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Authors:

L. Ji

P. Bonnin-Nartker

M.G. Klidas

R. Zhang

Babcock & Wilcox

Power Generation Group, Inc.

Barberton, Ohio, U.S.A.

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Abstract

Babcock & Wilcox Power Generation Group, Inc. (B&W PGG) is conducting a comprehensive CO₂ solvent selection methodology in support of the commercial deployment of B&W PGG's RSAT™ CO₂ scrubbing process. Solvent screening at B&W PGG focuses on the next generation of CO₂ solvents with fast CO₂ absorption kinetics, high capacity, and low heat of absorption. Solvent related physicochemical properties such as chemical stability and environmental impact were also seriously considered when judging the potential of a specific candidate solvent.

Various apparatus were used at different scales to collect necessary data for solvent screening. Laboratory scale fundamental kinetic and thermodynamic data were collected, and pilot scale tests were performed for potential solvents. A semi-empirical model developed at B&W PGG was used to estimate solvent performance. A solvent ranking system was also developed and was used to rank potential solvents with promising performance from the model predication. The ranking system concentrates on comparing different solvent properties that contribute to various CO₂ avoidance cost components. It enables a comprehensive solvent selection process. A number of promising CO₂ solvents was identified through solvent screening. Solvents B and C were used as an example to illustrate the solvent selection protocol developed at B&W PGG.

Introduction

The increased concern with climate impact requires the acceleration of the pace for commercial deployment of

carbon mitigation processes, especially in the utility industry. Among potential technology for post-combustion CO₂ capture, a solvent-based chemical absorption process is so far the most mature technology and has been commercially applied to oil and natural gas flue gas clean-up for more than seventy years. The most common solvents used in those applications include monoethanolamine (MEA), diethanolamine (DEA), and promoted N-methyldiethanolamine (MDEA). There are extensive studies regarding solvent selection, from both academia and industry, trying to identify alternative solvents for coal flue gas CO₂ capture with better overall performance than those of historical solvents.

When conducting solvent screening, CO₂ absorption kinetics, capacity, and heat of absorption are parameters that attract the most attention of researchers. Kinetics determines the absorption efficiency and it would ultimately affect the capital cost of the absorber; capacity is related to the solvent flow rate and the sensible heat requirement; and heat of absorption would be an important factor affecting reboiler heat duty. Solvents with fast kinetics will require a shorter absorber design and less packing for the same CO₂ recovery rate. Higher CO₂ absorption capacity would require less solvent flow and subsequent less steam demand for bringing the solvent to the regeneration temperature. Lower heat of absorption will require less energy input to reverse the chemical reaction and release absorbed CO₂.

Other than the three key parameters mentioned above, solvent stability, operational issues and environmental impact are factors that should be evaluated when selecting solvents. Solvent degradation and corrosion will cause an

increase in operation and maintenance (O&M) costs by making up solvent and reducing the lifetime of the equipment. Higher solvent viscosity would increase the pump work in circulating the solvent between absorber and regenerator. Cost and availability of potential solvents in commercial scale could contribute to limitations of the process feasibility. Environmental impacts such as solvent toxicity and volatility deserve serious attention when judging a solvent potential, since causing secondary pollution while capturing CO₂ is not a scenario the public would be willing to take.

B&W PGG is pursuing the commercial deployment of B&W PGG's RSAT™ CO₂ scrubbing process by means of a rigorous solvent selection strategy. A solvent screening protocol was established at the Babcock & Wilcox Research Center (BWRC) with primary focus on the selection of next generation CO₂ solvents. Potential solvents were tested at three different facilities including a wetted-wall column (WWC), an RSAT simulator, and an RSAT pilot plant to evaluate their absorption-regeneration performance. Independent long-term degradation and corrosion tests are in progress on promising solvents and will be complete before commercial deployment.

This paper presents a status update on the solvent selection activities at B&W PGG with the representative, experimental, and simulation data to illustrate the protocol used to screen CO₂ solvents. A ranking system based on test results and literature information was developed for potential solvent comparison.

Solvent screening

Wetted wall column

A WWC was built and used to measure the kinetics and vapor-liquid equilibrium (VLE) data under typical operational conditions. Figure 1 shows the schematic of the apparatus. Kinetics of a specific solvent was determined by extracting liquid film mass transfer coefficient, k_g' , according to equation 1 shown below^[1]:

$$\frac{1}{K_G} = \frac{1}{k_g} + \frac{1}{k_g'}$$

where K_G is the overall mass transfer coefficient, k_g is the gas film mass transfer coefficient and k_g' is the liquid film mass transfer coefficient. K_G can be obtained from analysis of the data from the WWC and the correlation for k_g was experimentally determined for this specific WWC and reported elsewhere^[2].

Figure 2 is a typical plot of WWC kinetic data for various solvents. The x-axis is the equilibrium partial pressure of CO₂ which corresponds to different loading conditions. The y-axis is the liquid film mass transfer coefficient, k_g' , which is the measure of the kinetics of a specific solvent. Solvents B and C are candidate solvents tested at BWRC. Solvent X is a commercial benchmark CO₂ solvent. It is

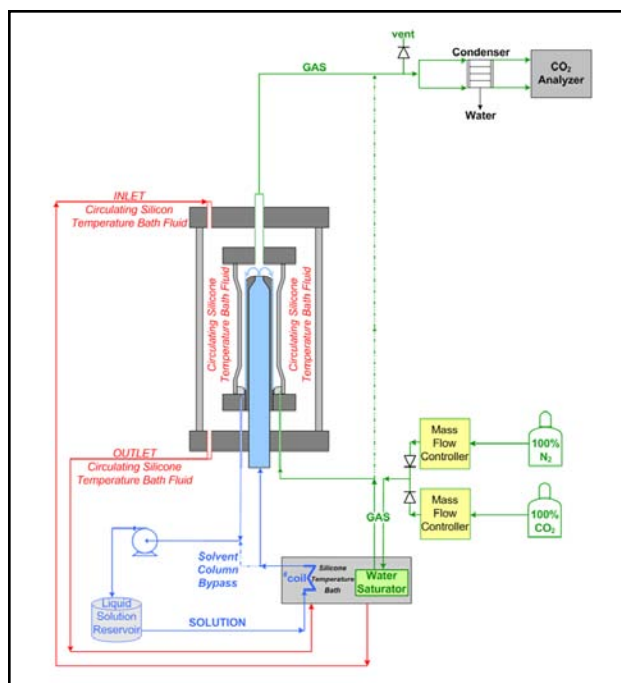


Fig. 1 Schematic of the B&W PGG WWC apparatus.

noticed that both new solvents showed faster kinetics, after comparing to Solvent X. Solvent B outperformed the other candidate in the entire CO₂ loading range.

CO₂ working capacity can also be estimated with the VLE data obtained from the WWC at different loadings. As can be seen from Figure 3, the theoretical maximum CO₂ capacity of Solvent B and C is from approximately 2.1 to 3.1 mol CO₂/kg solvent, which is a significant number, as compared to that of Solvent X.

B&W PGG RSAT simulator

The RSAT simulator is a modular bench-scale test facility used to investigate potential solvents encouraged by the WWC test results. Figure 4 shows the schematic of this facility. This unit consists of an absorber and a regenerator with 2 in. internal diameter and 4 ft of packing height. This unit has the capability to capture 1.0 kg/h of CO₂. One of the

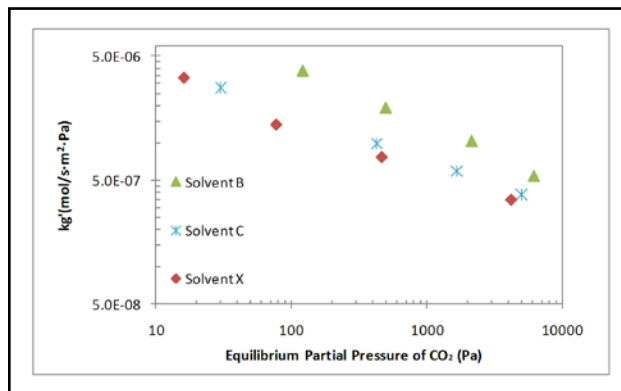


Fig. 2 Comparison of CO₂ absorption rate at 40C.

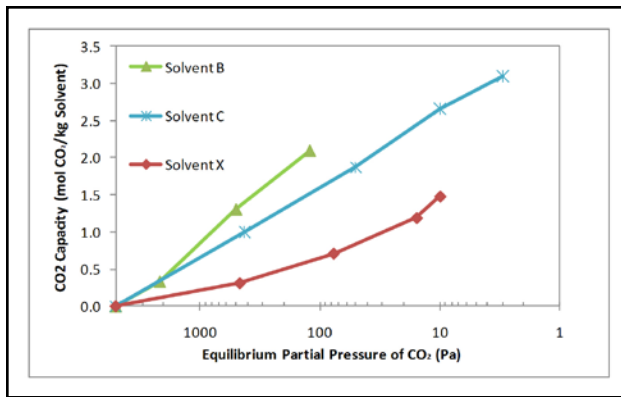


Fig. 3 Comparison of CO₂ capacity with 40C VLE data.

advantages of this facility is that it allows testing solvents in a relatively larger scale and in an integrated system. It can also be operated in three different modes: absorber and regenerator columns independently of each other; partially integrated absorber and regenerator column; and as a completely integrated system to simulate the industrial operational configuration. It is a very versatile facility because it is also a see-through unit in which solvent hydraulics are evaluated by observation.

With the capability of operating this unit in different modes, the RSAT simulator provides insights when investigating the impacts of different operation conditions such as absorber temperature profile and bulge determination, L/G ratio, regenerator pressure, and the effect of loading on the solvent performance. Since packing can be easily replaced, the effect of various packing on the mass transfer of the absorption/regeneration process can also be understood.

Figure 5 shows a temperature profile of a typical RSAT simulator test for Solvent B.

B&W PGG RSAT pilot plant

Figure 6 is the generic process flow diagram of the RSAT pilot plant at BWRC. The absorber and regenerator have an internal diameter of 2 ft and 60 ft in height. The designed

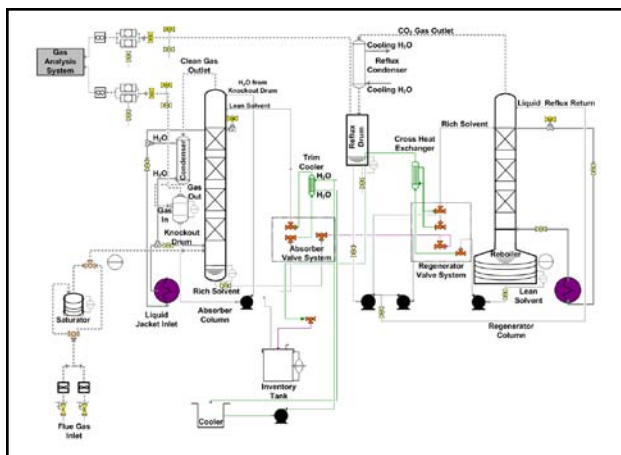


Fig. 4 Schematic of the B&W PGG RSAT™ simulator.

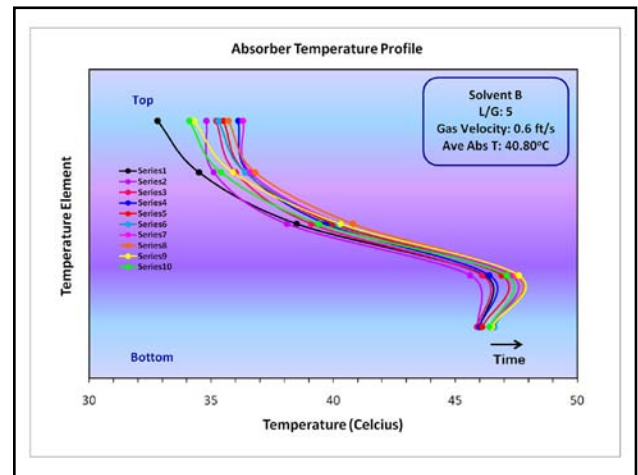


Fig. 5 Temperature profile of a typical RSAT™ simulator test.

CO₂ capture capacity is 7 tons/day at the removal rate of 90%. The RSAT pilot plant was built next to a Small Boiler Simulator II (SBSII) research facility which enables the operation for both recirculation mode with synthetic flue gas and once-through mode with coal flue gas generated from SBSII.

In addition, the pilot plant has a wide range of flexibility regarding the process flow sheet. Aside from the general absorption/regeneration system, supplemental equipment is also available for process improvements and solvent characterization. This equipment includes absorber inter-cooling, multiple flash tank and regenerator configurations, numerous temperature controls and other equipment. The supplemental equipment has been designed such that it can be put into or taken out of service easily, allowing for performance improvements applicable to each solvent.

Pilot tests for promising solvents were performed and the key parameters, such as reboiler heat duty, were compared. A semi-empirical model was developed for potential solvents and used to estimate the key parameters for these promising solvents^[3]. Pilot test data was used to fine-tune the semi-empirical model for a specific solvent; in addition, this data provides insights on solvent performance at a large-

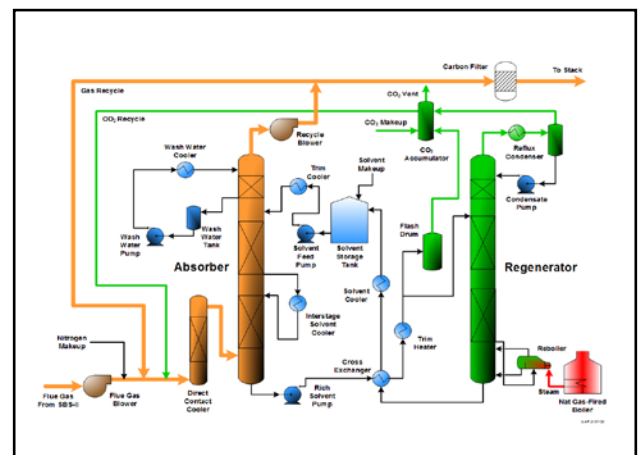


Fig. 6 Schematic of the generic B&W PGG RSAT™ pilot plant.

Table 1			
Comparison of Candidate CO₂ Solvents			
Solvent	Absorber Packing Height (ft)	Reboiler Duty (Btu/lb CO ₂)	L/G (wt)
B	0.9H _b	0.74Q _b	0.57(L/G) _b
C	H _b	0.75Q _b	0.40(L/G) _b
X	H _b	Q _b	(L/G) _b

scale which is helpful for evaluating their potential. Table 1 shows some key parameters estimated by the as-developed semi-empirical model for Solvents B and C, for a 500 MWe power plant with the absorber internal diameter fixed at 60 ft. This estimation is based on a generic RSAT process flow diagram, as shown in Figure 6 without process optimization.

Evaluation of potential solvents

The cost breakdown for CO₂ capture using the industrial benchmark solvent, MEA, is shown in Figure 7. It is noticed that regeneration energy represents approximately 45% of the total cost, compression work requires about 15% of the cost, and 21% of the cost goes to the capital. MEA solvent accounts for about 10% of the total cost. The rest is the O&M cost associated with the process. This different cost category should also be applicable to a generic CO₂ solvent.

As for the regeneration energy, it can be further broken down into sensible heat, heat of absorption, and the stripping heat. Solvents with large CO₂ capacity would require less sensible heat. Stripping heat is related to the heat of absorption, reversibility of the solvent, and the regenerator

temperature. Size of the absorber and associated packing are major parts of the capital cost. A solvent with fast kinetics will require a shorter and/or thinner absorber design and less packing for the same CO₂ recovery rate.

Solvent stability is another important parameter to consider when screening solvents. Other solvent characteristics such as viscosity, surface tension, toxicity, volatility, and foaming tendency are also important factors to consider when judging a solvent's potential. To screen solvents effectively, a table of solvent properties was made with the identification of relative importance on a scale of 0 to 10, with 10 being the most important property and 0 the least important property (Table 2).

Solvent selection with relative importance of properties listed in Table 2 was used to screen potential CO₂ solvents. Table 2 also listed the methods on how to obtain necessary information to evaluate a certain solvent property. It can be seen from the table that heat of absorption, capacity and kinetics are the three most important properties in evaluating potential CO₂ solvents, as CO₂ avoidance costs associated with these properties, primary energy and capital cost, contribute a significant part of the total cost.

Table 2			
Evaluation of Solvent Properties			
Property	Importance	Potential Show-Stopper	Evaluation Methods
Heat of absorption	10	Yes	Literature, Calorimetry Measurement, Calculation from VLE
Capacity	10	Maybe	Calculation from VLE
Kinetics	10	Yes	Literature, WWC
Toxicity	6	Yes	Literature/MSDS
Volatility	4	Maybe	Literature
Corrosivity	6	Maybe	Literature, Laboratory Test
Degradation	6	Yes	Literature, Laboratory Test
Foaming	4	Maybe	Literature
Viscosity	4	Yes	Literature, Pilot Test
Surface tension	4	Maybe	Literature
Cost	2	Maybe	Vendor

Oxidative and/or thermal degradation of a solvent would increase the operational cost dramatically. This could be a show-stopper for a potential solvent. Other physicochemical properties like viscosity, corrosivity, surface tension and foaming tendency are also important factors to consider since they all contribute to the CO₂ avoidance cost.

Environmental impact of the solvent is another challenge when selecting a solvent. The toxicity of a specific solvent could well become a show-stopper. It needs serious attention when screening a potential CO₂ solvent.

A ranking system was developed for screening different solvents with the consideration of various solvent properties and their impact on the total CO₂ avoidance cost. Solvents B and C were used as examples and the results are summarized in Table 3.

The attributes were categorized into four different parts: regeneration energy cost, which is essentially regeneration steam consumption; capital cost, which is primarily absorber, regenerator and the associated packing material cost; O&M cost, which is mainly solvent cost including make-up solvent due to degradation, and the operational cost associated with solvent properties such as corrosion, viscosity and foaming; and lastly environmental impact, which is primarily associated with the toxicity and volatility of a specific solvent.

The ranking system was based on a 0 to 10 scale with 10 corresponding to the most favorable condition for the overall CO₂ avoidance cost. In addition, weighting factors were estimated and assigned to different attributes, referenced from the CO₂ avoidance cost breakdown for MEA, as shown in Figure 7. Ranking of parameters contribute to the regeneration energy and capital cost were based on results summarized in Figures 2 and 3 and Table 1. Solvent stability and operation characters contributing to the O&M cost were ranked based on literature reports. Environmental impacts such as toxicity and volatility of the solvents were ranked from literature data. Total score for an ideal CO₂ solvent would be 10. Ranking scores for Solvents B and C are similar indicating their comparable yet competitive overall performance.

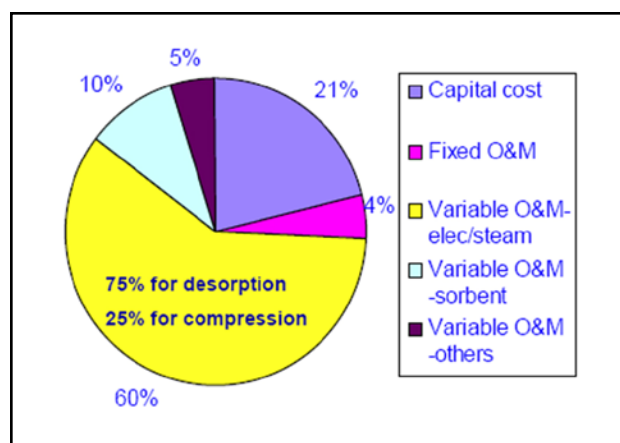


Fig. 7 CO₂ avoidance cost breakdown for MEA^[4].

This as-developed ranking system provided a convenient way to compare different solvents, with combined knowledge of test results and literature information.

Conclusions

A comprehensive CO₂ solvent selection protocol was developed at B&W PGG to support the commercial deployment of the RSAT CO₂ scrubbing process. It combines experimental test results, overall solvent performance predicted by as-developed semi-empirical model, and a solvent ranking system based on a total CO₂ avoidance cost analysis.

It has been proven to be an efficient yet accurate protocol for selecting solvents. Several promising solvents were identified through this process. Long-term degradation and corrosion tests were planned for these potential CO₂ solvents to further narrow the list of candidate solvents for commercial deployment.

Table 3 Potential Solvent Screening						
Attribute						
	Regeneration Energy		Capital Cost	O&M Cost	Environmental Impact	Total
	Heat of Absorption	Capacity	Kinetics, Surface Tension	Degradation, Corrosivity, Viscosity, Foaming	Toxicity, Volatility	84%
Impact on Total CO ₂ Avoidance Cost	25%	20%	20%	20%	15%	
Solvent B	9	8	9	8	7	8.30
Solvent C	8	9	8	7	9	8.15
Solvent X	7	7	8	8	7	7.40

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