

CO₂ Capture by Absorption with Potassium Carbonate

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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. Progress has been made in this reporting period on three subtasks. A simple thermodynamic model has been developed to represent the CO₂ vapor pressure and speciation of the new solvent. A rate model has been formulated to predict the CO₂ flux with these solutions under absorber conditions. A process and instrumentation diagram and process flow diagram have been prepared for modifications of the existing pilot plant system.

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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 will expand on parallel bench scale work with system modeling and pilot plant measurements to demonstrate and quantify the solvent process concepts.

Effort has been initiated on three subtasks:

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

Work has been initiated on a rigorous electrolyte-NRTL model to simulate the thermodynamic data for promoted by piperazine. This initial model uses a stand-alone FORTRAN code. As a continuation of work funded by the Texas Advanced Technology Program, a simple thermodynamic model was developed to predict the equilibrium and speciation in piperazine (PZ) promoted potassium carbonate.

Subtask 1.2 – Modify Point Rate Model

In conjunction with the equilibrium model, a rate model capable of predicting the flux of CO₂ into aqueous solutions was developed.

Subtask 2.2 - Design, Modifications, Order Equipment and Packing Materials

A process and instrument diagram (PID) and process flow diagram (PFD) have been developed.

Future Work

We expect the following accomplishments in the next quarter:

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

We will initiate work with the electrolyte-NRTL model in AspenPlus.

Subtask 1.3 – Develop Integrated Absorber/Stripper Model

Integrated modeling will be initiated with simple forms of the equilibrium and rate models.

Subtask 2.1 – Pilot Plant Test Plan

Analytical methods will be developed for the solvent.

Subtask 2.2 - Design, Modifications, Order Equipment and Packing Materials

Purchasing of equipment and materials for the pilot plant will be initiated. The column packing and internals will be selected.

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

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

Rigorous Modeling

We have initiated work on an electrolyte NRTL model to simulate thermodynamic data obtained by Cullinane for K₂CO₃ promoted by piperazine. The model will make use of an existing, stand-alone FORTRAN code.

The MS work by Cullinane (2002) contains 19 measurements of CO₂ vapor pressure with variable composition and temperature. It also has data for piperazine speciation for 8 compositions at three temperatures. Work in progress funded by the Texas Advanced Technology Program will approximately double this data set.

The computer code was most recently modified and used by Bishnoi to simulate the system MDEA/piperazine/CO₂/water. The framework in this code has been adapted by setting the pK_a value of MDEA to a large value so that it only exists as MDEAH⁺ and using that species to represent K⁺. The activity coefficient parameters for carbonate and bicarbonate have been adjusted to fit the VLE data for K₂CO₃/KHCO₃/CO₂.

This modified rigorous FORTRAN model is now being used to regress the speciation data for 0.6 m PX/3.6 m K₂CO₃. The regressed variables will be equilibrium constants and activity coefficient parameters for the piperazine species

Simple Modeling

In lieu of using activity coefficients, equilibrium constants were adjusted to match piperazine speciation data gathered from experiments that included high potassium concentrations. A procedure, as outlined in Cullinane (2002), was followed to match data for the speciation of PZ in the solutions, with each equilibrium constant treated independently. For a 20 wt% K₂CO₃ solution containing 0.6 m PZ at 60°C, the equilibrium constants were adjusted by matching predictions to experimental speciation data gathered using proton NMR such that

$$K_{PZCOO^-}' = 0.75 \cdot K_{PZCOO^-} \quad (1)$$

$$K_{PZ(COO^-)_2}' = 0.70 \cdot K_{PZ(COO^-)_2} \quad (2)$$

Table 1. Equilibrium Equations in Equilibrium Model, Mole Fraction-Based

Eq. #	Equilibrium Constant	$\ln K_i = A + B/T + C \ln T$			Source
		A	B	C	
3	$K_{HCO_3^-} = \frac{x_{HCO_3^-} \cdot x_{H_3O^+}}{x_{CO_2} \cdot x_{H_2O}^2}$	231.4	-12092	-36.78	Edwards <i>et al.</i> (1978), Posey (1996)
4	$K_{CO_3^{2-}} = \frac{x_{H_3O^+} \cdot x_{CO_3^{2-}}}{x_{HCO_3^-} \cdot x_{H_2O}}$	216.0	-12432	-35.48	Edwards <i>et al.</i> (1978), Posey (1996)
5	$K_w = \frac{x_{H_3O^+} \cdot x_{OH^-}}{x_{H_2O}^2}$	132.9	-13446	-22.48	Edwards <i>et al.</i> (1978), Posey (1996)
6	$K_{PZH^+} = \frac{x_{PZ} \cdot x_{H_3O^+}}{x_{PZH^+} \cdot x_{H_2O}}$	-11.91	-4351	None	Pagano <i>et al.</i> (1961)
7	$K_{PZCOO^-} = \frac{x_{PZCOO^-} \cdot x_{H_3O^+}}{x_{PZ} \cdot x_{CO_2} \cdot x_{H_2O}}$	-29.31	5615	None	Bishnoi (2000)
8	$K_{H^+PZCOO^-} = \frac{x_{PZCOO^-} \cdot x_{H_3O^+}}{x_{H^+PZCOO^-} \cdot x_{H_2O}}$	-8.21	-5286	None	Bishnoi(2000)
9	$K_{PZ(COO^-)_2} = \frac{x_{PZ(COO^-)_2} \cdot x_{H_3O^+}}{x_{PZCOO^-} \cdot x_{CO_2} \cdot x_{H_2O}}$	-30.78	5615	None	Bishnoi (2000)

The continuous lines in Figure 1 through Figure 3 are speciation predictions of the equilibrium model. Throughout the range of loading, the model performs well. There is a slight discrepancy at high loading where the model over-predicts the conversion of piperazine to its carbamate form and the conversion of carbamate to dicarbamate. Model accuracy diminishes as temperature moves away from 60°C, the temperature of the equilibrium constant regressions, indicating that ionic strength may affect the temperature dependence of piperazine equilibrium constants.

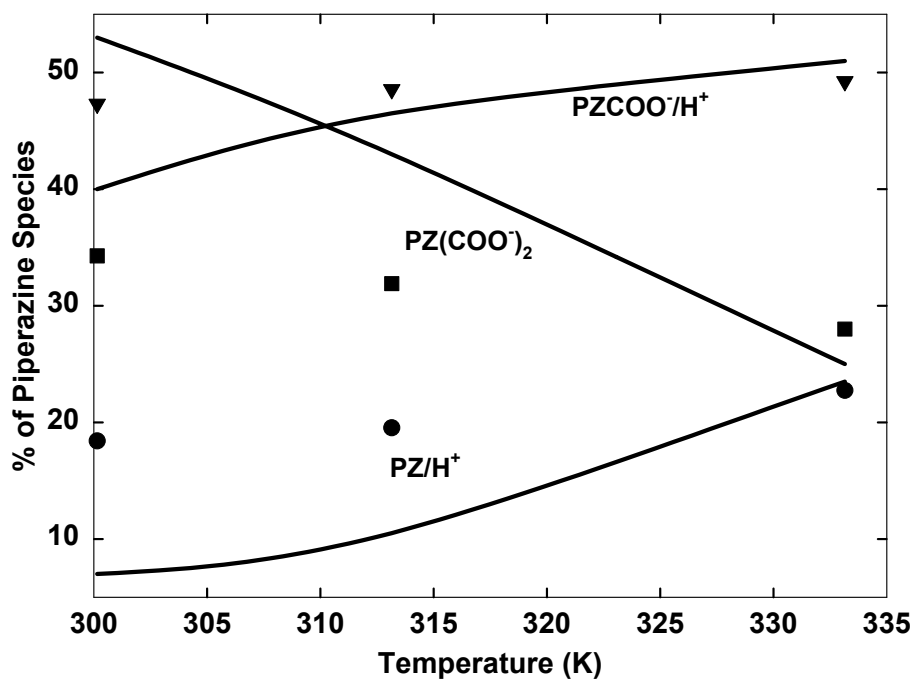


Figure 1. Piperazine Speciation in 3.6 m K⁺/0.6 m PZ at $\alpha = -0.032$, Points: NMR Data, Lines: Model Predictions

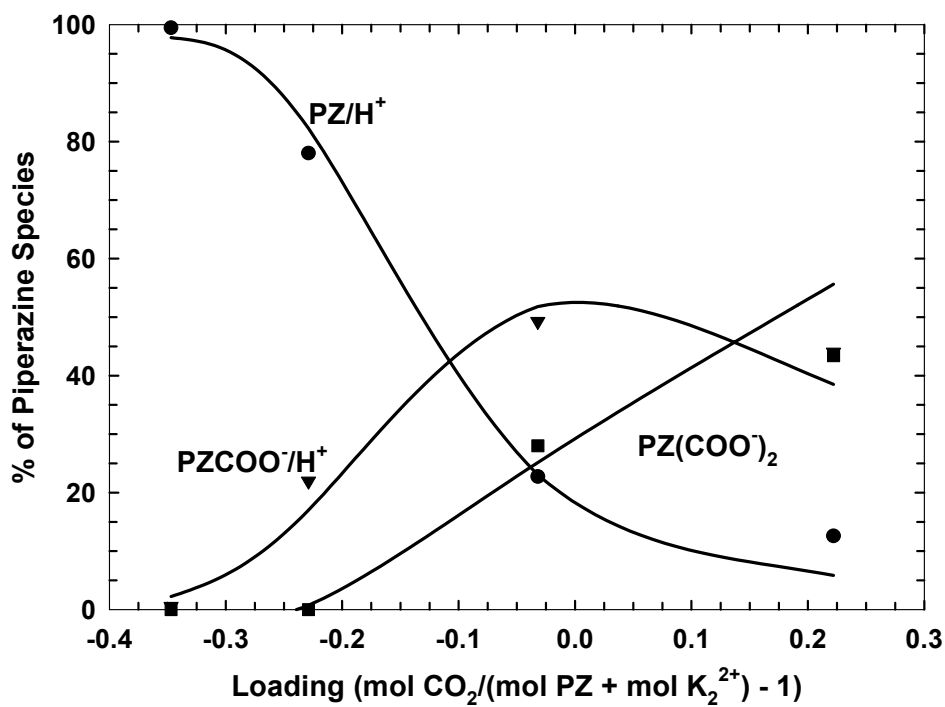


Figure 2. Piperazine Speciation in 3.6 m K⁺/0.6 m PZ at 60°C, Points: NMR Data, Lines: Model Predictions

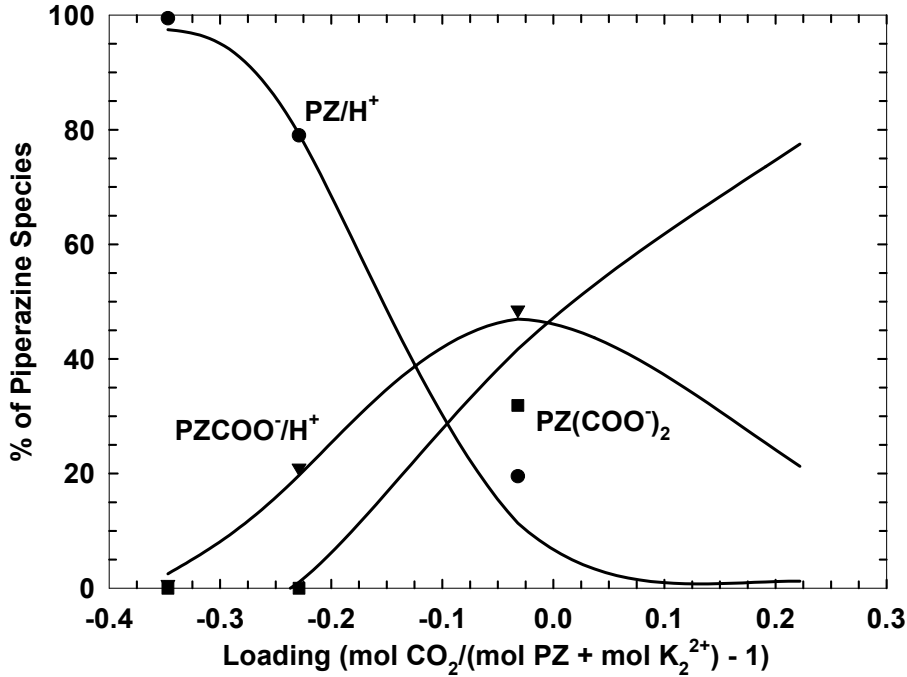


Figure 3. Piperazine Speciation of 3.6 m K^+ /0.6 m PZ at 40°C, Points: NMR Data, Lines: Model Predictions

An un-promoted potassium carbonate solution at 60°C was used as a starting point for the CO_2 equilibrium modeling. Adjustments, notated as Adj, to the equilibrium constants were made such that the new equilibrium constants are represented as

$$K_{HCO_3^-}' = Adj \cdot K_{HCO_3^-} \quad (10)$$

$$K_{CO_3^{2-}}' = Adj^2 \cdot K_{CO_3^{2-}} \quad (11)$$

Using a least squares regression of the model predictions, the equilibrium constants were altered such that the model fits smoothed $P_{CO_2}^*$ data reported in Tosh *et al.* (1959).

For a 20 wt% K_2CO_3 solution, no adjustment was necessary indicating that the ratio of adjustment factors, $Adj^2:Adj$ as seen in Equations 10 and 11, must equal approximately one. The resulting model predictions are shown in Figure 4. The model was also compared to the 30 wt% K_2CO_3 solution investigated by Tosh *et al.* (1959). The value of Adj, in this case, was found to be 0.31 demonstrating the non-idealities associated with high ionic strength solutions.

As demonstrated in Figure 4 by the continuous lines, the combination of the speciation fit and the CO_2 equilibrium fit produces a model capable of accurate predictions in both un-promoted and promoted potassium carbonate. The less

satisfactory fit at low loading suggests that the selected relationship for the adjustment factors does not hold at low loading conditions.

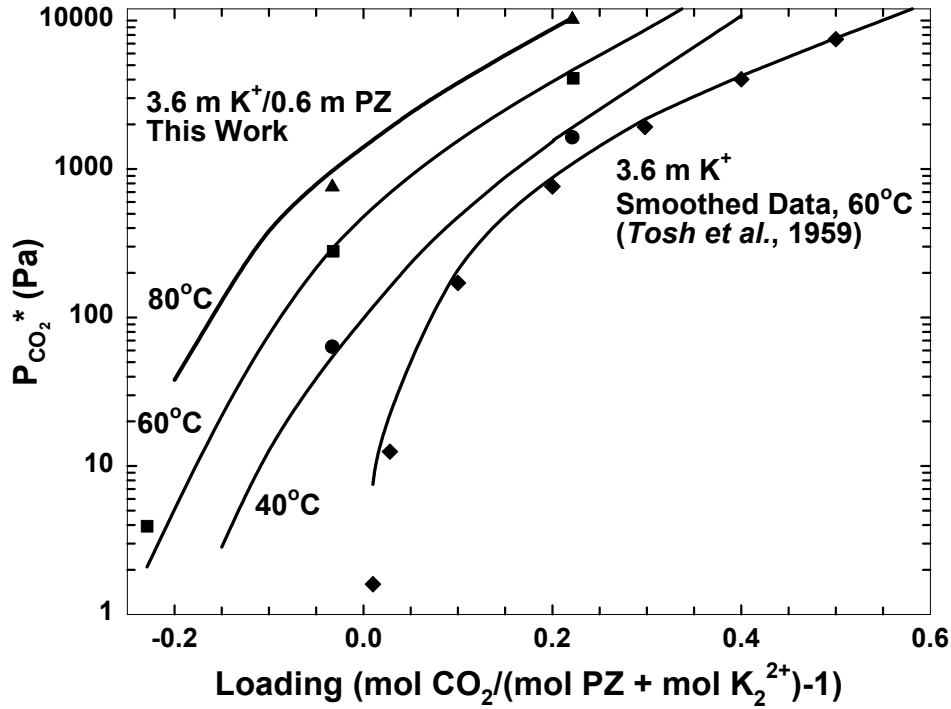


Figure 4. CO₂ Equilibrium in Promoted and Un-promoted K₂CO₃, Points: Experimental Data, Lines: Model Predictions with Adj = 1.0

Subtask 1.2 – Modify Point Rate Model

In conjunction with the equilibrium model, a rate model capable of predicting the flux of CO₂ into aqueous solutions was developed (Bishnoi, 2000). For this work, the model has been modified for potassium carbonate and piperazine mixtures. The predicted flux is based on the iterative solution to the eddy diffusivity theory at multiple nodes across a dimensionless boundary layer. The equilibrium model provides one boundary condition, the bulk solution composition. Each iteration of the secant method gives a new value for the gas-liquid interface partial pressure until convergence criteria are satisfied. The flux and kinetic information can then be extracted.

The rate model successfully predicted values of flux by using regressed rate constants and temperature dependence. GREG, a non-linear regression package, was used to arrive at rate constants suitable for a rate expression shown in Equation 12 (Caracotsios, 1986). The regression results, including values from Bishnoi (2000) for aqueous piperazine, are shown in Table 2.

$$r = \left\{ k_{PZ-OH^-} [PZ][OH^-] + k_{PZ} [PZ] + k_{PZCOO^-} [PZCOO^-] \right\} [CO_2] \quad (12)$$

Table 2. Specific Rate Constants Regressed From Various Rate Equations, $\Delta H_a = 3.36e4$ kJ/mol for Piperazine and Piperazine Carbamate (Bishnoi, 2000)

	Piperazine- Hydroxide	Piperazine	Piperazine Carbamate
	$k_{\text{PZ-OH}^0}$ ($\text{m}^6/\text{kmol}^2\text{-s}$)	k_{PZ^0} ($\text{m}^3/\text{kmol}\text{-s}$)	k_{PZCOO^0} ($\text{m}^3/\text{kmol}\text{-s}$)
Bishnoi (2000)	N/A	5.38e4	4.70e4
This Work (Figure 5)	N/A	1.29e6	1.93e4
This Work (Figure 6)	2.69e6 ^b	2.85e5	4.70e4 ^a

a. Not Regressed

b. $\Delta H_a = 0$ kJ/mol

Piperazine and piperazine carbamate rate constants used in the model were of the form shown in Equation 13 to account for temperature dependence. The PZ-hydroxide rate constant neglects temperature dependence, or $\Delta H_a = 0$.

$$k = k_{25^\circ C} \cdot \exp\left[-\frac{\Delta H_a}{R} \left(\frac{1}{T} - \frac{1}{298.15K}\right)\right] \quad (13)$$

Two regressions of the data were performed, one with and one without the PZ-hydroxide rate constant (Cullinane, 2002). The resulting fits of data for 3.6 m K^+ /0.6 m PZ are shown in Figure 5 and Figure 6. The simple rate expression (i.e. no PZ-hydroxide term) failed to accurately predict the rate behavior of piperazine/ K_2CO_3 . By including a term prevalent only at low loadings, the PZ-hydroxide rate constant, the fit is improved and more reasonable rate constants are obtained.

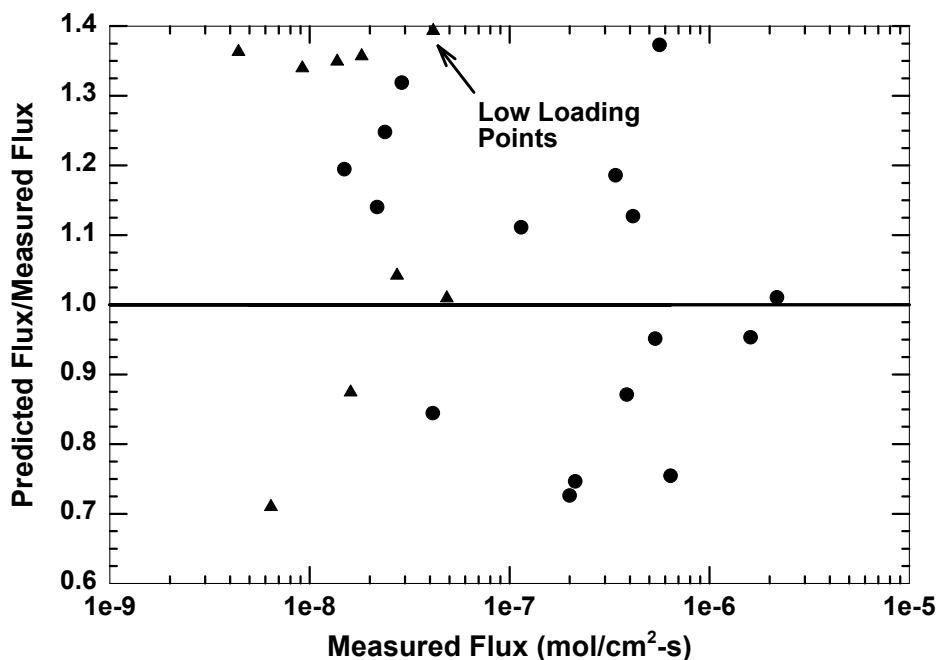


Figure 5. Parity Plot of Promoted K_2CO_3 Fluxes with Two Regressed Rate Constants: $k_{PZ}^0 = 1.29e6 M^{-1}s^{-1}$ and $k_{PZCOO^-}^0 = 1.93e4 M^{-1}s^{-1}$

Using the low loading interaction term, the PZ rate constant is increased by a factor of five from its value in water as reported in Bishnoi (2000). The rate constant for piperazine carbamate gives satisfactory results when its value in 4.0 M MDEA is used (Bishnoi, 2000). Previous research suggests the accelerated rate behavior is a result of a catalytic effect of carbonate or of increased ionic strength. Laddha and Danckwerts (1982) compared effects of K_2CO_3 and K_2SO_4 on MEA and DEA and found that potassium carbonate significantly increases the kinetics of DEA above ionic strength contributions from potassium sulfate addition, suggesting a catalytic effect of the carbonate. The kinetics of MEA are affected equivalently by K_2CO_3 and K_2SO_4 . Sartori and Savage (1983) and Tseng *et al.* (1988) also report accelerated rate behavior of DEA/carbonate solutions. Pohorecki *et al.* (1988) find, however, that the rate constant of ethylaminoethanol, another secondary amine, is a function of ionic strength, not carbonate concentration. The current data on PZ/ K_2CO_3 does not support attributing the increased kinetics specifically to ionic strength or to carbonate concentration.

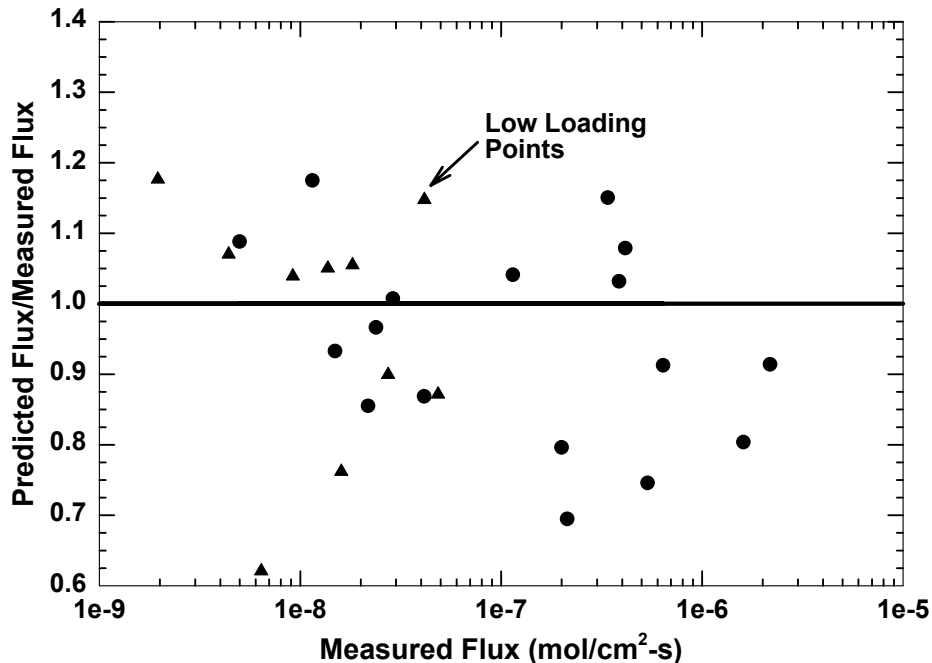


Figure 6. Parity Plot of Promoted K_2CO_3 Fluxes With Three Regressed Rate Constants: $k_{PZ-OH^-} = 2.69e6 M^{-2}s^{-1}$, $k_{PZ^0} = 2.85e5 M^{-1}s^{-1}$, and $k_{PZCOO^-} = 4.70e4 M^{-1}s^{-1}$

The PZ-hydroxide term at a high concentration of hydroxide, 0.45 M, in 3.6 m K^+ gives an apparent rate constant 22 times faster than in water. This may indicate that the proton extraction, rather than the formation of the zwitterion intermediate, is the rate-limiting step. With large amounts of hydroxide, it would be expected that this term would be required at low loading. If the proton extraction is rate-limiting even at the low loading conditions (i.e. more base), it is implied that it should be rate-limiting at high loading conditions where there is less base for the catalysis effect.

Regardless of the mechanism, values show, relative to one another, that the CO_2 -piperazine reaction in water is much faster than the CO_2 -MEA reaction. Additionally, the piperazine rate is increased over its value in water in the presence of aqueous potassium carbonate.

Task 2 – Pilot Plant Testing

Subtask 2.2 Design, Modifications, Order Equipment and Packing Materials

A process and instrument diagram (PID) and process flow diagram (PFD) have been developed. The detailed PFD and PIDs are provided in Attachments 1, 2a and 2b.

Absorption/Stripping Process – The process utilizes two columns, an absorber and stripper, each containing twenty continuous feet of a high performance packing. Centrifugal pumps transfer liquids and a vacuum pump and blower transfer air. Operating

temperatures are controlled by shell-and-tube heat exchangers. Temperatures are measured by Type J thermocouples, liquid and steam flows are measured by differential pressure transmitter/orifice plates, and air flow is measured by an annubar.

Air-actuated control valves are used to control temperature, pressure, steam (heat) flow and feed flows. A state-of-the-art Delta-V distributed control system is used to monitor, control and log process data.

The simplified PFD is shown in Attachment 1. Recycled air from the top of the absorber is mixed with recovered carbon dioxide and the mixture is fed to the suction of the blower. The heat of compression is removed by air cooler. The air/carbon dioxide is fed to the absorber just below the packed bed. The air leaving the top of the absorber is fed to an air/water separator (to remove liquid entrainment) and then is remixed with recovered carbon dioxide. Lean solvent from the stripper is fed to the absorption feed tank from which it is pumped to the top of the absorber. The solvent passes through a liquid distributor located in the column immediately above the packed bed. The rich solvent leaves the bottom of the absorber and flows through a feed heater to the stripper column. The composition of the solvent is monitored, with make-up water added as needed. The composition of the air feed is also monitored, with make-up carbon dioxide added when necessary.

As mentioned, the rich solvent is fed to a preheater, with the outlet temperature carefully controlled to minimize flashing of carbon dioxide. The heated two-phase liquid is fed to the top of the stripper, where a special two-phase distributor is used to minimize liquid entrainment. The lean solvent from the bottom of the stripper is cooled and returned to the absorber section. Heat is added to the stripper by condensing steam in a reboiler. Thus, the reboiler heat vaporizes water internally to provide stripping steam which in turn provides the necessary heat of desorption as well as favorable conditions for mass transfer. The steam and stripped carbon dioxide travels overhead to an overhead condenser. The condensed steam is returned to the top of the stripper as reflux, and the uncondensed carbon dioxide is fed to the suction of the vacuum pump for recycle to the absorber.

The proposed process will require a number of modifications to existing equipment. These modifications are primarily required to recover carbon dioxide and lower the operating costs of the project. A detailed list of modifications appears as Attachment 3. The modifications include the addition of stainless steel piping, stainless steel heat exchangers and entrainment separators.

Bid information has been obtained for each of the modifications. Vendor information is given in Attachment 4. A budget modification has been requested to prevent delay of the pilot testing and to increase the reliability and operating range of the equipment. Additional control equipment is being added with no additional cost to the project. Emerson Process Management will donate approximately \$200,000 of control equipment.

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Attachments

1. Process Flow Diagram
- 2a. Stripper PID
- 2b. Absorber PID
3. List of Modifications
4. Vendor Bid List

Attachments 1 and 2 (PIDs) are too large to include here. We have provided electronic versions of these files only.

Attachment 3 – List of Modifications

- 1) Purchase and install new stainless steel stripper bottoms cooler, absorber inlet cooler, stripper feed heater, stripper reflux heater and air cooler
- 2) Purchase absorber de-entrainment column section
- 3) Install new associated chilled water piping associated with bottoms cooler
- 4) Modify blower suction assembly
- 5) Add vacuum pump discharge oil/water filter/separator

Piping

- 6) P-3008, 3007, 3011, 3016, 3017, 3018, stripper gas accumulator discharge to vacuum pump
- 7) AA-4001&AA-4008, absorber air inlet & outlet
- 8) P-4017, absorber feed flow control loop
- 9) P-4014, absorber feed header to absorber column
- 10) P-2010, stripper feed flow control valve
- 11) P-2010, stripper bottoms product to cooler, including cooler bypass
- 12) P-4013, stripper bottoms to absorber feed tank
- 13) P-4014, stripper overhead condenser liquid to outlet
- 14) P-3003, stripper reflux level control loop
- 15) P-3012, stripped vapor from condenser to gas accumulator

Instrumentation

- 16) Install new absorber level transmitter
- 17) Analysis of absorber gas inlet and outlet composition
- 18) Install stripper gas accumulator outlet valve
- 19) Install absorber CO₂ make-up control valve and control loop
- 20) Fabricate and install stripper column extension

Attachment 4-
Table 1. Project DE-FC26-02NT41440 Equipment Costs

Item	Vendor	Cost
304 L Stainless Steel Pipe, Fittings	PAC Stainless 5250 Brittmore RD Houston, Texas 77041 1-800-535-0386	\$13,100
Carbon Steel pipe and Fittings, 304 L Stainless Steel Valves	Ferguson Supply 504 Industrial Blvd Austin, Texas 78758 512-444-3218	\$1,500
Stainless Steel Valves	Zy-Tech Global Industries, Inc. 10600 Corporate Dr. Stafford, TX 77477 1-800-231-3530	\$3,500
Stainless Steel and Carbon Steel Welding Services	Ted Romer Welding 8989 FM 1411 Dime Box, TX 77853 512-260-0035	\$44,000
PVC Piping and Fittings	Ryan Herco 3106 Industrial Terrace Austin, TX 78758	\$2,800
Pipe Insulation	Star Insulation 11401 Rand Dr Austin, TX 78726 512-385-9780	\$4,500
Solvent Heater (H-101-DI) Solvent Cooler (H-107-DI) Air Cooler (H-112-DA)	Kinetic Engineering 2055 Silber Rd Houston, TX 77055 713-666-2200	\$10,366 \$ 7,934 \$ 4,236
Orifice Flanges	Crane MFG 5531 E. Admiral Place Tilisa, OK 74115	\$1,144
Flange Gaskets	American Packing and Gaskets 6309 Armour Dr Houston, TX 77020 800-888-5223	\$550
Flange Bolts	Austin Bolt 2001 Rutland Austin, TX 78758 512-836-1611	\$250

Attachment 4-
Table 1. Project DE-FC26-02NT41440 Equipment Costs (cont)

Item	Vendor	Cost
DP Transmitters	The Transmitter Shop 2531 Preston Pasadena, TX 77503 281/482-3115	1,290
Fabricate New Column Sections	Inland Machine Houston, TX 713-686-2200	\$7,500
Fabricate New Column Suction Shroud (C-103)	Vought Sheet Metal 3402 Andtree Blvd Austin, TX 78724 512-926-8790	\$2,335
Weld New Piping Supports/Removal and Disposal of Old Carbon Steel Piping	University of Texas Physical Plant 512-471-3609	\$10,500
Process Filters	Rosedale 13700 Gilman Park Houston, TX 77073	\$6,200
Stripper Vent Valve to Recycle	Puffer Swievan 154 W. San Antonio St New Branfels, TX 78130 830-624-8400	\$3,965
	Total	\$125,670