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Rate-Based Simulation Model For Potential CO₂ Solvent-Performance Predication and Comparative Study with Baseline Solvent

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babcock & wilcox power generation group

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Abstract

Regenerable solvent absorption technology (RSAT™) process development activities at The Babcock & Wilcox Company (B&W) have been focused on the selection of next generation CO₂ solvents with rapid absorption rate, high CO₂ capacity and low heat of absorption. Screening of different amine-based solvents is underway in our CO₂ Control Laboratory. Kinetic and solubility data of selected CO₂ solvents was collected with high accuracy using our established experimental protocols. A semi-empirical, rate-based model was developed for screening potential solvents which can be used by making only a few key laboratory measurements.

The as-developed model provides a reasonable prediction of key parameters in commercial-scale application. It has been proven to be a convenient tool for fast solvent screening. A solvent screening protocol for use with the as-developed model was established. Promising solvents identified through this protocol will be subjected to a more extensive rate-based model development with Aspen Plus™ as a platform. In addition, with larger scale test data available for the promising solvents, the semi-empirical model will be upgraded from a solvent-screening tool to an easy-to-use design tool.

Introduction

In post-combustion capture processes the CO₂ is removed from the flue gas of a traditional coal-fired power plant. A typical flue gas contains approximately 12-15% (vol., wet) CO₂ at a total pressure of about one atmosphere[1]. Since the partial pressure of CO₂ in coal-fired flue gas is relatively

low, and the amount of flue gas to be treated is very large, it is commonly agreed that a chemical solvent-based absorption scrubber is the most suitable process for near-term deployment[1]. Among chemical absorption processes, monoethanolamine (MEA)-based CO₂ scrubbing is the most mature technology. Fluor's Econamine FG Plus™ is an example of an MEA-based commercialized post-combustion CO₂ capture process[1]. In addition to corrosion and degradation issues associated with SO_x, NO_x, and oxygen, the major disadvantage of MEA-based processes is the high regeneration energy required, which is around 4 GJ/ton CO₂ (1700 Btu/lb CO₂) removed[2].

Significant research efforts have been aimed at developing an alternative solvent as well as optimizing the MEA-based absorption process. Different amines and amine mixtures have been studied extensively as potential solvent for CO₂ capture. Piperazine (PZ) promoted potassium carbonate, PZ promoted methyldiethanolamine (MDEA), 2-amino-2-methyl-1-propanol (AMP), MEA/AMP blends, and Diglycolamine (DGA) are examples of potential alternative CO₂ solvents that have been studied[1, 3-5]. Most of these solvent screening studies focus on either kinetic measurement or CO₂ capacity estimation through solubility data collection. A few of them use simulation tools like Aspen Plus to simulate large-scale solvent performance which involves significant model development effort, especially for amine mixtures.

B&W has been working on screening next-generation solvents for post-combustion CO₂ capture. The methodology adopted at B&W is to collect fundamental kinetic and thermodynamic data for pre-screened solvent candidates using our CO₂ Control Laboratory. A rate-based semi-empirical

model is then developed with only bench-scale data for a specific solvent. This model is used to predict large scale solvent performance in terms of reboiler duty, absorber height, etc., to further screen solvents. Having identified the most promising solvent from semi-empirical model predictions, more extensive fundamental data measurements are then performed for that solvent. Experiment data is then regressed with the data regression system (DRS) in the Aspen Plus simulator to generate the required parameters for model development. An Aspen Plus model is then built for that solvent to enable more detailed large scale performance prediction. Finally, the previously established semi-empirical model is upgraded with the help of the Aspen Plus model and larger scale test data to expand the capability from a solvent-screening tool to a user-friendly process design model.

This paper focuses on establishing a solvent screening protocol with the use of a semi-empirical model. One specific solvent, Solvent A, is used as an example to illustrate the methodology for solvent screening with the help of the as-developed model.

Experimental

Chemicals

MEA was supplied in 2.5 liter amber glass bottles at 99% purity and is in liquid form under ambient conditions. AMP is in solid form and is supplied in 1 liter amber glass bottles. Solvent A is a sterically hindered amine commercially available from a chemical supplier.

Carbon dioxide gas blends in balance nitrogen (0.1%, 1%, 10%, 20%, 30%) were supplied in 1A size (213 ft³) gas cylinders to allow for variation of CO₂ concentrations during

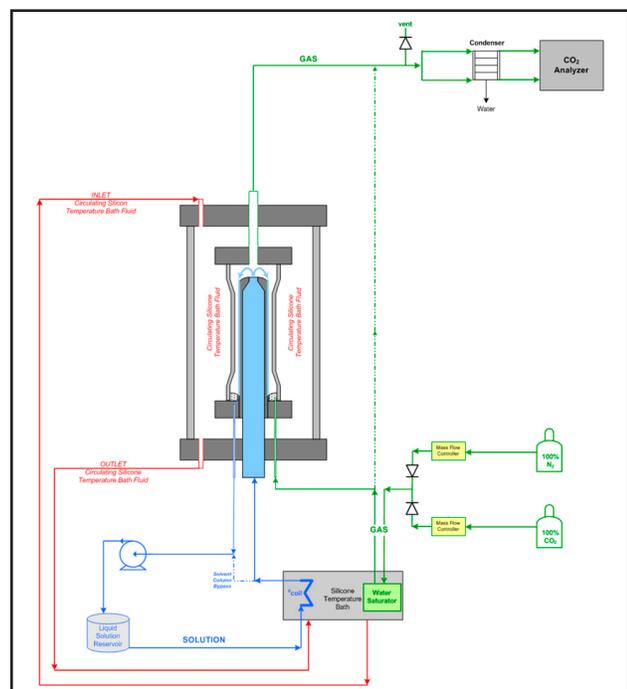


Fig. 1 Schematic of the WWC apparatus.

the experiments. High-purity (99.999%) house nitrogen gas is supplied from a liquefied storage tank and then vaporized for distribution.

Solution analysis via titration

A Chittick apparatus was used to analyze solvent concentration and CO₂ loading via titration methods. The apparatus and a detailed description of the titration method can be found elsewhere[6].

WWC apparatus

Figure 1 shows a schematic of our wetted-wall column (WWC) apparatus. The column in this study is made of stainless steel and has a diameter of 1.27 cm. The hydraulic diameter and height of the annulus are 0.43 cm and 9.13 cm, respectively. A detailed description can be found in another paper[6].

Methods

The chemical reaction kinetics of a specific solvent were expressed in terms of the liquid-side mass transfer coefficient, k'_g , which was defined as:

$$\frac{1}{k'_g} = \frac{H_{CO_2}}{\sqrt{k_2[Am]D_{CO_2}}} \quad (1)$$

The overall mass transfer resistance during CO₂ absorption process was expressed as follows:

$$\frac{1}{K_G} = \frac{1}{k_g} + \frac{1}{k'_g} \quad (2)$$

Where K_G is the overall mass transfer coefficient, k_g is the gas film mass transfer coefficient (the correlation for k_g for the specific WWC in our laboratory was obtained and reported in another paper[6]), H_{CO_2} is the Henry's law constant for CO₂ in amine solution, D_{CO_2} is the diffusion coefficient of CO₂ in amine solution, $[Am]$ is the free amine concentration, and k_2 is the second order reaction rate constant. More detailed explanations of above equations were described in a separate technical paper[6].

Results and discussion

Fundamental data from WWC

Kinetic and vapor-liquid equilibrium (VLE) data for the sterically hindered amine, A, were obtained from our WWC under different experimental conditions and are summarized in Table 1. These data are compared to those for MEA reported by Dugas et al.[7].

Table 1
CO₂ Equilibrium Partial Pressure and Rate Data for Solvents MEA and A at 40 °C and 60 °C

| Solvent | 40 °C | | | 60 °C | | |
|--------------------------------|-------------------------|-------------------------------|-------------------------|-------------------------|-------------------------------|-------------------------|
| | CO ₂ Loading | P _{CO₂} * | k _g ' | CO ₂ Loading | P _{CO₂} * | k _g ' |
| | mol/mol _{alk} | Pa | mol/s·m ² Pa | mol/mol _{alk} | Pa | mol/s·m ² Pa |
| MEA ^[7] (30 wt%) | 0.252 | 15.7 | 3.34E-6 | 0.252 | 109 | 2.92E-6 |
| | 0.351 | 77 | 1.40E-6 | 0.351 | 660 | 1.70E-6 |
| | 0.432 | 465 | 7.66E-7 | 0.432 | 3434 | 9.28E-7 |
| | 0.496 | 4216 | 3.47E-7 | 0.496 | 16157 | 3.76E-7 |
| A (30 wt%) | 0.201 | 56 | 2.78E-6 | 0.201 | 230 | 1.16E-6 |
| | 0.397 | 196 | 1.16E-6 | 0.397 | 1090 | 1.03E-6 |
| | 0.565 | 860 | 6.55E-7 | 0.565 | 4540 | 4.23E-7 |
| | 0.620 | 1550 | 3.13E-7 | 0.620 | 7150 | 3.13E-7 |
| A (40 wt%) | 0.16 | 116 | 2.78E-6 | 0.16 | 379 | 2.76E-6 |
| | 0.36 | 284 | 1.16E-6 | 0.36 | 1815 | 1.03E-6 |
| | 0.56 | 1395 | 4.24E-7 | 0.56 | 6710 | 4.23E-7 |
| | 0.807 | 8830 | 9.11E-8 | 0.807 | 33470 | 8.09E-8 |

Experiment temperatures of 40 °C and 60 °C were selected to simulate absorber conditions to evaluate CO₂ absorption rate. Comparison of absorption kinetics of CO₂ was first made between 30 wt% Solvent A and 30 wt% MEA. As can be seen from Figure 2, Solvent A has similar k_g' values to those of MEA at all CO₂ loading conditions. In addition, it seems that temperature does not have a significant effect on k_g' for Solvent A at rich loadings.

Another comparison of k_g' was done for 30 wt% and 40 wt% Solvent A. It can be seen from Figure 3 that 30 wt% Solvent A has faster kinetics than 40 wt% Solvent A, especially under rich loading conditions. Additionally, temperature does not have a significant impact on k_g' for 40 wt% Solvent A.

CO₂ capacity (moles CO₂/kg solvent), which is directly related to the sensible heat requirement and solvent flow rate, was calculated for Solvent A and MEA based on 40 °C CO₂ solubility data presented in Table 1 and is compared in Figure 4. A rich solution with an equilibrium partial pressure of CO₂ equal to 5000 Pa was selected for both solvents. Figure 4 shows the CO₂ capacity as a function of the equilibrium partial pressure of CO₂ at various lean loading conditions.

Regardless of the concentration of Solvent A, it consistently shows higher CO₂ working capacity compared to that of 30 wt% MEA. This is due to the fact that an unstable carbamate specie is formed during the CO₂ absorption process with Solvent A, which gives it up to a 1 mol CO₂/mol amine theoretical CO₂ capacity, compared to 0.5 mol CO₂/mol amine for MEA.

Semi-empirical model

It will accelerate the solvent screening process if a model could be developed to predict large scale solvent performance with only limited lab data. This would enable quantitative evaluation of potential candidate solvents and would help to avoid unnecessary significant effort on extensive fundamental data collection and detailed model development.

A rate-based semi-empirical model was developed at B&W for this purpose. The key simulation conditions and assumptions of the model are: a 500 MW power plant with 12 vol% CO₂ (wet) and a total flue gas mass flow rate of 5.31*10⁶ lb/hr. The total flue gas pressure is 1.04 bars,

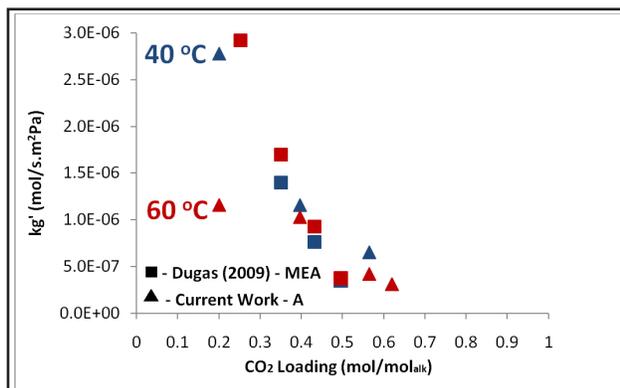


Fig. 2 CO₂ absorption rate data for 30 wt% Solvent A and MEA at 40 °C and 60 °C.

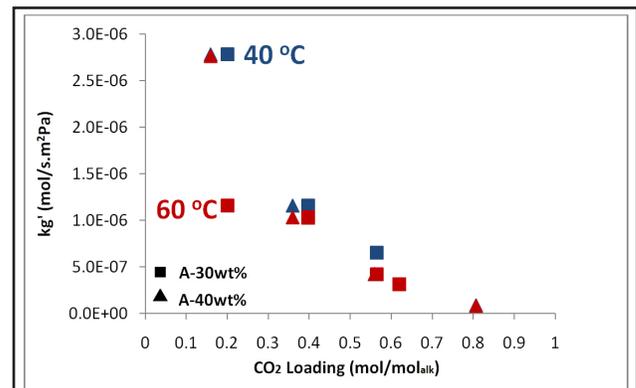


Fig. 3 CO₂ absorption rate data for 30 wt% and 40 wt% Solvent A at 40 °C and 60 °C.

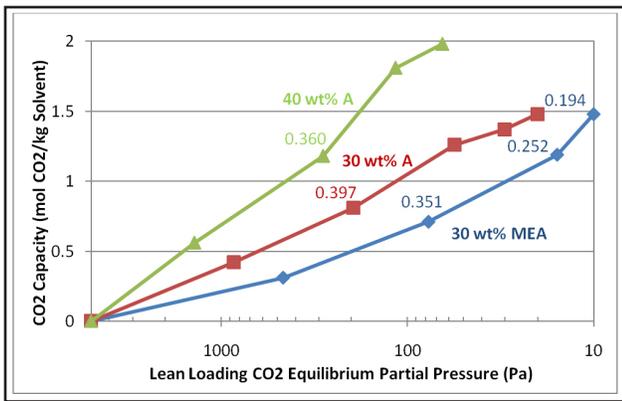


Fig. 4 CO₂ capacity of MEA and A at 40 °C assuming a 5000 Pa rich solution.

structured packing is used in the absorber, and the absorber diameter is kept the same for all solvents. CO₂ recovery rate is 90%. The approach temperature (ΔT) across the heat exchanger is 10 K. A comparison of the performance of the baseline solvent, MEA, Solvent A, and AMP is summarized in Table 2.

It can be observed from Table 2 that for 30 wt% MEA, with an absorber diameter of about 60 feet, the absorber packing height is 40 feet for 90% CO₂ removal. The reboiler heat duty is approximately 1794 Btu/lb CO₂ and the L/G ratio is 3, where L and G are solvent and flue gas mass flow rates, respectively. For the same absorber packing diameter and height with 90% CO₂ capture, the regeneration energy and L/G ratio predicted by an Aspen Plus model for 30 wt% MEA are about 1550 Btu/lb CO₂ and 2.8-3.0, respectively. Considering the fact that Aspen Plus model predictions are under optimum conditions, the semi-empirical model yields reasonable large-scale performance estimates. Solvent A, regardless its concentration, shows a significant reduction in reboiler heat duty, as well as a smaller solvent mass flow. However, Solvent A, at both concentrations, requires a higher absorber packing height compared to that of MEA under these non-optimized conditions. When compared to another CO₂ solvent candidate, AMP, Solvent A showed a smaller regeneration heat requirement, a lower solvent flow rate, and a much lower absorber packing height.

As for Solvent A at two different concentrations, the 40 wt% solution has a lower reboiler duty and L/G ratio, which is consistent with the higher CO₂ capacity for the 40 wt% Solvent A, as can be seen from Fig.4. The 30 wt% Solvent

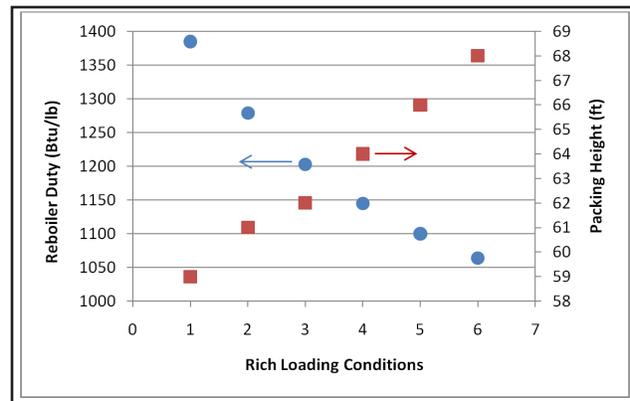


Fig. 5 Optimum rich loading condition for 40 wt% Solvent A with a fixed lean loading.

A solution has a lower absorber packing height than that of 40 wt% which is an indication of faster kinetics, which can be seen from Table 1 and Fig.3.

It seems that Solvent A has good potential as a CO₂ solvent relative to another hindered amine, AMP. The 40 wt% Solvent A looks more attractive than 30 wt% in terms of a smaller reboiler duty and lower solvent flow rate. The key parameters estimated in Table 2 were simulated under fixed rich and lean loading conditions for different concentrations of Solvent A. These fixed conditions may not be optimal. It is necessary to identify optimum rich and lean loading conditions for 30 wt% and 40 wt% Solvent A. The performance parameters estimated for Solvent A under optimized conditions will give a more accurate judgment.

Optimum rich loading was estimated by comparing reboiler duty and absorber packing height under different rich loading conditions with lean loading fixed, as shown in Fig.5. The optimum rich loading was identified to be between 3 and 4 for 40 wt% Solvent A.

With this pre-determined optimum rich loading, regeneration energy and packing height under different lean loading conditions were compared and the optimum lean loading was determined for 40 wt% Solvent A, as shown in Fig. 6.

Similar exercises were performed for 30 wt% Solvent A and the corresponding optimum rich and lean loading conditions were also identified.

With the determined optimum conditions for 30 wt% and 40 wt% Solvent A, performance parameters were re-estimated for Solvent A at the two different concentrations. Table 3 summarizes those predicted parameters.

Table 2
Comparison of Different Solvent Candidates to MEA

| Solvent | Absorber Packing Height (ft) | Reboiler Duty (Btu/lb CO ₂) | L/G (wt) |
|---------------------------|------------------------------|---|----------|
| MEA (30 wt%) | 40 | 1794 | 3.0 |
| A (30 wt%) | 54 | 1302 | 2.5 |
| A (40 wt%) | 62 | 1203 | 2.0 |
| AMP (30 wt%) ¹ | 189 | 1402 | 2.8 |

1. WWC data is from Professor Gary Rochelle' research group at The University of Texas, Austin.

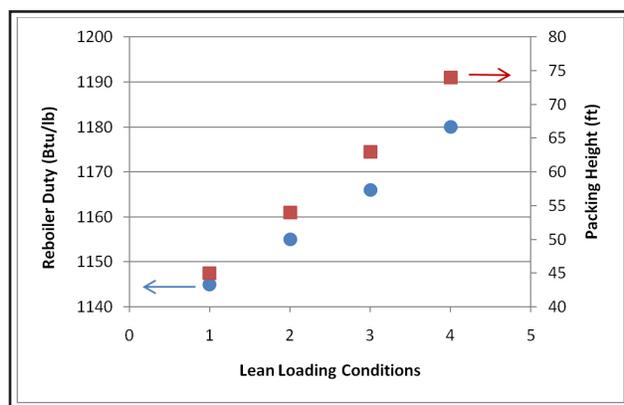


Fig. 6 Optimum lean loading condition for 40 wt% Solvent A with rich loading fixed at optimum.

It can be seen from Table 3 that 40 wt% Solvent A requires approximately 10% less regeneration heat, 23% less solvent flow, 12.5% higher absorber packing than those of 30 wt% Solvent A. It seems 40 wt% Solvent A is a better choice than 30 wt% one according to these preliminary estimated parameters. This estimation is purely based on the lab-scale kinetic and thermodynamic data analysis without considering solvent corrosion, viscosity and other operational issues related to the physical properties of Solvent A. It is therefore not the whole story. However, it provides useful insight into the performance of a potential solvent using only a minimal amount of laboratory solvent data.

Table 3

Comparison of Solvent A Under Optimized Conditions with Different Concentrations

| Solvent | Absorber Packing Height (ft) | Reboiler Duty (Btu/lb CO ₂) | L/G (wt) |
|------------|------------------------------|---|----------|
| A (30 wt%) | 40 | 1274 | 2.2 |
| A (40 wt%) | 45 | 1145 | 1.7 |

Conclusions

A semi-empirical, rate-based model was developed at The Babcock & Wilcox Company. It conveniently estimates the key parameters for judging the potential of a candidate CO₂ solvent. Optimum rich and lean loading conditions can also be determined with this model. Only limited bench-scale, WWC experimental data is required to develop such a semi-empirical model for a specific solvent, which makes the solvent screening process much quicker and easier as compared to the more extensive model development with commercial simulators such as Aspen Plus.

A protocol for solvent screening with the help of the semi-empirical model was established and proven to be quite efficient. Solvent A, which was identified using this protocol, seems to offer great potential as a new CO₂ solvent. Solvent screening with this protocol continues in our CO₂ Control Laboratory.

More extensive bench- and large-scale tests on Solvent A is scheduled in order to develop a more rigorous rate-based Aspen Plus model for Solvent A, which will provide more detailed performance information. The capability of the semi-empirical model already developed for Solvent A will be expanded to serve as a design tool, with the help of the to-be-developed Aspen Plus model and larger scale test data.

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