The gas flow rates are regulated by a rotameter located downstream of the Horiba analyzer.

A large weather-proof electrical cabinet was purchased and modified to fit two sampling pumps. A temperature controlled fan was added to help dissipate the buildup of heat inside the cabinet and to prevent the sampling pump from overheating or melting the diaphragm.

A new CO₂ makeup heater was constructed and installed. The previous heater was not sized for loading large amounts of CO₂ into the solution. As a result of being undersized, the heater began to leak due to the continuous stress resulting from differential thermal expansion. At high flow rates, the CO₂ was not adequately heated and the exchanger and makeup lines would freeze. The new double-pipe heat exchanger was constructed out of 1-inch black pipe and ½-inch stainless-steel tubing. The heater consisted of two 10-foot sections and was operated in parallel. Steam flow was on the shell side and the liquid CO₂ was on the tube side. In the new design, steam flow was directed in parallel to the heat exchangers and to the CO₂ regulator, whereas before, the steam flowed in series with the heat exchanger and regulator. The new design seems to have worked well so far.

A new stainless-steel reboiler has been ordered. The original reboiler was constructed out of carbon steel. Over time, it appeared that the reboiler had developed a pinhole-sized leak and ultimately needed to be replaced. The bid for the new reboiler has gone out, the drawings have been approved, and the reboiler is schedule for June delivery.

After completion of the MEA campaign, additional modifications will be made to the existing pilot plant configuration. The inadequate preheat of the stripper feed will be rectified using the existing solvent cooler as the new cross-exchanger. The current solvent pre-heater will be used as the trim heater and will be located downstream of the cross-exchanger. A new solvent cooler with approximately 40 ft² will be purchased to replace the existing one.

Subtask 2.5a – Campaign 2 Pilot Plant - Results for Absorber

by Eric Chen
(Supported by EPA Star Fellowship)

Experimental – Campaign 2

A portion of diluted liquid samples from Campaign 2 were analyzed with the inorganic carbon (IC) analyzer located on the main UT campus. The results from the campus IC and from the Shimadzu total organic carbon (TOC) analyzer located at the Pickle Research Center (PRC) were plotted against online pH measurements. The results are shown in Figure 9. It was found that the campus loading numbers were systematically lower than that analyzed by the Shimadzu TOC.

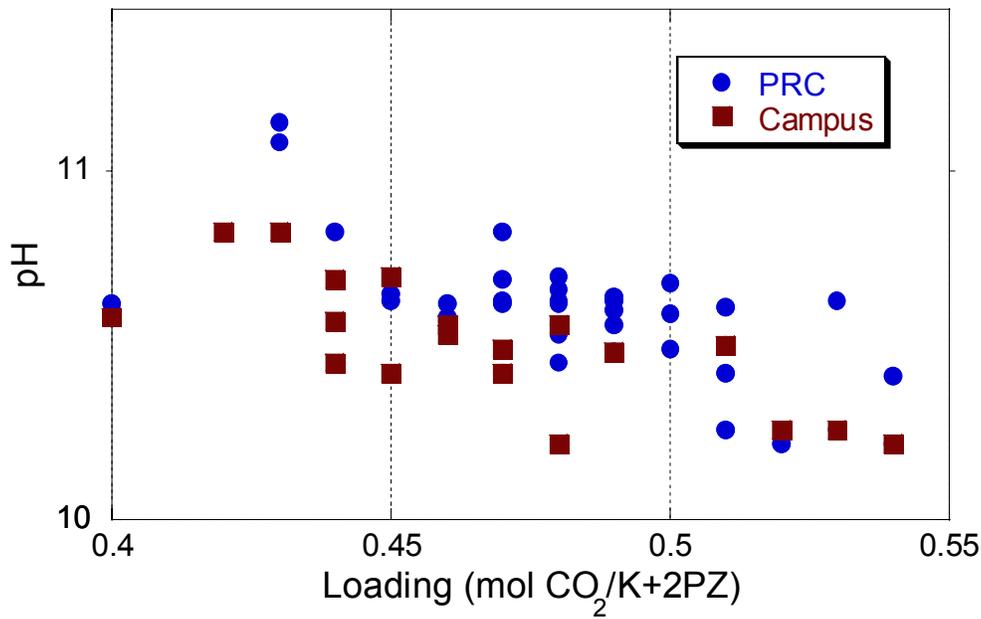


Figure 9. CO₂ Loading Comparison

It was discovered that the diluted sample solutions and the IC standard solutions absorbed CO₂ when left open to the atmosphere. The PRC IC standards are made up to a concentration of 1000 ppm of inorganic carbon using sodium carbonate and sodium bicarbonate. The on-campus IC standard is made up to a concentration of 7 molar (84 ppm) using sodium carbonate.

An experiment was conducted where the IC standard was parafilmmed and the diluted samples were left open to the atmosphere and were analyzed over a period of five days (Figure 10). The results show that at concentrations below 200 ppm, the diluted samples will absorb between 20-30 ppm of CO₂ from the atmosphere within a 17-hour period. In the past the TOC has been operated over a period of 12 hours. Therefore, if the samples were not parafilmmed, a fairly large amount of CO₂ may have been absorbed. In the future, all of the samples will be parafilmmed.

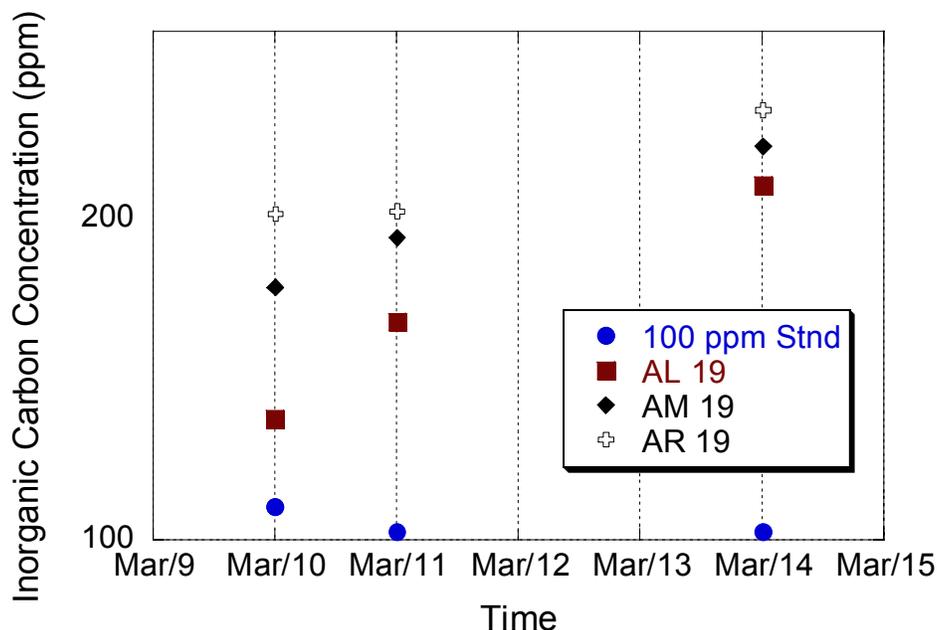


Figure 10. CO₂ Absorption into Diluted Piperazine/Potassium Carbonate Samples

It was also observed that the 100 ppm IC standards consisting of sodium carbonate and bicarbonate will absorb up to 10 ppm of CO₂ when left open to the atmosphere overnight. Three sets of IC standards consisting of 100, 150, 200 ppm were made at PRC and analyzed by the on-campus IC. The values were found to be about 10-15 percent lower by the on-campus IC. The PRC standards were freshly prepared; however, the on-campus standard that was used to calibrate the analyzer was not. Therefore, it is conceivable that the on-campus standard may have absorbed CO₂.

Finally, the sodium carbonate standard used for the main campus IC was measured by the Shimadzu and determined to be 96 ppm when the actual concentration should have been 84 ppm. This supports the observation that CO₂ is absorbed by the IC standard. The on-campus standard is stored in a stopped glass flask at ambient temperature and not in the refrigerator. Overtime, the standard may absorb CO₂ from the atmosphere. Therefore, the new procedure will be to use fresh standards diluted from concentrated standards and to store the concentrated standards in a capped vessel inside a refrigerator.

A density correlation for the piperazine promoted potassium carbonated solvent was developed by Cullinane (2005a). The correlation depends on the potassium and piperazine concentration, temperature, and CO₂ loading. The correlation is most sensitive to potassium concentration. The corresponding solvent parameters from the first and second campaigns were introduced into the density correlation and plotted against the actual density determined by the online density measurements. The results are shown in Figure 11. The plot shows that there is slight deviation in density measurements between Campaigns 1 and 2. The potassium measurement is the most critical variable in the correlation. Therefore, slight differences in measurement may

result in the observed deviations. In the second campaign, the titration method used for determining potassium and piperazine was performed with samples diluted at a ratio of 1:4, whereas in Campaign 1, the titration was performed with undiluted liquid samples. The dilution of the sample may have changed the titration endpoints and resulted in a slightly different potassium and piperazine concentration. Independent analyses using inductively-coupled plasma (ICP), gas chromatography (GC), or ionic chromatography (IC) will be needed to verify the potassium and piperazine concentrations.

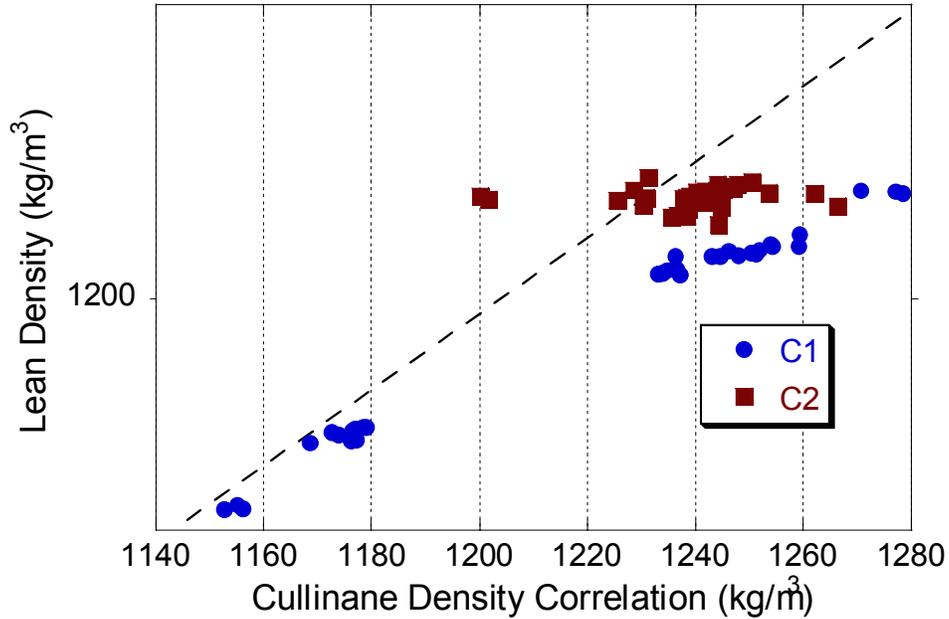


Figure 11. Density Correlation using Pilot Plant Analytical Results

Conclusions and Future Work

The CO₂ loading analysis for Campaign 2 will need to be reconciled before further data analysis can be done. In addition, ICP, GC, or IC analysis will be done to determine potassium, piperazine, iron and vanadium concentrations. The data between Campaigns 1 and 2 will need to be reconciled. The absorber model will be modified to fit the data obtained from the pilot plant experiments.

Subtask 2.7 – MEA Baseline Campaign

by Ross Dugas
(Supported by this contract)

Introduction

This section contains information pertaining to the MEA pilot plant campaign which took place in March and April of 2005. The purpose of this campaign was to study the carbon dioxide absorption/stripping performance of a 30 wt% monoethanolamine solution. The results have yet to be compiled and analyzed but observations of the campaign are included in this report.

Campaign 3 Modifications to the Pilot Plant

To ensure high-quality data and prevent physical limitations to the pilot plant operations, it was necessary to make various modifications to the Separation Research Program's pilot plant. These modifications took place in the months leading up to the MEA campaign.

Air flow measurements entering the absorber were measured by an annubar located in an 8" PVC pipe. At lower flow rates, the pressure drop across this annubar was very small and thus gave a high degree of uncertainty. To prevent this potential inaccuracy, the 8" PVC was replaced with 3 and 4" PVC lines. The system was designed such that either flow path or both flow paths could be used depending on the system's gas flow. This ensures sufficiently high velocities and pressure drops across the annubars and gives flow rates with a greater degree of confidence.

Operating conditions that included low lean loadings and high gas rates in the absorber required that large quantities of CO₂ be cycled through the absorber and stripper. In the previous campaign with vacuum stripping, the stripper was not able to handle this vast quantity of CO₂. Previously, the CO₂ exiting the top of the stripper's condenser flowed through a 1" line which contains multiple elbows and approximately 30 linear feet before it reached the gas accumulator. With the high flow rate and low density of the CO₂ at vacuum conditions, the velocity created very high pressure drops through the piping. As a result, the lower stripper pressure had to be compromised to handle the CO₂ flow. To avoid this limitation, an alternate flow path for the CO₂ was created. A 2" pipe was added the top of the liquid accumulator below the condenser to the gas accumulator.

A steam flow measurement on the solvent preheater and a gas flow measurement out of the gas accumulator were also installed. The steam flow measurement will help in the total heat balance of the system. The gas flow measurement will help in verifying the mass balance and in determining the energy requirements of the process.

To prevent flashing and avoid two phase flow problems for the stripper feed, two modifications were made. The absorber outlet pump was connected to another pump in series to increase the pressure of the stream and possibly prevent flashing upstream of the valve. The valve before the stripper was moved from a vertical run to a horizontal run

immediately before the stripper. This new valve location will prevent slug flow if the liquid flashes across the valve.

An FTIR was connected to the system to analyze the absorber outlet gas stream. The FTIR should give information about MEA volatility and ammonia accumulation in our system.

MEA Campaign Test Plan

A test plan was devised to evaluate the performance of the absorption/stripping system using high and low lean loadings, high and low gas rates, and three different CO₂ removals. The pilot plant tests also included some vacuum stripping in addition to a typical stripping pressure. Flexipac 1Y, a structured packing, and IMTP 40, a random metal packing, were tested in both the absorber and the stripper. For all runs the solvent was 30 wt% MEA and the absorber inlet gas was approximately 12% CO₂. The loading is defined as moles CO₂ per mole MEA. The CO₂ removal is the percentage of CO₂ entering the absorber that is removed by the solvent. The solvent rate was varied to achieve the desired CO₂ removal. The operating matrix can be seen below in Table 8.

Table 8. Operating Matrix for the MEA Campaign

Run	Lean Loading	Stripper Pressure (atm)	Gas Rate (ACFM)	CO ₂ Removal
Packing: Absorber - Flexipac 1Y, Stripper - IMTP 40				
1,2,3	0.2	1.6	500	75,90,95%
4,5,6	0.2	1.6	250	75,90,95%
7,8,9	0.3	1.6	500	75,90,95%
10,11,12	0.3	1.6	250	75,90,95%
Packing: Absorber - IMTP 40, Stripper - Flexipac 1Y				
13,14,15	0.2	1.6	500	75,90,95%
16,17,18	0.2	1.6	250	75,90,95%
19,20,21	0.3	1.6	500	75,90,95%
22,23,24	0.3	1.6	250	75,90,95%
25,26,27	0.3	0.3	500	75,90,95%
28,29,30	0.2	0.3	500	75,90,95%

Observations

One of the issues that prevented ideal operation of the plant was the absorber gas inlet temperature. The absorber gas inlet temperature was intended to be 55°C to model industrial operation. However, the absorber gas line does not have a heater to control temperature and the air cooler has little control over cooling water flow rates. A smaller orifice plate was installed in the cooling water stream during the packing changout, between runs 12 and 13. Some heating was accomplished by adjusting manual valves before the stripper and around the blower recycle. The process was very painstaking and

not very effective, especially at the lower gas rates. The absorber gas inlet temperatures for the first 12 runs can be seen below in Figure 12.

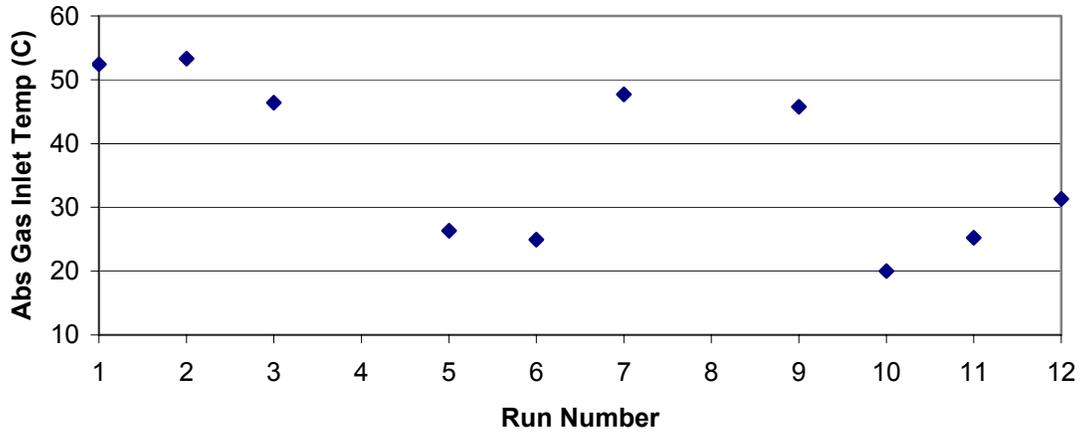


Figure 12. Absorber Gas Inlet Temperature for Runs 1-12 of the MEA Campaign

The stripper feed temperature was intended to have a 10°C approach with the reboiler. This would simulate a 10°C approach in the cross exchanger. However, this approach was often not possible due to an undersized stripper feed heater. This limitation was compounded by the lower absorber gas temperatures which produced a cooler rich solution exiting the absorber. Figure 13 shows the stripper temperature approach for the first twelve runs of the campaign.

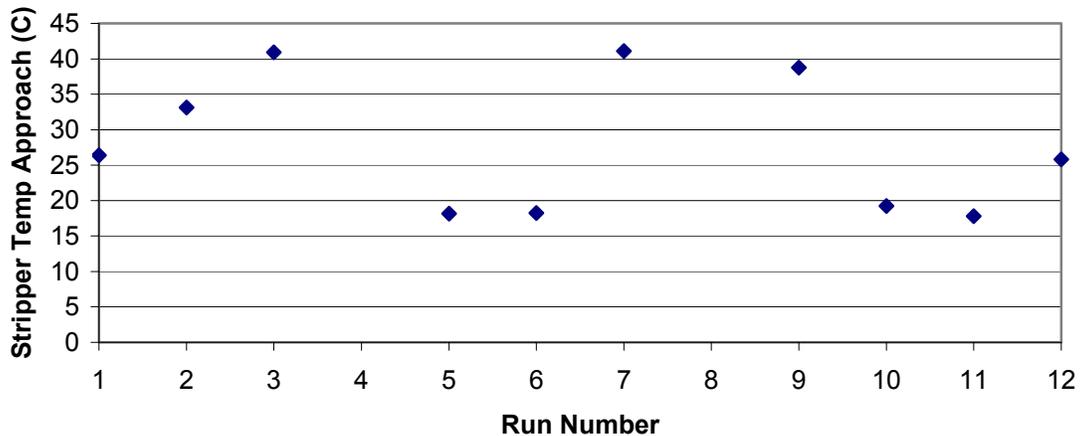


Figure 13. Stripper Feed Temperature Approach for Runs 1-12 of the MEA Campaign

Another issue that limited operation was stripper pressure. A pressure of 0.3 atmospheres was attempted unsuccessfully with a 0.3 lean loading. The stripper exhibited a pinch which would not allow the CO₂ to leave the solution. An increased heat rate only resulted in a higher liquid reflux. Slightly raising the pressure allowed more of the CO₂ to be released from solution. The pressure was raised to 0.7 atmospheres before a 0.3 lean loading could be achieved. Vacuum stripping at a lean loading of 0.2 was not attempted since an even higher stripper pressure would be required.

Future Work

The results of the MEA baseline campaign will continue to be compiled and analyzed. The results of the campaign will be presented in a Master's thesis within a few months.

Modifications to the plant will be made to remove physical limitations. After all the needed modifications have been completed, the fourth and final piperazine/potassium carbonate campaign will commence. The results from this MEA campaign should be very useful in comparing with piperazine/potassium carbonate and any future solvents.

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