OPTIMIZED SOLVENT FOR ENERGY-EFFICIENT, ENVIRONMENTALLY-FRIENDLY CAPTURE OF CO_2 AT COAL-FIRED POWER PLANTS

FINAL REPORT

FINAL REPORT – VOLUME 1

PERIOD OF PERFORMANCE
OCTOBER 1, 2011 TO APRIL 30, 2014

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ABSTRACT

The overall goal of this project, as originally proposed, was to *optimize* the formulation of a novel solvent as a critical enabler for the cost-effective, energy-efficient, environmentally-friendly capture of CO_2 at coal-fired utility plants. Aqueous blends of concentrated piperazine (PZ) with other compounds had been shown to exhibit high rates of CO_2 absorption, low regeneration energy, and other desirable performance characteristics during an earlier 5-year development program conducted by B&W. The specific objective of this project was to identify PZ-based solvent formulations that *globally* optimize the performance of coal-fired power plants equipped with CO_2 scrubbing systems. While previous solvent development studies have tended to focus on energy consumption and absorber size, important issues to be sure, the current work seeks to explore, understand, and optimize solvent formulation across the full gamut of issues related to commercial application of the technology: capital and operating costs, operability, reliability, environmental, health and safety (EH&S), etc. Work on the project was intended to be performed under four budget periods. The objective of the work in the first budget period has been to identify several candidate formulations of a concentrated PZ-based solvent for detailed characterization and evaluation. Work in the second budget period would generate reliable and comprehensive property and performance data for the identified formulations. Work in the third budget period would quantify the expected performance of the selected formulations in a commercial CO_2 scrubbing process. Finally, work in the fourth budget period would provide a final technology feasibility study and a preliminary technology EH&S assessment. Due to other business priorities, however, B&W has requested that this project be terminated at the end of the first budget period. This document therefore serves as the *final report* for this project. It is the first volume of the two-volume final report and summarizes Budget Period 1 accomplishments under Tasks 1-5 of the project, including the selection of four solvent formulations for further study.

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NOMENCLATURE

2-PE	2-piperidineethanol
AA	Amino acid
AAS	Amino acid salt
AAAS	Amine amino acid salt
AMP	Aminomethylpropanol
Arg	Arginine
ASME	American Society of Mechanical Engineers
B&W	Babcock & Wilcox Power Generation Group, Inc.
CSDS	Continuous Solvent Degradation Facility
DCC	Direct contact cooler
DEA	Diethanolamine
DEEA	Diethylethanolamine
DGA®	Diglycolamine®
DIPA	Diisopropanolamine
DMAE	Dimethylethanolamine
DMAPA	3-(Dimethylamino)propylamine
Dmg	Dimethylglycine
EFG+	Fluor Econamine FG Plus^{SM}
EH&S	Environmental, health, and safety
EOR	Enhanced oil recovery
ESP	Electrostatic precipitator
HAZOP	Hazard and operability methodology
IECM	Integrated Environmental Control Model, Carnegie Mellon University/NETL
IGCC	Integrated gasification combined cycle
LCOE	Levelized cost of electricity
L/G	Liquid to gas flow ratio
LNB	Low-NO_X burner
LSFO	Limestone forced-oxidation
Lys	Lysine
MAPA	3-(Methylamino)propylamine
MDEA	Methyldiethanolamine
MEA	Monoethanolamine
MW_e	Electrical output in megawatts

NCCC	The National Carbon Capture Center in Wilsonville, Alabama
NGCC	Natural gas combined cycle
OFA	Over-fire air
PC4	Post-Combustion Carbon Capture Center at the NCCC
ppm	Parts per million
Pro	Proline
PSO	Pseudo first order
PSTU	Pilot Solvent Test Unit at the NCCC
PTFE	Polytetrafluoroethylene
PZ	Piperazine
Sar	Sarcosine
SCR	Selective catalytic reduction
SEER	Safety and Environmental Evaluation Request
SNCR	Selective non-catalytic reduction
Sulf	Sulfolane
Tau	Taurine
TCLP	Toxicity Characteristic Leaching Procedure
TEA	Triethanolamine
Tyr	Tyrosine
UC	University of Cincinnati
UT	The University of Texas at Austin
US DOE-NETL	U. S. Department of Energy National Energy Technology Laboratory
VOC	Volatile organic compound
VLE	Vapor-liquid equilibrium
WWC	Wetted-wall column
α	CO_2 loading (mol/mol$_{alk}$)
μ	Dynamic viscosity
v	Kinematic viscosity
ρ	Density

1.0 EXECUTIVE SUMMARY

1.1 Overview of the Technology

The capture and storage or utilization of carbon dioxide produced by coal-fired power plants is one promising approach for enabling the continued use of coal (and fossil fuels in general) in a carbon-constrained world. CO_2 scrubbing systems that employ a regenerable liquid solvent offer several potential advantages for realizing this goal. These systems are:

- Commercially available, although there is limited experience with large coal-fired applications,
- Applicable to both new and existing coal-fired power plants, unlike the integrated gasification combined cycle (IGCC) approach, and
- Applicable in either full-flow or slipstream (partial) capture scenarios, unlike both the IGCC and oxy-combustion approaches.

A schematic of a typical regenerable CO_2 scrubbing process, commonly referred to as absorption-stripping, is shown in Figure 1.1. These processes effect the removal of CO_2 from power plant exhaust gas using a wet scrubber, or absorber, similar to absorbers used to remove SO_2 from flue gases. Energy, often in the form of low-pressure steam, is used to recover the CO_2 from the solvent in the regenerator. The recovered CO_2 is dried and compressed for subsequent storage or utilization, and the regenerated solvent is pumped back to the absorber for reuse. CO_2 scrubbing systems using simple amines have been successfully applied in the petrochemical industry for decades. A major disadvantage of these systems, however, when applied to coal-fired power plants, is their high cost. It is estimated that a conventional amine-based CO_2 scrubbing process would reduce the net electrical output of the power plant by nearly one-third, and increase the cost of electricity by 60 to100%. Reducing these costs is, in the broadest sense, the rationale for the project described, herein.

1.2 Goals and Objectives of the Project

The overall goal of this project is to optimize the formulation of a novel solvent as a critical enabler for the cost-effective, energy-efficient, environmentally-friendly capture of CO_2 at coal-fired utility plants. The prototype solvent formulation is an aqueous solution of concentrated piperazine (PZ), a solvent that has been shown to exhibit high rates of CO_2 absorption, low regeneration energy, and several other desirable performance characteristics during tests conducted both by B&W and by other investigators. Through recent testing B&W has been able to further show that it is possible to modify many of the performance characteristics of a concentrated PZ solvent by adding other compounds to the formulation *while maintaining the desirable performance characteristics of the PZ solvent.*

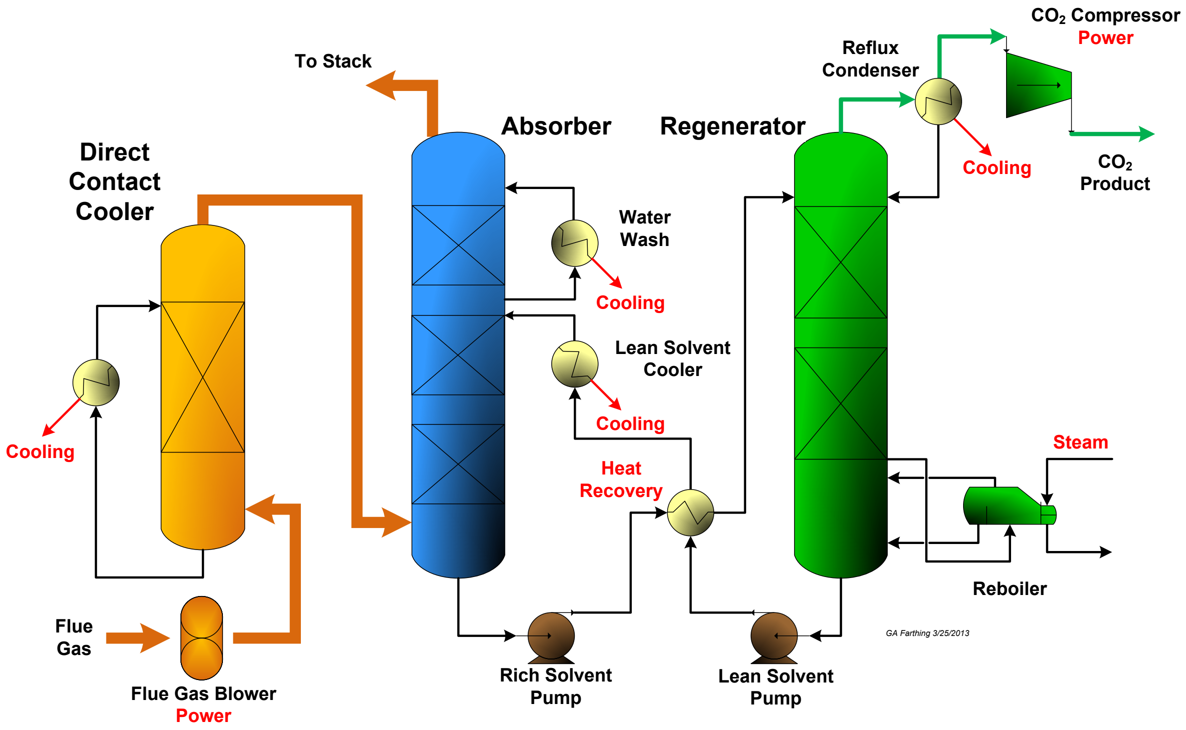

Figure 1.1 Regenerable Solvent Process

The feasibility of using solvent formulations containing high concentrations of PZ is not immediately obvious. In aqueous solution, PZ exhibits a room temperature solubility limit of about 14 wt%. Professor Gary Rochelle and his research group at the University of Texas at Austin (UT) pointed out, however, that the solubility of PZ is strongly affected by CO_2 loading, and that clear solutions containing more than 40 wt% PZ can be prepared in the presence of CO_2. The UT team ultimately described how, through the proper control of CO_2 loading, a “solubility window” can be maintained in which an absorption/stripping process can be successfully operated[1].

Concentrated PZ provides extremely high rates of absorption, reasonably good CO_2 carrying capacity, low regeneration energy (due to favorable thermodynamic characteristics), relatively

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[1] Rochelle, G.T., et al., United States Patent 7,938,887 B2, May 10, 2011.

low volatility, and reduced CO_2 compression costs provided by regeneration at high pressure (enabled by PZ's good resistance to thermal degradation). A solvent comprising concentrated PZ, alone, is not a panacea, however. Solid-phase piperazine hexahydrate ($PZ \cdot 6H_2O$) and protonated piperazine carbamate monohydrate ($H^+PZCOO^- \cdot H_2O$) can precipitate from the solvent solution if CO_2 loadings are allowed to get too low or too high, respectively. This significantly limits the CO_2 loading range permissible which, in turn, limits the solvent's CO_2 carrying capacity. Operation near saturation can also impact the operability and reliability of the system if troublesome deposits tend to form during normal operation, or during system upsets. Piperazine is more expensive than the more conventional monoethanolamine (MEA) solvent, although this cost might be offset by piperazine's lower rates of degradation and evaporation. PZ is somewhat less biodegradable than MEA, and is harder to handle due to its higher freezing temperature. Finally, the performance of concentrated PZ solvents is simply not as well studied or well understood as that of more conventional solvents such as MEA.

Previous development work at B&W, in-house work conducted over several years at a cost of many millions of dollars, has quantitatively demonstrated the desirable performance characteristics of concentrated PZ-based solvents through testing programs at laboratory, bench, and pilot scales.

It is important to state that the work being conducted under this project is therefore *not* simply directed at establishing the technical feasibility of using PZ-based solvents for CO_2 scrubbing at coal-fired power plants. Rather, this project has the specific objective of identifying PZ-based solvent formulations that *globally* optimize the performance of coal power plants equipped with CO_2 scrubbing systems. While previous solvent development studies tended to focus on energy consumption and absorber size, important issues to be sure, the current work seeks to explore, understand, and optimize solvent formulation across the full gamut of issues related to commercial application of the technology: capital and operating costs, operability, reliability, environmental, health and safety (EH&S), etc.

The underlying premise is that solvent deficiencies such as those described above can be minimized or eliminated, and solvent advantages can be enhanced, through the novel addition of other chemical species to the basic PZ-based solvent. Formulations of interest comprise solutions containing at least 14 wt% PZ in combination with hindered amines, tertiary amines, inorganic amino acid salts, organic amino acid salts, inorganic carbonate salts, and/or other soluble organic compounds.

1.3 Project Participants

In addition to US DOE-NETL and B&W, the following organizations comprise the project team:

University of Cincinnati: Professor Stephen W. Thiel, Associate Professor, School of Energy, Environmental, Biological, and Medical Engineering, University of Cincinnati (UC), and his research team would use the facilities of their Adsorption and Ion Exchange Laboratory to provide heat capacity, vapor-liquid equilibrium, and heat of absorption data for candidate solvent formulations. These data are critical for accurate simulation model predictions. Laboratory work at the University of Cincinnati would occur during Budget Period 2 of the project.

First Energy: Ms. Eileen M. Buzzelli, Director, FE Technologies and Corporate METT, serves on the project Advisory Committee along with B&W management personnel. The Committee will meet periodically to review and advise on the commercial applicability of project plans and results.

1.4 Scope of Work

Work on the project was planned to be performed under four budget periods as illustrated in Figure 1.2. The objective of the work in the first budget period has been to identify several candidate formulations of a concentrated PZ-based solvent for detailed characterization and evaluation. The objective of work in the second budget period was to generate reliable and comprehensive property and performance data for the identified formulations. The objective of work in the third budget period was to quantify the expected performance of the candidate formulations in a representative CO_2 scrubbing process. The overall objectives of the fourth budget period were to complete a final technology feasibility study and a preliminary technology EH&S assessment. These assessments would serve to establish the feasibility of the chosen solvent formulation on economic, technical, environmental, and safety grounds. Due to other business priorities, however, B&W has requested that this project be terminated at the end of the first budget period.

The project makes extensive use of *existing* laboratory, bench, and pilot facilities at B&W's Research Center located in Barberton, Ohio. Specialized equipment for solvent development and characterization includes a wetted-wall column for solvent thermodynamic and chemical kinetics characterization, electrochemical cells for corrosion studies, a bench-scale process simulator for process optimization and operability studies, and a 7 ton/day, pilot-scale CO_2 scrubbing system for obtaining representative solvent and process performance data. A new bench-scale continuous solvent test apparatus has been constructed to characterize solvent degradation under conditions representative of a coal-fired flue gas application. Planned laboratory calorimetric work at the University of Cincinnati would provide vapor-liquid equilibrium (VLE) data, heat of absorption and heat capacity information. Experimental work has and would be supported by performance predictions using B&W's in-house semi-empirical and Aspen Plus® rate-based simulation computer models.

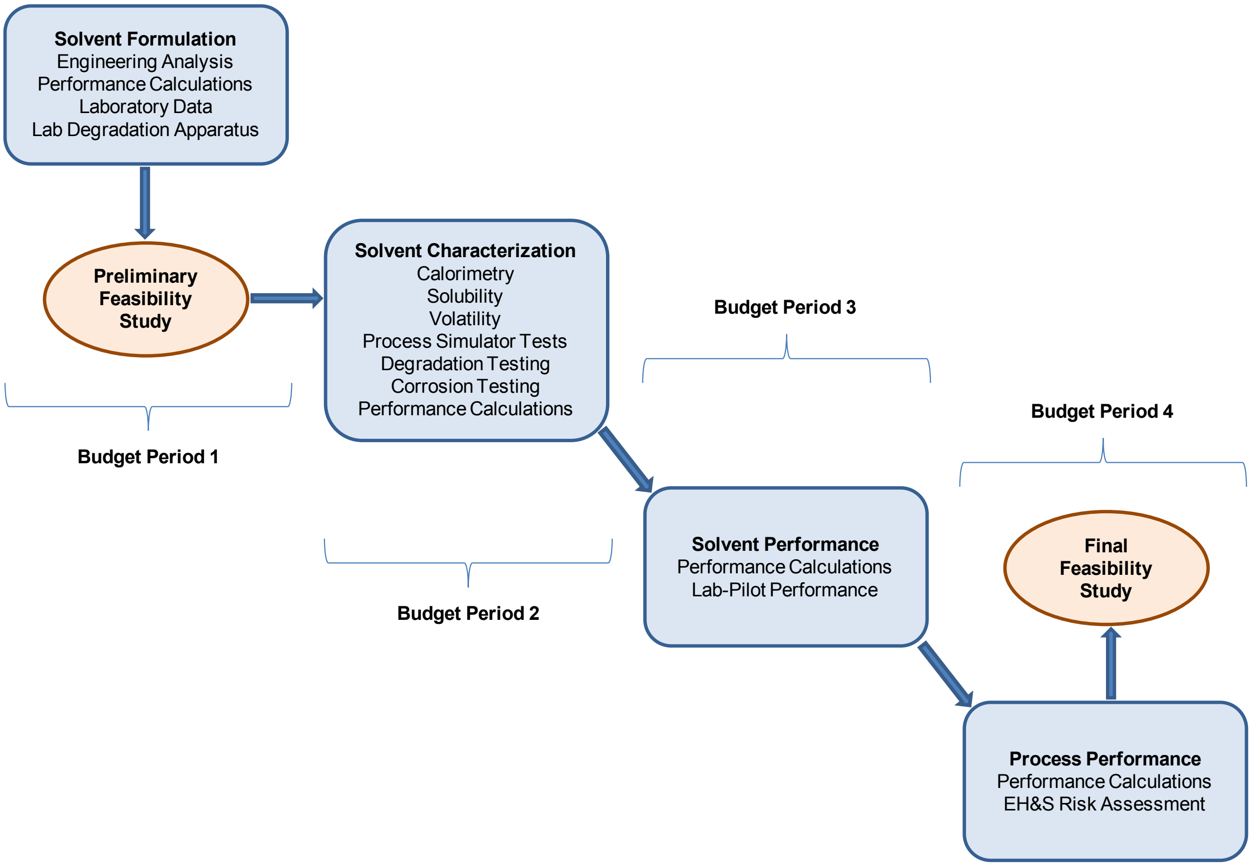
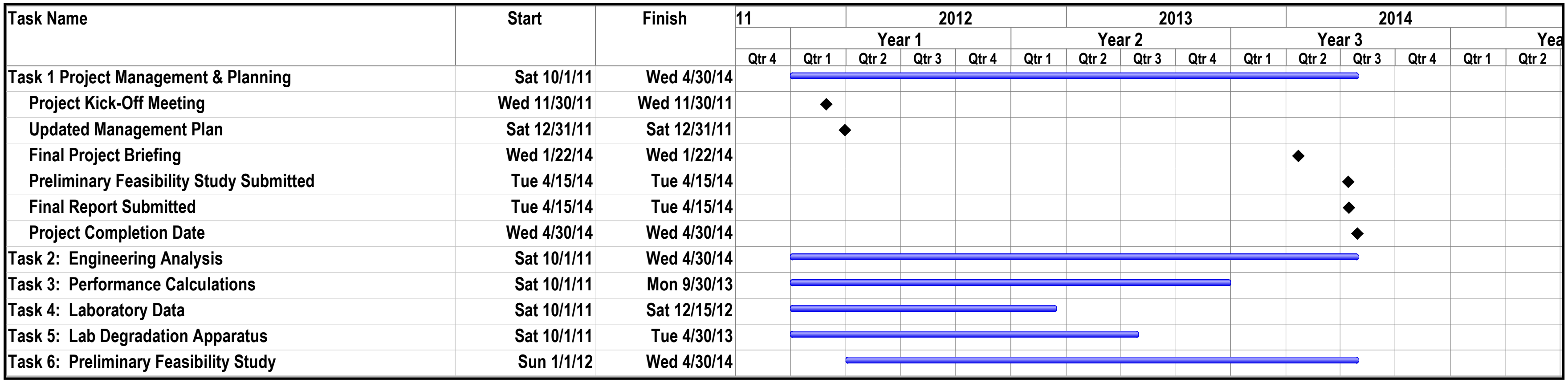


Figure 1.2 Overall Project Scope of Work

1.5 Project Schedule

The abbreviated project schedule (Budget Period 1) is shown in Figure 1.3, comprising 6 tasks spanning a total of 31 months.



Task Name	Start	Finish
Task 1 Project Management & Planning	Sat 10/1/11	Wed 4/30/14
Project Kick-Off Meeting	Wed 11/30/11	Wed 11/30/11
Updated Management Plan	Sat 12/31/11	Sat 12/31/11
Final Project Briefing	Wed 1/22/14	Wed 1/22/14
Preliminary Feasibility Study Submitted	Tue 4/15/14	Tue 4/15/14
Final Report Submitted	Tue 4/15/14	Tue 4/15/14
Project Completion Date	Wed 4/30/14	Wed 4/30/14
Task 2: Engineering Analysis	Sat 10/1/11	Wed 4/30/14
Task 3: Performance Calculations	Sat 10/1/11	Mon 9/30/13
Task 4: Laboratory Data	Sat 10/1/11	Sat 12/15/12
Task 5: Lab Degradation Apparatus	Sat 10/1/11	Tue 4/30/13
Task 6: Preliminary Feasibility Study	Sun 1/1/12	Wed 4/30/14

Figure 1.3 Project Schedule

1.6 Purpose of This Report

Due to the termination of the project at the end of the first budget period, this document serves as the *final report* for this project. It is the first volume of the two-volume final report and summarizes Budget Period 1 accomplishments under Tasks 1-5 of the project, including the selection of four solvent formulations for further study. Work completed under Task 6 is described in a separate report volume entitled “Optimized Solvent for Energy-Efficient, Environmentally-Friendly Capture of CO_2 at Coal-Fired Power Plants, Final Report – Volume 2, Preliminary Technical and Economic Feasibility Study”.

1.7 Summary of Budget Period 1 Activities

1.7.1 Task 1 – Project Management and Planning

Objectives

The objectives of this task are to provide:

- Coordination and communication with US DOE-NETL and other project participants
- Timely and efficient execution of the project scope
- Monitoring and control of project scope, cost, schedule, and risk
- Maintenance and revision of the Project Management Plan as required

Work under this task also ensures that all technical project performance information is supplied to US DOE-NETL through the timely delivery of topical reports and a comprehensive final project report:

- *Preliminary Technical and Economic Feasibility Study (Task 6)*
- *Final Project Report*
- *Research Performance Progress Reports and Financial Reports (Quarterly)*
- *Other Periodic and Topical Reports.* Issued as required in accordance with the Project Management Plan and the "Federal Assistance Reporting Checklist"

Accomplishments

Work performed under Task 1 comprised coordinating activities related to the various tasks, providing the necessary resources, and completing the appropriate reports. Other specific activities included:

- A project *Kick-off Meeting* was held at the US DOE-NETL Pittsburgh campus on November 30, 2011.
- The *Project Management Plan* was updated based on changes made to the Statement of Project Objectives during contract negotiations, input from proposal reviewers, discussions with the US DOE-NETL Project Manager, and discussions held during the project Kick-off Meeting.
- A *technical presentation* was made at the annual NETL CO_2 Capture Technology Meeting held in Pittsburgh on July 9-12, 2012.
- A final project briefing was held at the US DOE-NETL Pittsburgh campus on January 22, 2014

1.7.2 Task 2 – Engineering Analysis

Objectives

The overall goal of this project is to identify, develop, and validate a concentrated piperazine-based solvent formulation that globally optimizes the technical, economic, and environmental performance of a CO_2 scrubbing system for coal-fired utility boilers. The initial stages of a solvent selection program (i.e., the work described, herein) are particularly challenging since initial candidate selections must be made without the benefit of good fundamental solvent property data, making it difficult to even roughly estimate the performance of a given candidate. Of course the work of this project builds on years of previous development work at B&W that had already narrowed the field to a family of solvent formulations comprising blends containing PZ in concentrations above about 14 wt%.

The specific objectives of Task 2 were to identify and evaluate promising solvent formulations, and to:

- Select *12 initial* candidates for more extensive evaluation under Tasks 3 and 4
- Select *4 final* candidates to carry forward

Methods

A 40.8 wt% PZ solvent formulation served as the prototype, or baseline, formulation throughout the Budget Period 1 work. It exhibits a variety of desirable characteristics that provided important quantitative measures of performance against which the predicted performance of new PZ-based candidates were judged. Further, the 40.8 wt% PZ solvent formulation had been well characterized by B&W through extensive testing at the laboratory, bench, and pilot scales supplemented by comprehensive rate-based computer simulation modeling. The 40.8 wt% PZ formulation also exhibits a variety of less-than-desirable performance characteristics that naturally served to establish initial performance goals for an improved PZ-based formulation.

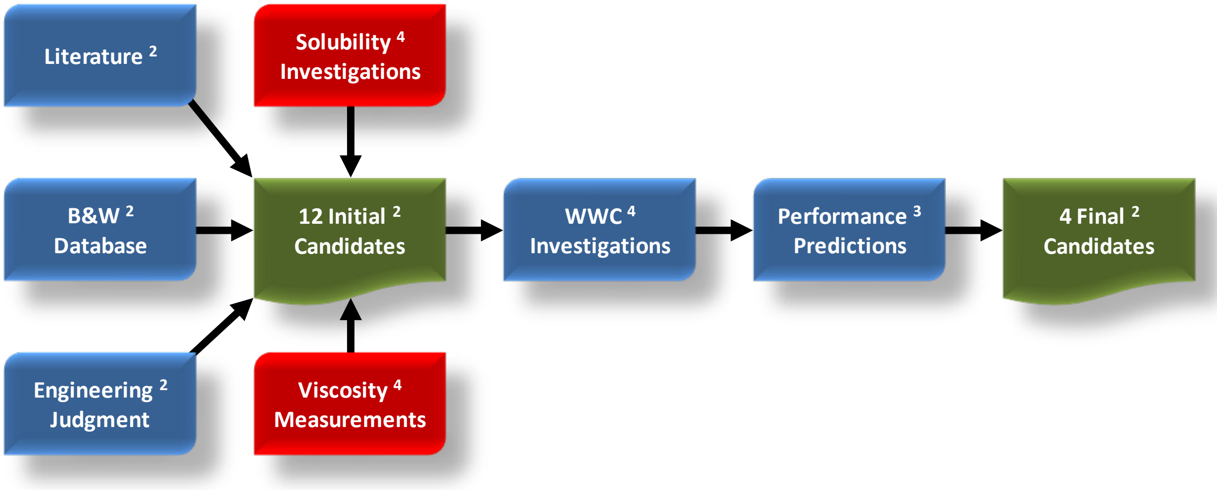


Figure 1.4 Overview of Budget Period 1 Solvent Selection Activities

The overall methodology used to identify, evaluate, and select promising solvent formulations is illustrated in Figure 1.4. The tasks under which each of the various supporting activities was performed are indicated by superscripts in the figure. The original project plans called for the “long list” of discovered solvents to be trimmed to 12 initial candidates using only *existing* B&W data, literature data, and engineering analysis. It soon became apparent, however, that existing information and theoretical considerations were not sufficient to make the needed judgments for innovative, never-been-tested, solvent formulations. Additional laboratory characterization tests, shown in red in Figure 1.4, were therefore conducted to provide the needed insights. The additional testing comprised solubility studies and the characterization of formulation viscosities.

Accomplishments

A “long list” of 55 potential PZ-based formulations, shown in Table 1.1, was developed based on literature review, previous B&W solvent work, and brainstorming activities. These formulations were then evaluated according their expected performance related to factors such as: heat of absorption, working capacity, kinetic rate, toxicity, solubility, degradation, volatility, corrosivity, viscosity, foaming tendency, surface tension, and raw material cost. It should be noted that quantitative information on these factors for these developmental formulations was, in general, not available at this early stage of the work. Many of the decisions made during this evaluation were of a very qualitative, “gut feel” nature. Information available in the literature or through earlier B&W work was supplemented by the added laboratory solubility and viscosity characterization studies.

Table 1.1 “Long List” of Candidate Solvent Formulations

Type	Formulation	Concentration *wt%*
Amine	PZ	40
	PZ	45
Amine Blend	PZ/DEEA	21/29
	PZ/2-PE/DMAE	12/7/30
Carbonate	K_2CO_3	20
	PZ/ Na_2CO_3	14/20
	PZ/ $(NH_4)_2CO_3$	14/20
	PZ/ K_2CO_3	13.8/22.14
	MAPA/ K_2CO_3	14/22
PZ / Organic	PZ/Sulfolane	40/5
	PZ/Sulfolane	40/10
	PZ/Sulfolane	40/15
	PZ/Sulfolane	40/20
	PZ/Sulfolane	40/30
	PZ/Methanol	40/2
	PZ/Ethanol	40/2
	PZ/Propanol	40/2
	PZ/Butanol	40/1
	PZ/Butanol	40/2
	PZ/Butanol	40/5
	PZ/Arg/Sulfolane	14.3/29.3/5
Amine Amino Acid Salt (AAAS)	MEA/Arg	7.4/20
	MEA/Pro	14.5/27.2
	MEA/Sar	15.2/22.6
	MEA/Tau	14/28.6
	PZ/(Arg/MAPA)	20/(20/10)
	PZ/(Arg/PZ)	20/(20/10)
	PZ/(Arg/Sar)	16/(25/3.6)
	PZ/(Sar/DMAPA)	20/(14/16)
	PZ/(SarMAPA)	20/(15/15)
	PZ/(Sar/MAPA)	20/(20/20)
	PZ/(Sar/PZ)	20/(15/15)
	PZ/(Dmg/DMAPA)	20/(30)
	PZ/(Dmg/MAPA)	20/(30)
	PZ/(Dmg/PZ)	20/(30)
	PZ/Dmg	20/23.9
	PZ/Arg	4/15
	PZ/Arg	9.9/19.6
	PZ/Arg	14/29
	PZ/His	15/27
	PZ/Lys	14.5/25
	PZ/Lys	16/26
	PZ/Lys	18.4/31.4
	PZ/Pro	19.2/25.7
	PZ/Pro	21/29
	PZ/Pro	22/29
	PZ/Pro	32/42
	PZ/Sar	20.3/21.1
	PZ/Sar	25/25
	PZ/Sar	26.5/27.7
	PZ/Tau	6.2/9
	PZ/Tau	12/17.8
	PZ/Tau	18.8/27
	PZ/Tau	21/30
	PZ/Tyr	13.7/29

This methodology resulted in the selection of 14 unique solvent formulations for further testing and evaluation under Tasks 3 and 4. The initial candidates are shown in Table 1.2.

Table 1.2 Selected Candidate Formulations

Category	Formulation	Composition (wt%)
Single Amine	PZ (baseline)	40.8
Amine Blend	PZ / DEEA	21 / 29
	PZ / 2-PE / DMAE	12 / 7 / 30
Amine/Amino Acid Salt	PZ / SarDMAPA	20 / 30
	PZ / SarMAPA	20 / 30
	PZ / SarMAPA	20 / 40
	PZ / SarPZ	20 / 30
	LysPZ	42
	ArgPZ	43
	ProPZ	50
	SarPZ	50
Inorganic Salt	MAPA / K_2CO_3	14 / 22
Organic Additive	PZ / Sulfolane	40 / 5
	PZ / Sulfolane	40 / 10

4 Final [2]
Candidates

Final candidate selection made use of the information generated during the initial selection process augmented by the results of laboratory characterization tests and performance predictions conducted under Tasks 4 and 3, respectively. Testing in the wetted-wall column provided CO_2 absorption rate and CO_2 solubility (VLE) data, and indirectly provided information on the enthalpy of CO_2 absorption. This information was then used in conjunction with B&W's existing in-house semi-empirical computer model to make preliminary predictions of solvent performance in a full-scale CO_2 scrubbing process. Key performance factors provided by the semi-empirical model included optimal lean and rich loadings, solvent CO_2 working capacity, absorber column liquid to gas mass flow ratio (L/G), required absorber packing height to achieve 90% CO_2 removal, heat of reaction for CO_2 absorption (ΔH_{abs}), and reboiler heat duty. Four final candidate formulations were thus chosen and are shown in Table 1.3. Had the project continued, these formulations would have been subjected to detailed characterization testing and performance evaluations in subsequent project phases.

Table 1.3 Final Candidate Formulations

Category	Formulation	Composition (wt%)
Amine Blend	PZ / DEEA	21 / 29
	PZ / 2-PE / DMAE	12 / 7 / 30
Amine/Amino Acid Salt	PZ / SarMAPA	20 / 30
Organic Additive	PZ / Sulfolane	40 / 5

1.7.3 Task 3 – Performance Calculations

Objectives

The objective of Task 3 was to provide CO_2 scrubbing process performance predictions for use in quantitatively evaluating the candidate formulations under Task 2. Process performance predictions are required to properly interpret the implications of the results of the wetted-wall column (WWC) tests, for example. WWC results do not directly provide information on regeneration energy requirements, for example, but it would be unreasonable to select candidate solvent formulations without considering this major performance factor. In the absence of actual process performance data, computer simulation modeling provides a means for estimating the needed information.

Methods

A rate-based semi-empirical process model was previously developed by B&W to support the early stages of solvent evaluation. A protocol for solvent screening using the semi-empirical model was subsequently established and validated against both more-rigorous simulation models and performance data from pilot-plant testing. The model can be used to estimate process performance on the basis of preliminary (and limited) laboratory data generated with the WWC. Some key parameters in the model include:

- 500 MW_e power plant
- CO_2 recovery rate is 90%
- Flue gas mass flow rate of 5,310,000 lbs/hr
- 12 vol% CO_2 (wet) in flue gas

- Flue gas pressure is 1.04 bars
- Structured packing is assumed
- Approach temperature for cross heat exchanger is 10 C
- Absorber diameter is kept the same *for all solvents*

While performance predictions could have been attempted using more rigorous Aspen Plus® simulations, the value of constructing such models in the early stages of solvent development work has been shown to be minimal in previous B&W studies.

Accomplishments

Performance 3
Predictions

The semi-empirical, rate-based model was used to estimate key performance parameters for the promising solvent formulation candidates. Only limited WWC experimental data is required to develop such a semi-empirical model for a specific solvent, which greatly enhanced the efficiency of the solvent evaluation and selection tasks. As described in the previous section, seven of the fourteen candidates carried through WWC testing were deemed of sufficient promise to warrant semi-empirical model evaluation. Both 40.8 wt% PZ, the baseline PZ-based formulation, and 30 wt% MEA, a widely-used acid gas removal solvent, were also included in the study for comparison purposes. Semi-empirical model studies were thus conducted on the following nine solvent formulations:

- 30 wt% MEA
- 40.8 wt% PZ
- 29 wt% DEEA / 21 wt% PZ
- 30 wt% DMAE / 7 wt% 2-PE / 12 wt% PZ
- 30 wt% SarMAPA / 20 wt% PZ
- 30 wt% SarPZ / 20 wt% PZ
- 5 wt% Sulf / 40.8 wt% PZ
- 43 wt% ArgPZ
- 50 wt% SarPZ

The B&W semi-empirical model was used to estimate optimal lean and rich loadings, solvent CO_2 working capacity (based on the optimal rich and lean loadings), absorber column liquid to gas mass flow ratio (L/G), required absorber packing height to achieve 90% CO_2 removal, heat of reaction for CO_2 absorption (ΔH_{abs}), and reboiler heat duty for each of the candidate formulations. The selections were primarily made on the basis of reboiler heat duty and cyclical, or working, capacity, since these two performance factors tend to encompass the net influences of the remaining factors. The four selected formulations include:

- 29 wt% DEEA/21 wt% PZ
- 30 wt% DMAE/7 wt% 2-PE/12 wt% PZ
- 5 wt% Sulf/40.8 wt% PZ
- 30 wt% SarMAPA/20 wt% PZ

The selection of the first three candidates on list was straightforward due to their low estimated reboiler heat duty requirements. Two of the formulations, 30 DMAE/7 2-PE/12 PZ and 5 Sulf/40.8 PZ, outperform 30 MEA by almost 30%. Further, the working capacity of the 5 Sulf/40.8 PZ formulation is over 100% higher than that of 30 MEA. Reboiler heat duty requirements for SarMAPA/PZ and SarPZ/PZ were quite similar to one another, however. The SarMAPA/PZ formulation was ultimately chosen as the fourth candidate due to its higher working capacity and slightly faster absorption rate.

Task 4 – Laboratory Data

Objectives

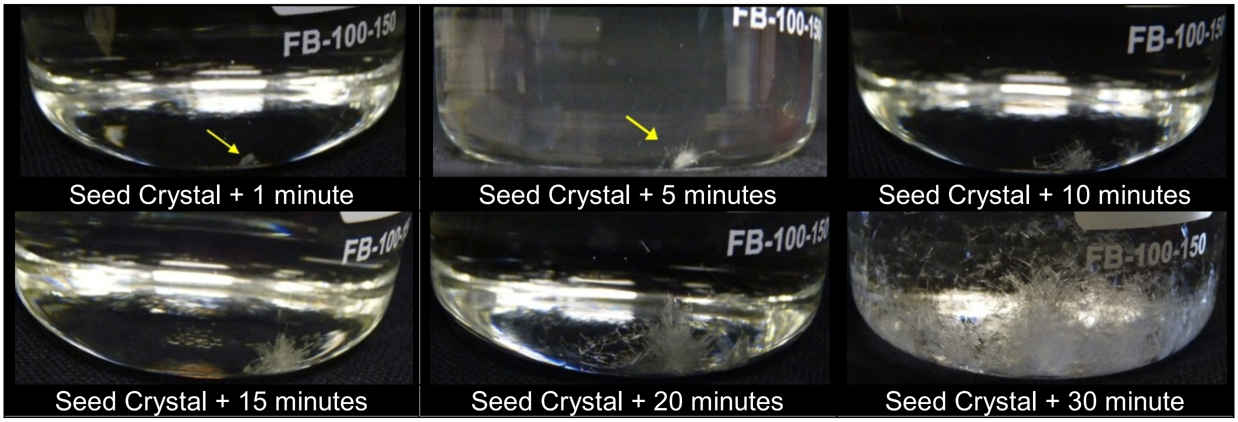
The objective of Task 4 was to enable meaningful solvent evaluations by providing preliminary but reliable property data for the candidate formulations. The original project plan called for the laboratory work to focus exclusively on WWC testing. However, as described earlier, it became necessary to also characterize the solubility and viscosity characteristics of the candidate formulations. This information, crucial to good decision making, simply could not be generated from first principles for the unique solvent formulations of interest in this study.

Methods

Solubility. Scoping experiments to determine the solubility characteristics of candidate formulations were conducted. Solutions were gravimetrically prepared using stock chemicals and high-purity water. The neat solutions were visually assessed for solubility during preparation, both immediately following mixing and after some time had elapsed. Then, CO_2 was gravimetrically reacted with the solvent to achieve a target CO_2 loading condition. Solubility observations were again made over time.

A significant complication was the tendency for $H^+PZCOO^-\cdot H_2O$ solutions to remain in a state of supersaturation for extended periods (months). The crystallization behavior of these relatively large-molecule crystals is apparently kinetically controlled, and the process by which the molecules become sufficiently well organized to form crystals can be quite slow. This behavior had been noted in our previous testing in the laboratory and also during pilot plant testing. It resulted in significant laboratory trial-and-error work to find ways to ensure that supersaturated solutions crystallized reliably, and in manageably short times. In the instances where the components appeared to be completely dissolved (clear solution), it became routine to add a seed crystal of the expected precipitate to ensure that the solution was not in a state of supersaturation. As a seed crystal was added to a supersaturated solution, crystal growth generally proceeded rapidly as illustrated in Figure 1.5.

Solutions that contained solids were heated and an approximate saturation temperature was thus obtained by observing the temperature at which all solids were dissolved. Approximate solubility operating "windows" were thus generated for the candidate formulations. These were then judged against the known operating window for the baseline formulation, 40.8 wt% PZ.



Seed Crystal + 1 minute

Seed Crystal + 5 minutes

Seed Crystal + 10 minutes

Seed Crystal + 15 minutes

Seed Crystal + 20 minutes

Seed Crystal + 30 minute

Figure 1.5 Crystal Growth in Rich PZ After Seeding

Viscosity. A highly viscous solvent may result in

- Low mass transfer rates in the absorber and regenerator,
- Low heat transfer rates in the cross heat exchanger and other heat transfer equipment, and
- High pumping power requirements.

These impacts of solvent viscosity have been clearly seen in previous bench- and pilot-scale testing of CO_2 scrubbing systems at B&W. Absorber performance has been seen to be surprisingly sensitive to even small changes in temperature due to its impact on solution viscosity. Through such testing it has been determined that solvent viscosity under absorber conditions (roughly 40-50 C) should be below about 10 cP – certainly below 20 cP.

The viscosity of candidate formulations depends on component type and concentration, CO_2 loading, and temperature. As with solubility behavior, it is difficult to accurately predict solution viscosity a priori. Viscosity measurements using a simple laboratory method were therefore made to ensure that the candidate formulations exhibited acceptable flow characteristics.

Wetted-Wall Column. B&W's wetted-wall column was used to collect CO_2 absorption rate and solubility data on candidate solvent formulations using previously established and validated experimental protocols. Such measurements were crucial to the proper selection of candidate solvent formulations. CO_2 absorption rate, or flux, and equilibrium CO_2 solubility data were obtained at different temperatures under various CO_2 loading conditions using the WWC. These data were then used to make preliminary performance predictions, as described under Task 3, which in turn were used to support the candidate selection methodology (Task 2).

Accomplishments

At least 141 solutions were prepared and evaluated in the laboratory.

Solubility ^{4} Investigations

Several candidate formulations of concentrated PZ solvents containing carbonates, other amines, and salts of amino acids, were investigated to establish a *very preliminary* understanding of their solubility behavior. Also evaluated were organic additives specifically designed to improve the solubility of PZ and its carbamates. Carbonate salts and the salts of amino acids, of interest primarily for reasons other than solubility improvement, tended to exhibit limited solubility under relevant CO_2 scrubbing conditions, adding a layer of complication onto the already complicated solubility behavior of PZ itself. Eight candidate formulations were eliminated from consideration based on their solubility characteristics, alone. Several other candidates exhibited what was considered to be only marginally acceptable solubility characteristics.

Viscosity ^{4} Measurements

A Cannon-Fenske style glass capillary viscometer was used to make preliminary measurements of the kinematic viscosity of several candidate solvent formulations at 20 and 40 C and various CO_2 loadings. Approximately 50 tests were conducted. Using B&W's "rule of thumb", six candidates with dynamic viscosities greater than about 10 cP at absorber conditions (about 40 C) were eliminated from further consideration. Several other candidates exhibited marginally acceptable viscosity characteristics.

WWC[4] Investigations

The 14 solvent formulations selected during the initial evaluation were characterized using the WWC. Several of the candidate formulations exhibited CO_2 absorption rates comparable to that of 40.8 wt% PZ, the baseline solvent for this study. Three solvents that exhibited impressive CO_2 absorption rates were PZ/2-PE/DMAE (12/7/30), PZ/Sulfolane (40/5) and PZ/Sulfolane (40/10). As anticipated, none of the candidate formulations exhibited absorption rates measurably higher than that of 40.8 wt% PZ.

CO_2 cyclical or working capacity was estimated using VLE data obtained from the WWC at different CO_2 loadings. Several of the candidate formulations exhibited higher theoretical maximum capacities than that of 40.8 wt% PZ. These included PZ/2-PE/DMAE (12/7/30), PZ/DEEA (21/29), PZ/Sulfolane (40/5), and PZ/Sulfolane (40/10).

During WWC testing, six of the 14 initial candidates were found to exhibit characteristics which made them noncompetitive and were eliminated from further consideration. In general, once a formulation was determined to be noncompetitive WWC testing was stopped. Overall, WWC testing resulted in eight candidate formulations being carried forward into the performance prediction (modeling) evaluation conducted under Task 3.

Task 5 – Laboratory Degradation Apparatus

Objectives

The objective of this task was to design and install a Continuous Solvent Degradation System (CSDS) to enable subsequent comprehensive solvent degradation investigations to be conducted. The final selection of an optimized solvent formulation will absolutely require high quality, representative, solvent degradation data.

Methods

Amine solvents such as MEA or PZ chemically degrade in a variety of ways including:

- *Thermal Degradation* due to exposure to the high temperatures of the regeneration process,
- *Oxidative Degradation* due the presence of oxygen in the flue gas,
- *Carbamate Polymerization* due to the presence of CO_2, and
- *Heat-Stable Salt Formation* resulting from reactions with flue gas constituents such as SO_X, NO_X, HCl, etc.

Degradation reactions can be accelerated by the presence of degradation or corrosion products and heat-stable salts, and through the catalytic effects of various metals. Metals can be present due to the corrosion of process equipment or the presence of fly ash or limestone from the upstream power plant processes.

The CSDS, shown schematically in Figure 1.6, is intended to simulate key features of industrial CO_2 capture processes in a representative way including cyclical absorption and regeneration process conditions, and the impacts of various contaminant species. The CSDS has been designed for continuous, unattended operation for tests lasting 100-1000 hours or more, and has been installed in an existing vented hood in B&W's CO_2 Control Laboratory. By design, it is *not* intended to replicate the entire CO_2 scrubbing process at small scale. Rather, it is designed to recreate the critical degradation-related conditions representative of an industrial CO_2 scrubbing process in a manner that can be safely operated unattended.

The oxidative reactor simulates low-temperature, atmospheric-pressure absorber conditions and the thermal reactor simulates high-temperature regenerator conditions in the range of 100-150 C (212-302 F). Solvent samples are switched between these systems for alternating exposure to oxygen and heat. Decoupling the two vessels is a practical simplification that provides several safety benefits by segregating the oxygen-containing and high-temperature vessels, and by reducing the complexity of high-pressure safeguards.

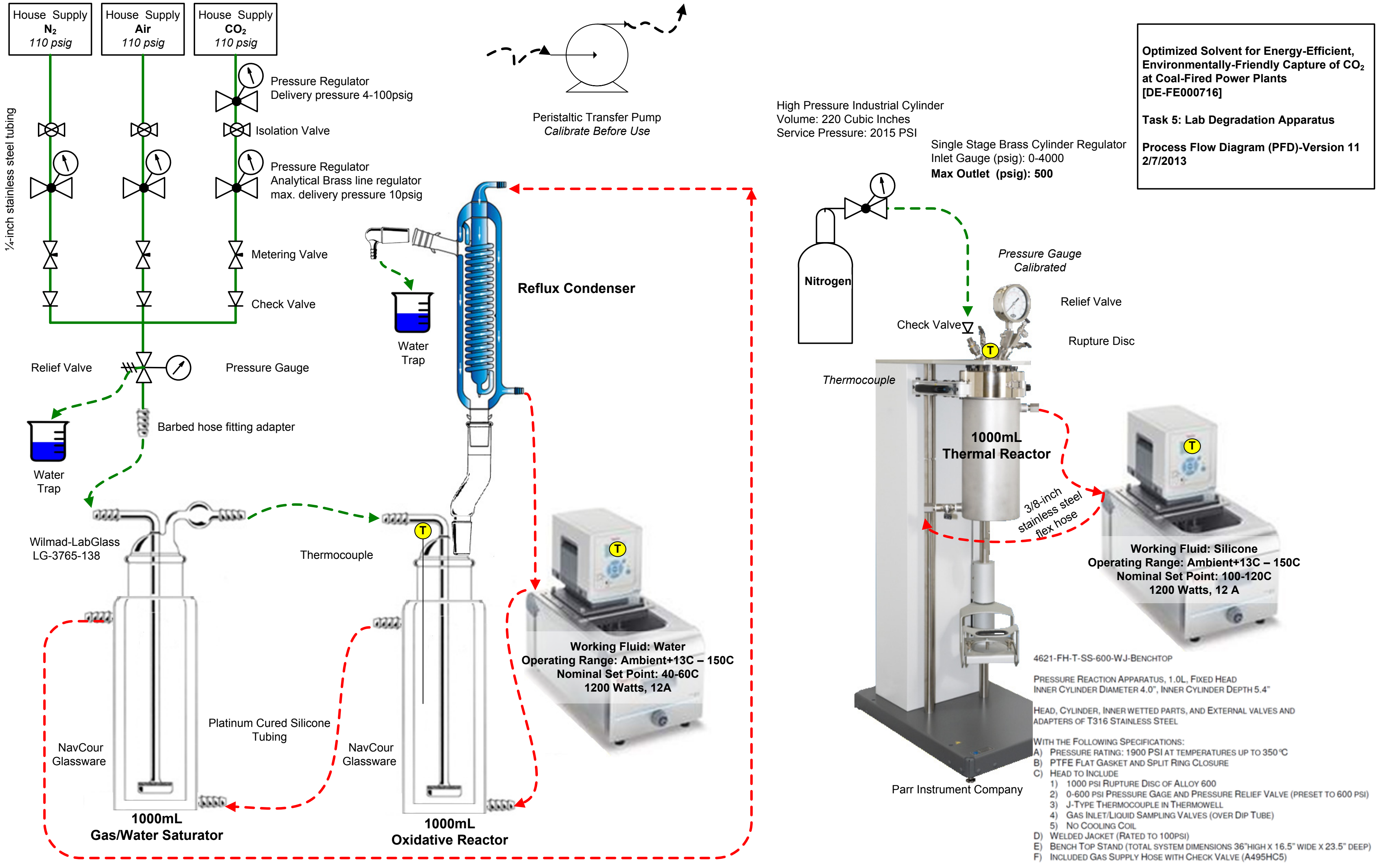


Figure 1.6 CSDS Detailed Design

Accomplishments

The CSDS has been installed in an existing 8-foot fume hood in the B&W CO_2 Control Laboratory (see Figure 1.7), and individual component shakedown has been completed. Approximately half of the hood space is dedicated to the CSDS apparatus, itself, while the remaining bench-top provides space for solvent preparation and wet chemistry analysis activities. All work under Task 5, and indeed all work under this project, has been conducted in accordance with the B&W Research Center Standard Practice Quality Assurance (QA) Manual which is compliant to ISO-9001:2008. All equipment has been installed; and the system is ready for use in subsequent project budget periods.

Figure 1.7 Continuous Solvent Degradation System (CSDS)

1.7.4 Task 6 – Preliminary Feasibility Study

Objectives

Work completed under Task 6 is described in detail in a *separate report volume* entitled "Optimized Solvent for Energy-Efficient, Environmentally-Friendly Capture of CO_2 at Coal-Fired Power Plants, Final Report – Volume 2, Preliminary Technical and Economic Feasibility Study".

For completeness and continuity, however, a few of the highlights of that study are included, below. The reader is referred to Volume 2 for a more complete description.

The objective of Task 6, Preliminary Technical and Economic Feasibility Study, was to further develop the proposed solvent concept and to establish a quantitative basis for subsequent process development and bench-scale testing. The overall approach was to consider the application of the new solvent/process concept to a 550 MW_e (net) coal-fired power plant. The study provides a quantitative measure of the potential performance improvements offered by the advanced process in terms of factors such as levelized cost of electricity (LCOE), cost of CO_2 capture, and parasitic power consumption. It also helps to identify gaps in system information needed for successful scale-up in later phases of process development, highlight additional laboratory data that may be required, and establish technology performance targets.

Methods

The Integrated Environmental Control Model (IECM), developed by Carnegie Mellon University's Department of Engineering & Public Policy with over two decades of continuous support from US DOE-NETL, was used to generate meaningful economic data for the performance of advanced solvent systems. IECM is a computer modeling program that facilitates systematic cost and performance analyses of emission control equipment at coal-fired power plants. The IECM allows the user to configure the power plant by selecting from a variety of pollutant control technologies:

Power Plants

- PC boilers (sub-, super-, and ultra-supercritical), integrated coal gasification & combined cycle (IGCC), natural gas combined cycle (NGCC), oxyfuel combustion

NO_X Control

- Wall, tangential, and cyclone firing, low NO_X burner (LNB) with over-fire air (OFA), selective catalytic reduction (SCR), selective non-catalytic reduction (SNCR), natural gas reburn

SO_2 Control

- Acid gas removal w/sulfur recovery, wet limestone w/forced oxidation (LSFO), wet limestone with dibasic acid, lime spray dryer, Mg-Lime Process

Particulate Matter Control

- Electrostatic precipitator (ESP), reverse gas fabric filter, reverse gas sonic fabric filter, shake and deflate fabric filter, pulse-jet fabric filter

Mercury Control

- Activated carbon injection (with and without spray cooling), intrinsic capture of mercury by other pollution control technologies

CO_2 Capture & Storage

- Amine scrubber, ammonia scrubber, membrane separation, pipeline transport, enhanced oil recovery storage (EOR), deep saline reservoir storage, ocean storage, enhanced coalbed methane storage, water-gas shift reactor, Selexol scrubber, chemical looping, O_2-CO_2 recycle (Oxyfuel)

The IECM also allows uncertainties in performance and costs to be characterized for key design criteria. The uncertainties can be iterated across the entire emission control system.

The IECM provided an ideal platform for estimating the performance impacts of an advanced PZ-based solvent formulation at this early stage of the project. A more rigorous, bottom-up approach to performance and cost estimation using the AspenPlus® platform, for example, would yield no more accurate results in light of the fact that the candidate formulations have not yet been properly characterized or subjected to performance testing. The model results presented, below, are therefore based on estimated properties of an advanced PZ-based solvent, and not on the specific properties of one of the four candidate formulations. A more detailed approach would have been used later in the project.

Assumptions for system boundaries, process design, and economic analysis used for the IECM evaluations were based on the guidelines provided in Attachment 3 of the original US DOE-NETL Funding Opportunity Announcement[1]. The IECM was used to estimate such factors as the levelized cost of electricity (LCOE), cost of CO_2 capture, and parasitic power consumption for various cases involving the application of the PZ-based process concept to a 550 MW_e (net) coal-fired power plant. For comparison purposes similar cases were developed using existing IECM input parameters based on the commercial Fluor Econamine FG Plus^{SM} CO_2 scrubbing process. In what follows these cases are referred to as the “Conventional Amine” process. All capture plant cases were compared to the Reference Plant case (Case-R) for the purposes of calculating such things as “Avoided Cost” and percentage increase in the LCOE.

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[1] “Bench-Scale and Slipstream Development and Testing of Post-Combustion Carbon Dioxide Capture and Separation Technology for Application to Existing Coal-Fired Power Plants”, US DOE-NETL, Funding Opportunity Number DE-FOA-0000403, Issued 1/31/2011.

Accomplishments

The results of seven case studies using the IECM are summarized in Table 1.4. The input plant design parameters and resulting performance of the Reference Plant (Case-R) are illustrated in Figure 1.8. It has been configured to match as closely as possible the US DOE-NETL evaluation guidelines, and is based on a state-of-the-art 550 MW_e (net) sub-critical pressure power plant firing an Illinois #6 bituminous coal. All cases are based on a 20-year plant life, an 85% capacity factor, and constant 2007 dollars. All capture plant cases include the cost of CO_2 compression to 2000 psia, but do not include CO_2 product transportation and storage costs.

It should be noted that the terms “new” and “retrofit” are used in a specific way in this study. *New plant* cases simply refer to simulations where the heat input (coal flow) to the power plant was *adjusted* to yield a net plant electrical output of 550 MW_e. In other words the size of the base plant was adjusted to accommodate the parasitic power requirements of the CO_2 scrubbing process and yield the desired plant output. *Retrofit plant* cases refer to simulations where the heat input (coal flow) to the power plant was *held constant* at the value equal to that of the Reference Plant. In other words the size of the base plant was held constant at that of the Reference Plant, and the plant output was allowed to drop according to the parasitic power requirements of the CO_2 scrubbing process – the idea being that this case reflects what would happen if the capture process were applied to an existing 550 MW_e (net) plant. The various capture plant cases are configured as follows:

Conventional Amine Capture Plant, Cases AM-N (new) and AM-R (retrofit): These cases are based on the use of the existing IECM configuration template for the Flour Econamine FG Plus^{SM} CO_2 scrubbing process, and are intended to provide a quantitative baseline for plant performance against which the performance of the advanced PZ-based process can be compared. The base plant configuration is identical to that of the Reference Plant in both cases, but its size in the two cases reflects the new and retrofit scenarios.

Advanced PZ-Based Capture Plant, Cases PZ-N (new) and PZ-R (retrofit): These cases are intended to estimate the performance of an advanced capture process based on the use of an advanced PZ-based solvent formulation. Each is directly comparable with the corresponding Conventional Amine case, *Cases AM-N (new) and AM-R (retrofit)*, respectively. All four cases are meant to conform to the US DOE-NETL evaluation guidelines, and therefore use the same base plant configuration. As an example, the input plant design parameters and resulting performance results for the Advanced PZ-Based Capture Plant (New), Case PZ-N (new), are illustrated in Figure 1.9.

The improved performance of the PZ-based plants relative to the conventional amine plants is primarily due to the following factors:

- *Absorber Size.* The absorber packing height required to achieve the target CO_2 removal efficiency is reduced due to the high absorption rates achievable with the PZ-based formulation.
- *Reboiler Heat Duty.* The required regeneration energy is lower due to the higher CO_2 working capacity and superior energetics and thermodynamics associated with the PZ-based formulation.
- *Compression Energy.* Parasitic power consumption associated with CO_2 compression is reduced due to the ability to regenerate the solvent at elevated pressure, which, in turn, is enabled by the good resistance to thermal degradation exhibited by the PZ-based formulation.
- *Solvent Makeup.* Solvent makeup is estimated to be significantly reduced due to the lower volatility and good resistance to degradation characteristic of the PZ-based formulation.
- *Reclaimer Waste.* Disposal costs associated with the disposal of reclaimer waste products are reduced due, again, to the solvent's resistance to degradation and, indirectly, to its lower corrosivity.

Advanced PZ-Based Capture Plant, Cases PZ-NU (new USC) and PZ-NUC (new USC, Compliant): These two cases use the same capture plant inputs as the other PZ-based cases. However, they depart from the US DOE-NETL evaluation guidelines by specifying a high efficiency, ultra-supercritical steam cycle plant as the base plant.

- Case PZ-NU (new USC) simply illustrates the impact of this substitution.
- Case PZ-NUC (new USC, Compliant) carries the analysis further by assuming that a CO_2 emission rate of only 1,100 lbs CO_2/MW-hr (net) must be achieved, rather than the 90% CO_2 capture assumed for all other cases. This emission rate actually exceeds the proposed carbon pollution standard for new power plants (1,100 lbs CO_2/MW-hr (gross)) issued by the U.S. Environmental Protection Agency on Sept. 20, 2013.

In summary, it can be seen from Table 1.4 that application of the advanced PZ-based process is projected to significantly reduce the cost and parasitic power impacts of CO_2 capture relative to application of the conventional amine process. Looking at just the "new" capture plant cases *relative to the performance of the Reference Plant*:

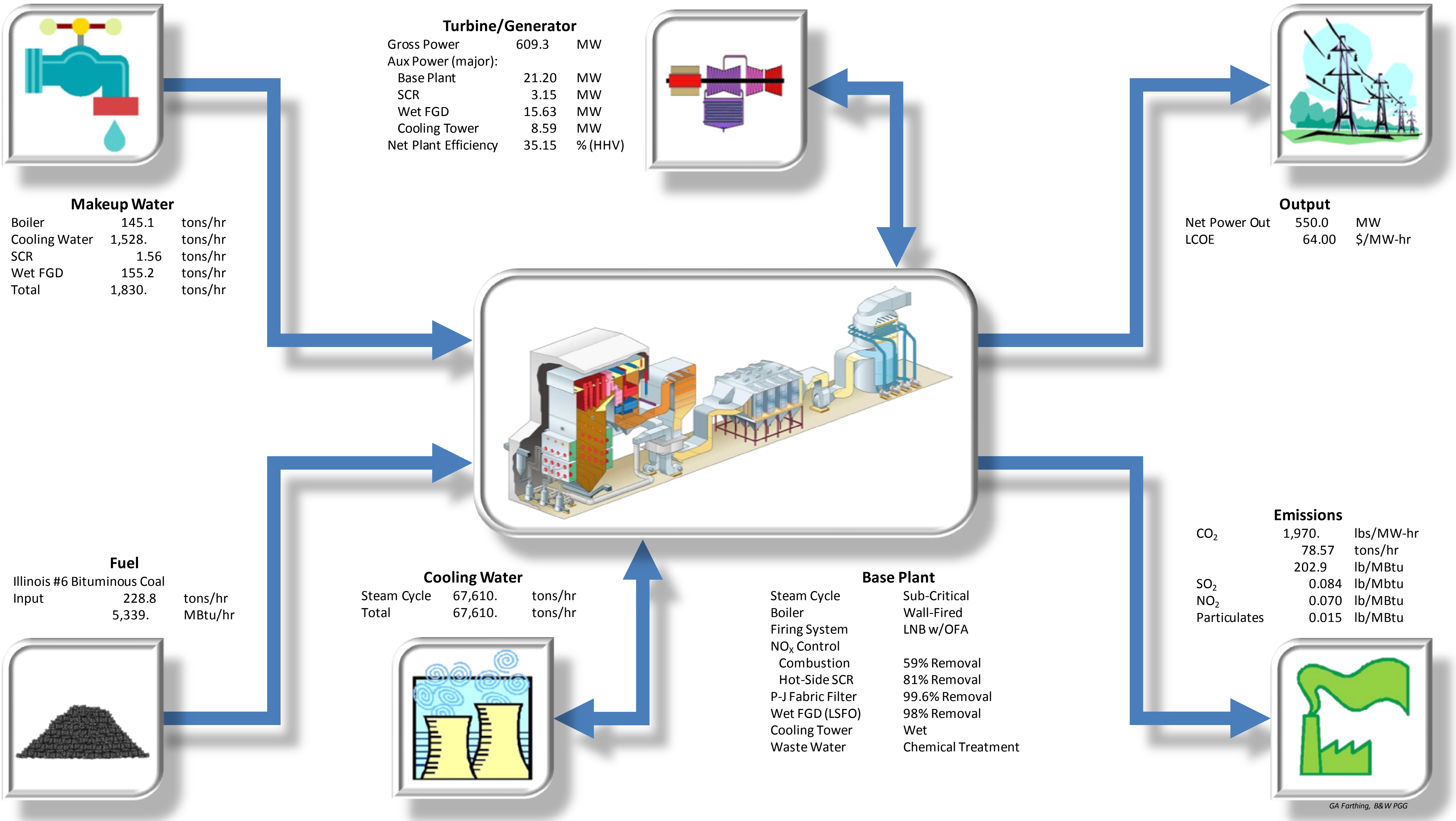
- The conventional amine process reduces net plant efficiency by 31% and increases the LCOE by 70%
- The advanced PZ-based process reduces net plant efficiency by 23% and increases the LCOE by 45%.

- The advanced PZ-based process used in conjunction with an ultra-supercritical base plant reduces net plant efficiency by only 4% and increases the LCOE by 36%.
- The advanced PZ-based process used in conjunction with an ultra-supercritical base plant and designed to meet a 1,100 lbs CO_2/MW-hr (net) emission rate actually *increases* net plant efficiency by 7% and increases the LCOE by only 16%.

Table 1.4 Capture Plant Case Studies

Performance Measures	**Reference Plant**	**Conventional Amine Capture Plant**		**Advanced PZ-Based Captue Plant**			
	Case-R Baseline	*Case AM-N New*	*Case AM-R Retrofit*	*Case PZ-N New*	*Case PZ-R Retrofit*	*Case PZ-NU New USC*	*Case PZ-NUC New USC Compliant*
Net Electrical Output, MW	550	550	379.2	550	425.4	550	550
CO_2 Capture Efficiency, %	-	90	90	90	90	90	40.2
Fuel Input (HHV), Mbtu/hr	5,339	7,743	5,339	6,902	5,339	5,535	4,982
Gross Electrical Output, MW	609.3	717.4	494.6	689.6	533.4	659.2	630.5
Net Plant Efficiency (HHV), %	35.15	24.24	24.24	27.19	27.19	33.91	37.67
CO_2 Emitted, lb/MW-hr	1,970	285.7	285.7	254.7	254.7	204.2	1,100
Cost of CO_2 Captured, $/ton	-	34.83	40.70	25.15	30.19	25.07	27.63
Cost of CO_2 Avoided, $/ton	-	59.78	69.58	39.46	46.85	31.08	29.20
LCOE, $/MW-hr	64.00	108.80	116.30	92.83	98.61	87.04	74.20
LCOE Increase, $/MW-hr	-	44.80	52.30	28.83	34.61	23.04	10.20
LCOE Increase, %	-	70	82	45	54	36	16

Case R: Reference Plant



Turbine/Generator

Gross Power	609.3	MW
Aux Power (major):		
Base Plant	21.20	MW
SCR	3.15	MW
Wet FGD	15.63	MW
Cooling Tower	8.59	MW
Net Plant Efficiency	35.15	% (HHV)

Makeup Water

Boiler	145.1	tons/hr
Cooling Water	1,528.	tons/hr
SCR	1.56	tons/hr
Wet FGD	155.2	tons/hr
Total	1,830.	tons/hr

Output

Net Power Out	550.0	MW
LCOE	64.00	$/MW-hr

Fuel

Illinois #6 Bituminous Coal

Input	228.8	tons/hr
	5,339.	MBtu/hr

Cooling Water

Steam Cycle	67,610.	tons/hr
Total	67,610.	tons/hr

Base Plant

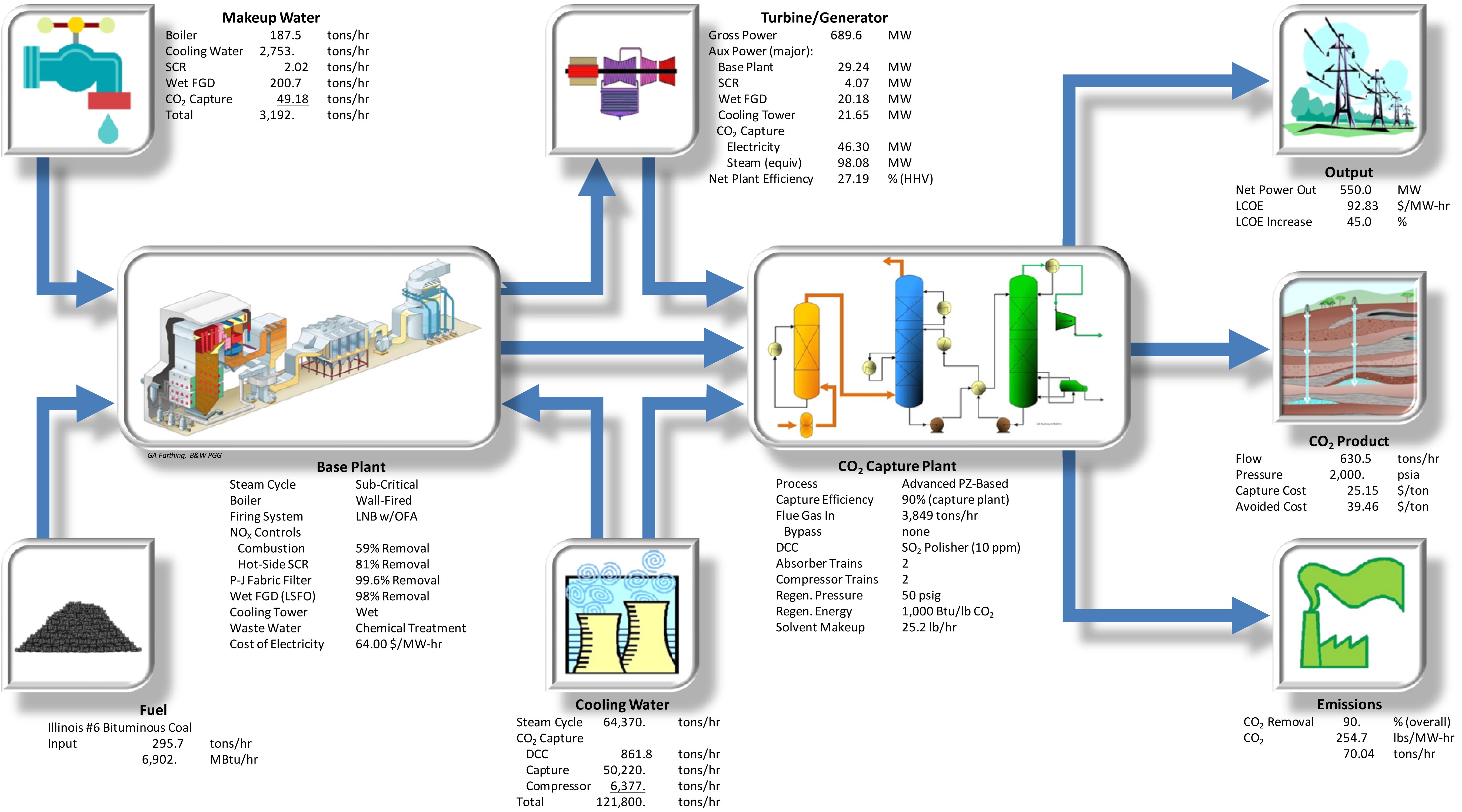
Steam Cycle	Sub-Critical
Boiler	Wall-Fired
Firing System	LNB w/OFA
NO_x Control	
Combustion	59% Removal
Hot-Side SCR	81% Removal
P-J Fabric Filter	99.6% Removal
Wet FGD (LSFO)	98% Removal
Cooling Tower	Wet
Waste Water	Chemical Treatment

Emissions

CO_2	1,970.	lbs/MW-hr
	78.57	tons/hr
	202.9	lb/MBtu
SO_2	0.084	lb/Mbtu
NO_2	0.070	lb/Mbtu
Particulates	0.015	lb/MBtu

Figure 1.8 Case R: Reference Plant

Case PZ-N: Advanced PZ-Based Capture Plant (New)



Makeup Water

Boiler	187.5	tons/hr
Cooling Water	2,753.	tons/hr
SCR	2.02	tons/hr
Wet FGD	200.7	tons/hr
CO_2 Capture	49.18	tons/hr
Total	3,192.	tons/hr

Turbine/Generator

Gross Power	689.6	MW
Aux Power (major):		
Base Plant	29.24	MW
SCR	4.07	MW
Wet FGD	20.18	MW
Cooling Tower	21.65	MW
CO_2 Capture		
Electricity	46.30	MW
Steam (equiv)	98.08	MW
Net Plant Efficiency	27.19	% (HHV)

Output

Net Power Out	550.0	MW
LCOE	92.83	$/MW-hr
LCOE Increase	45.0	%

Base Plant

Steam Cycle	Sub-Critical
Boiler	Wall-Fired
Firing System	LNB w/OFA
NO_x Controls	
Combustion	59% Removal
Hot-Side SCR	81% Removal
P-J Fabric Filter	99.6% Removal
Wet FGD (LSFO)	98% Removal
Cooling Tower	Wet
Waste Water	Chemical Treatment
Cost of Electricity	64.00 $/MW-hr

CO_2 Capture Plant

Process	Advanced PZ-Based
Capture Efficiency	90% (capture plant)
Flue Gas In	3,849 tons/hr
Bypass	none
DCC	SO_2 Polisher (10 ppm)
Absorber Trains	2
Compressor Trains	2
Regen. Pressure	50 psig
Regen. Energy	1,000 Btu/lb CO_2
Solvent Makeup	25.2 lb/hr

CO_2 Product

Flow	630.5	tons/hr
Pressure	2,000.	psia
Capture Cost	25.15	$/ton
Avoided Cost	39.46	$/ton

Fuel

Illinois #6 Bituminous Coal

Input	295.7	tons/hr
	6,902.	MBtu/hr

Cooling Water

Steam Cycle	64,370.	tons/hr
CO_2 Capture		
DCC	861.8	tons/hr
Capture	50,220.	tons/hr
Compressor	6,377.	tons/hr
Total	121,800.	tons/hr

Emissions

CO_2 Removal	90.	% (overall)
CO_2	254.7	lbs/MW-hr
	70.04	tons/hr

Figure 1.9 Case PZ-N: Advanced PZ-Based Capture Plant (New)

1.8 Conclusions

Project accomplishments during Budget Period 1 may be summarized as follows:

- The planned scope of work of Budget Period 1 has been successfully completed within the original project budget.
- Over 55 PZ-based solvent formulation candidates were identified and evaluated including PZ solutions containing other amines, amino acid salts, inorganic carbonate salts, and organic additives.
- Laboratory characterization work involved the preparation of over 140 solvent solutions. In addition to the planned WWC testing, the laboratory work comprised additional, unplanned testing to characterize candidate solubility and viscosity characteristics. This additional work was necessitated by the difficulties associated with predicting such properties for innovative solvent formulations where little previous work had been done.
- An initial set of 14 promising candidate formulations were comprehensively evaluated using B&W's WWC to provide quantitative vapor-liquid equilibrium (VLE), mass transfer, and heat of reaction data. The 14 formulations tested included 40.8 wt% PZ, which served as the baseline formulation throughout the Budget Period 1 work.
- The results of the WWC testing were used in conjunction with B&W's in-house semi-empirical process simulation model to predict required absorber packing height and L/G, reboiler heat duty, and solvent CO_2 working capacity for 7 remaining candidates. Model results were also developed for 30% MEA and 40.8% PZ for comparison purposes.
- Engineering evaluation augmented by laboratory data and performance predictions resulted in the selection of 4 final candidate formulations. The 4 recommended candidates are:
  - ✓ Piperazine (21 wt%) / Diethylethanolamine (29 wt%)
  - ✓ Piperazine (12 wt%) / 2-Piperidineethanol (7 wt%) / Dimethylethanolamine (30 wt%)
  - ✓ Piperazine (20 wt%) / { Sarcosine (15 wt%) / 3-(Methylamino)propylamine (15 wt%) }
  - ✓ Piperazine (40 wt%) / Sulfolane (5 wt%)
- A Continuous Solvent Degradation System (CSDS) was designed, fabricated, and installed in B&W's CO_2 Control Laboratory to enable comprehensive solvent degradation investigations to be conducted. The CSDS has been designed to representatively simulate solvent exposure conditions in an industrial CO_2 scrubbing process, and to provide for continuous, unattended operation for tests lasting 100-1000 hrs or more.
- A Preliminary Technical and Economic Feasibility Study was completed to further develop the proposed solvent concept and to establish a quantitative basis for subsequent process development and bench-scale testing. The study provides a quantitative measure of the potential performance improvements offered by the advanced process in terms of factors such as levelized cost of electricity (LCOE), cost of CO_2 capture, and parasitic power consumption.

2.0 BACKGROUND AND PRIOR WORK

2.1 Process Considerations

In the process of interest, traditionally referred to as an absorption-stripping process, CO_2 is removed from the flue gas using a wet scrubber, or absorber, very much akin to the wet scrubbers used for removing SO_2 from flue gases. There are some important differences between CO_2 and SO_2 scrubbers, however. CO_2 is present in much larger quantities than SO_2, meaning that, in general, throwaway processes are not attractive and the solvent must be regenerable, or reusable. CO_2 is also more difficult to remove from flue gases than SO_2, primarily due to its lower reactivity and very slow rate of hydration in water.

A schematic of a regenerable solvent CO_2 scrubbing process is shown in Figure 2.1. The flue gas stream from which CO_2 is to be removed is contacted with lean solvent (solvent which has not yet absorbed much CO_2) in an absorber vessel, or scrubber. CO_2 is absorbed by the solvent, and the clean flue gas is exhausted through the stack. The rich solvent (solvent which has absorbed a significant amount of CO_2) is then pumped to a regenerator wherein a temperature-swing process is used to remove (more-or-less distill, or strip) the absorbed CO_2 from the solvent for subsequent storage. Energy, often in the form of low-pressure steam supplied to a reboiler, is required to free the CO_2 from the rich solvent. The regenerated solvent is then pumped back to the absorber for reuse.

As a concrete example, monoethanolamine (NH_2 CH_2 CH_2 OH, or MEA), a primary amine, reacts with CO_2 by way of a reversible, exothermic reaction in the absorber to form (primarily) carbamate. The rich amine solution is then sent to the regenerator, wherein CO_2 is released by driving the chemical equilibrium from carbamate back to amine. This is accomplished in the regenerator by heating the solution to 110-120 C using steam supplied to the reboiler. Heating the solution not only causes the equilibrium solubility of CO_2 to decrease, but also evaporates some of the water in the solvent. The water vapor reduces the partial pressure of CO_2 in the gas phase, thereby increasing the driving force for CO_2 desorption and “stripping” the CO_2 from the MEA solvent. The regenerator requires energy input on the order of 3.7-4.0 GJ/tonne CO_2. This is a great deal of energy, amounting to about 40% of the heating value of the original carbon in the coal! At a power plant it is generally anticipated that this large amount of energy would be supplied to the reboiler in the form steam extracted ahead of the low-pressure turbine, dramatically reducing the amount of electricity produced by the power plant.

For most regenerable solvent processes the reboiler heat duty comprises three factors:

- Sensible heat – the heat required to raise the temperature of the solvent from the temperature of the rich solvent leaving the absorber to the operating temperature of the regenerator
- Heat of reaction – the energy required to reverse the exothermic CO_2 absorption reaction
- Stripping steam – the latent heat associated with the vaporization of water from the solvent in the regenerator column

The sensible heat component depends on the heat capacity of the solvent and the solvent circulation rate which, in turn, depends on the CO_2 carrying capacity of the solvent. The stripping steam component depends on the thermodynamic characteristics of the solvent-CO_2 system, and on the pressure at which the regenerator operates. The heat of reaction component obviously depends on the mechanism and thermodynamic details of the chemical reaction(s) of CO_2 with the solvent.

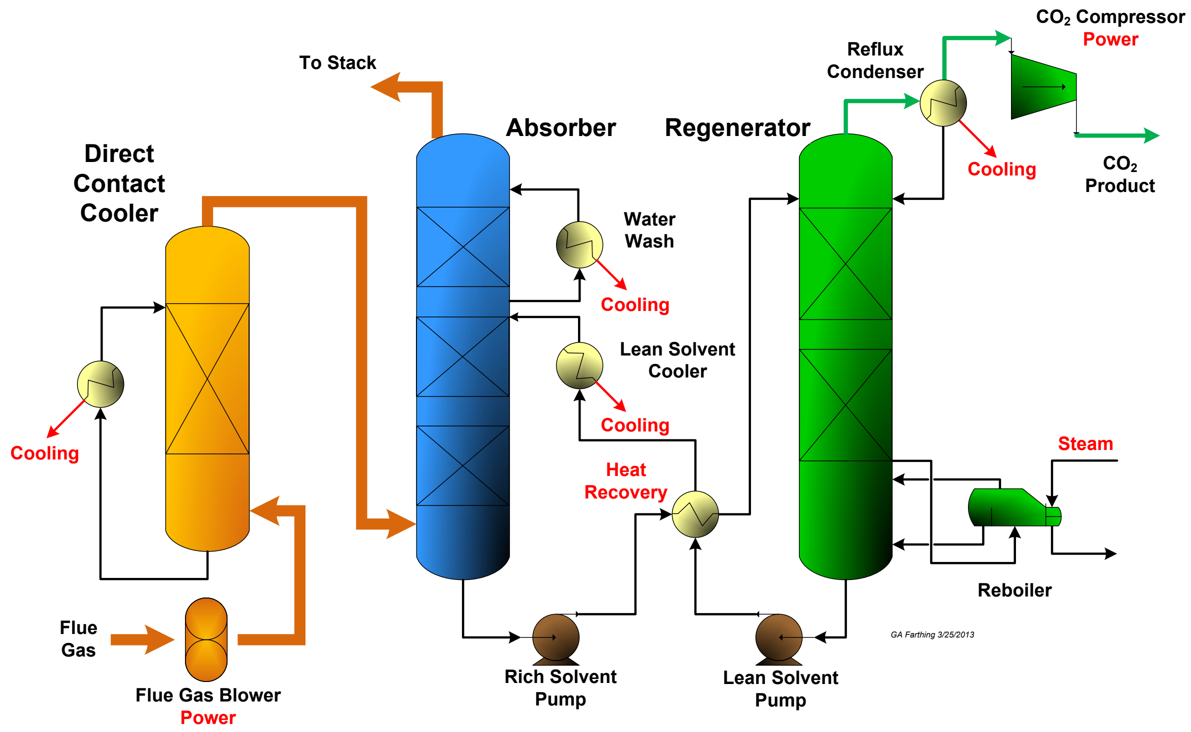


Figure 2.1 Regenerable Solvent Process

The performance of the scrubbing process can be impacted in significant ways by constituents and impurities in coal combustion flue gas. Solvent reactions with SO_X, NO_2 and other acid gas species can lead to the formation of heat-stable salts. Unlike CO_2, these gases are not released during the solvent regeneration process and slowly render the solvent unreactive. The inlet concentrations of SO_X and NO_2 must therefore be kept low, possibly as low as ~1 ppm. The CO_2 scrubbing process is therefore placed downstream of conventional pollution control equipment as illustrated in Figure 2.2, to minimize these and other detrimental impacts of flue gas impurities on process performance.

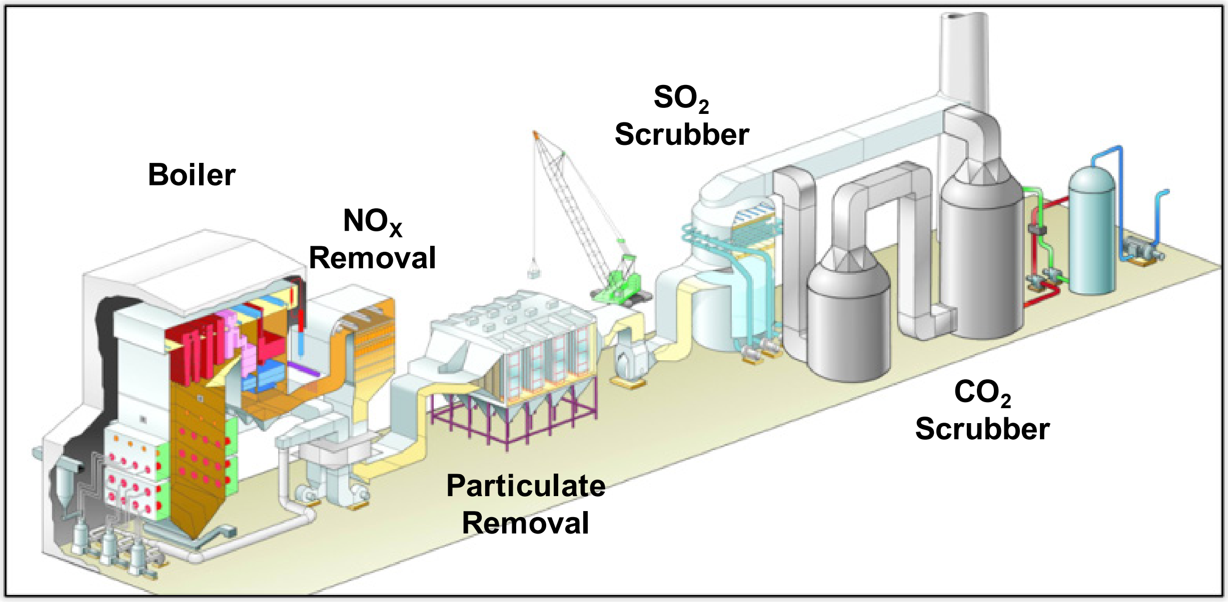


Figure 2.2 CO_2 Capture at Coal-Fired Power Plant

2.2 Solvents

There are two broad classes of CO_2 scrubbing solvents: physical and chemical. Physical solvents *dissolve* CO_2, whereas chemical solvents chemically *react* with CO_2. Figure 2.3 illustrates the impact of CO_2 partial pressure on the equilibrium concentration, or loading, of CO_2 in the liquid phase for the two classes of solvents. It is apparent from the figure that chemical solvents load with CO_2 much better than physical solvents at low CO_2 partial pressures. Also illustrated in the figure is the concept of CO_2 carrying capacity, or simply capacity. If a pressure-swing absorption/stripping process is run between pressures p_1 (absorber) and p_2 (regenerator), the net amount of CO_2 captured and released by the process is shown as ΔL. This is the CO_2 carrying capacity of the illustrated solvents for that particular pressure-swing process.

Physical solvents are well-suited to applications where the feed gas provides a high partial pressure of CO_2 and a pressure-swing process can be used to advantage. Examples of physical solvents include Selexol™, Purisol®, and propylene carbonate. For low pressure applications such as coal-fired flue gas, however, physical solvents are largely ineffective. Chemical solvents, on the other hand, load well with CO_2 at low partial pressures and, due to the energetics of their exothermic chemical reaction with CO_2, respond well to a temperature-swing process. The remainder of this report therefore exclusively deals with chemical solvents for the scrubbing of CO_2 from coal-fired flue gases. Examples of chemical solvents include amines, carbonates (e.g., K_2CO_3), ammonia, and caustic (e.g., NaOH). For conventional temperature-swing CO_2 scrubbing applications, caustic is too reactive and therefore not regenerable, and ammonia is too volatile. Amines have been found to strike a good balance between alkalinity and volatility, and have therefore found widespread application.

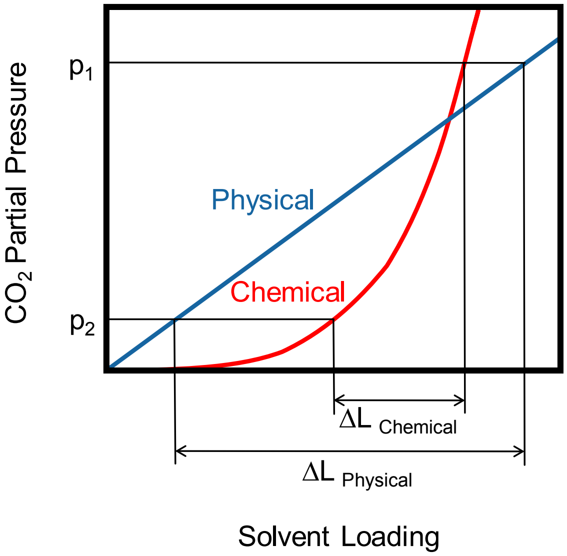


Figure 2.3 Comparison of Physical and Chemical Solvents

Amine solvents are grouped according to their molecular structure. Primary and secondary amines in aqueous solutions can reversibly react with CO_2 to form carbamate species:

$CO_2 + 2RNH_2 \leftrightarrow RNHCOO^- + RNH_3^+$ (Primary Amine)

$CO_2 + 2R_2NH \leftrightarrow R_2NCOO^- + R_2NH_2^+$ (Secondary Amine)

Two moles of the primary or secondary amine are required to absorb 1 mole of CO_2, limiting the CO_2 loading that can be achieved. These amines tend to have high heats of reaction with CO_2, and generally yield high CO_2 absorption rates. Examples of primary amines include monoethanolamine (MEA) and diglycolamine (DGA). Examples of secondary amines include diethaolamine (DEA), Diisopropanolamine (DIPA), and piperazine (PZ), a cyclic diamine.

Hindered and tertiary amines do not react directly with CO_2 to form carbamate species. Instead, they react indirectly in the presence of water to form bicarbonate:

$$CO_2 + RNH_2 + H_2O \leftrightarrow HCO_3^- + RNH_3^+ \qquad \text{(Hindered Primary Amine)}$$

$$CO_2 + R_3N + H_2O \leftrightarrow HCO_3^- + R_3NH^+ \qquad \text{(Tertiary Amine)}$$

One mole of the tertiary or hindered amine is required to absorb 1 mole of CO_2. Tertiary and hindered amines tend to have lower heats of reaction with CO_2, and generally yield lower CO_2 absorption rates. Examples of tertiary amines include methyldiethanolamine (MDEA) and triethanolamine (TEA). Aminomethylpropanol (AMP) is an example of a hindered amine.

Carbonate and amine reactions with CO_2 can be summarized as shown in Table 2.1

Table 2.1 Absorption Characteristics of Conventional Solvents[1]

Solvent	**Reaction**	**ΔH Absorption kcal/gmol**	**Kinetics**
Carbonates	$CO_3^= + CO_2 + H_2O \leftrightarrow 2\ HCO_3^-$	~ -5	very slow
Hindered and tertiary amines	$CO_2 + RNH_2 + H_2O \leftrightarrow HCO_3^- + RNH_3^+$ $CO_2 + R_3N + H_2O \leftrightarrow HCO_3^- + R_3NH^+$	~ -14	slow
Primary and secondary amines	$CO_2 + 2RNH_2 \leftrightarrow RNHCOO^- + RNH_3^+$ $CO_2 + 2R_2NH \leftrightarrow R_2NCOO^- + R_2NH_2^+$	~ -22	fast

2.3 Solvent Considerations

The physical, chemical, and thermodynamic properties of the solvent are of critical importance in determining the performance of a CO_2 scrubbing process. They have a wide variety of impacts on overall system performance measures such as capital cost, operating cost, operability and reliability, and safety and environmental considerations. A few examples of these considerations are illustrated in Figure 2.4.

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[1] Rochelle, G.T., *CO_2 Capture by Aqueous Absorption/Stripping – Thermodynamics*, short course presented to B&W, 7/24/2008.

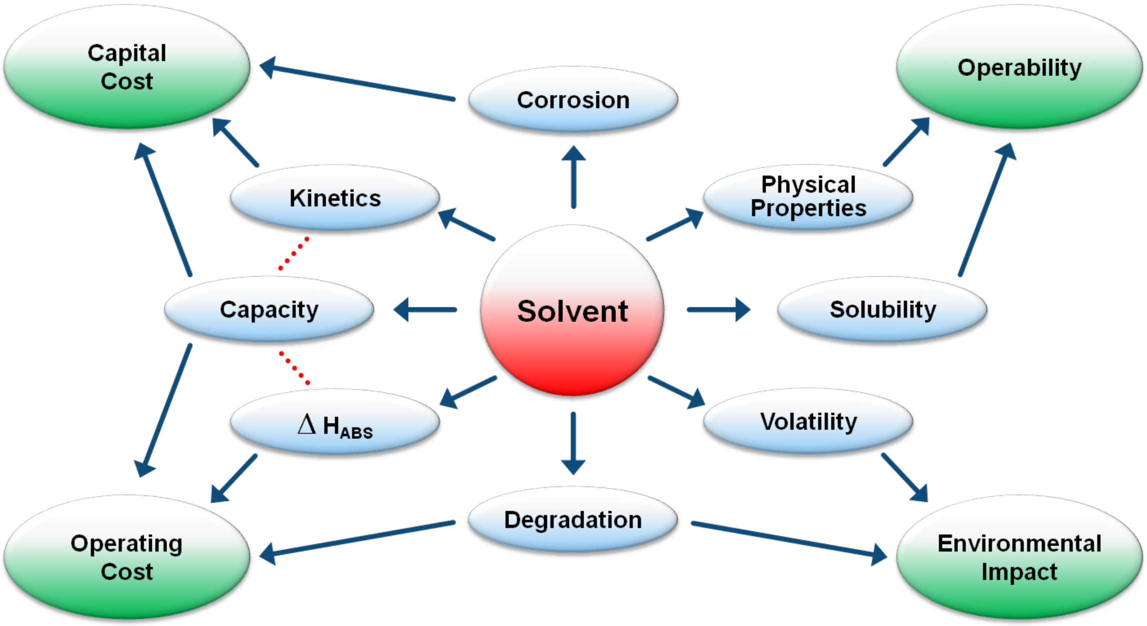


Figure 2.4 Solvent Selection Considerations

Chemical Kinetics. The CO_2 absorption process may be characterized as comprising mass transfer accompanied by chemical reaction. The chemical reaction greatly enhances the rate of mass transfer by removing (through chemical reaction) absorbed CO_2 in the liquid phase from the region of the gas-liquid interface, thereby providing a strong concentration driving force for CO_2 absorption. For the solvents of interest, here, the kinetic rate of the chemical reaction between CO_2 and the solvent helps to determine the rate of CO_2 absorption which, in turn, directly affects the height of the absorber required to achieve the desired CO_2 removal efficiency.

CO_2 Working Capacity. The difference in CO_2 concentration between the rich and lean solvent streams determines the amount of solvent that must be circulated to yield the desired amount of CO_2 removal. The capacity is an important performance characteristic of a solvent because it helps to determine the sizes of the absorber and regenerator vessels, as well as the size of related pumps, heat exchangers, etc. It also greatly impacts the amount of energy required for the process, primarily through the sensible heat component of reboiler duty, but also through its impact on pump power requirements. The capacity of a solvent is determined by the thermodynamic characteristics of the solvent at the relevant process operating conditions.

Heat of Reaction. The chemical reaction between CO_2 and the solvent in the absorber is exothermic. The heat needed to reverse this reaction in the regenerator directly contributes to the energy required for regeneration. All things being equal, it would seem to be desirable to choose a solvent with a low heat of reaction if the goal is to reduce the regeneration energy required. All things are not equal, however, and such solvents rarely perform well on flue gas. As seen previously, solvents with lower heats of reaction tend to have lower absorption rates and have vapor-liquid equilibrium (VLE) characteristics less suitable to a temperature-swing regeneration process. There are good fundamental thermodynamic reasons why these solvent characteristics are not truly independent variables (as indicated by the dotted lines in Figure 2.4). Selection of a solvent therefore almost always involves a compromise which seeks to optimally balance competing effects.

Volatility. The volatility of the solvent at the conditions at the top of the absorber greatly impacts overall process performance. Volatile solvent allowed to escape the absorber through the stack becomes a volatile organic compound (VOC) emission, potentially creating an important and undesirable environmental impact. Attempting to contain these emissions through the use of a water wash section at the top of the absorber increases cost and can also impact the process water balance. This can result in a contaminated wastewater discharge stream, another possible environmental impact. Finally, any solvent lost from the process through evaporation must be replaced, contributing to solvent make-up cost.

It is important to note that predicting the volatility (and many of the other thermodynamic properties) of a new solvent under process conditions from first principles is a difficult task. Volatility is a complicated function of solvent properties, process conditions, CO_2 loading, reaction product speciation, and the non-ideal nature of concentrated electrolyte solutions.

Solubility. The operating range in terms of allowable CO_2 loading, for example, can be significantly limited by the solubility of the solvent and/or its reaction products. Ammonia, sodium and potassium carbonates, piperazine, and amino acid systems are all significantly impacted by issues of solubility. Solubility, like volatility, is a complicated issue in these concentrated electrolyte solutions, and existing thermodynamic packages are rarely adequate to predict behavior. In addition to its impact on system CO_2 removal performance, solubility issues can greatly impact process operability and reliability due to the potential for the formation of troublesome deposits during normal process operation, system transients, and solvent handling operations.

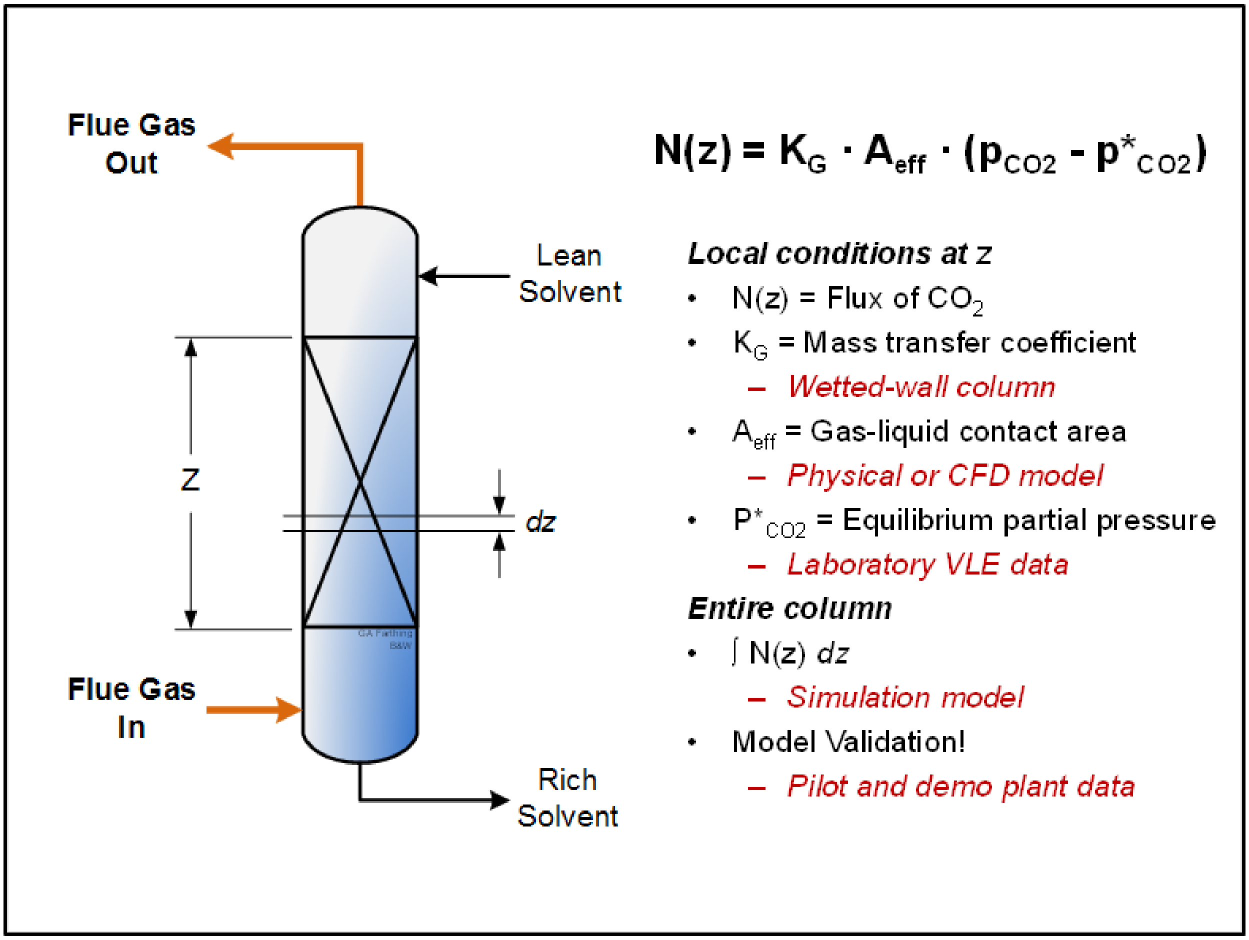
Degradation. Amine solvents chemically degrade in a variety of ways: thermal degradation due to exposure to the high temperatures of the regeneration process, oxidative degradation due the presence of oxygen in the flue gas, carbamate polymerization, etc. The solvent is also degraded through reaction with flue gas contaminants such as SO_X, NO_X, HCl, and others which form heat-stable salts. Degradation reactions can be accelerated by the presence of degradation or corrosion products and heat-stable salts, and through the catalytic effects of various metals (possibly originating with the coal fly ash). Degradation results in the need for additional solvent makeup, and for solvent reclaiming to remove degradation products and heat-stable salts from the circulating solvent. Many of the possible degradation products removed by the reclaiming process are hazardous and result in a hazardous solid waste stream. Volatile degradation products can also contribute to VOC emissions at the stack. The formation and emission of nitrosamines are of particular concern

Corrosion. Solvent solutions under consideration for CO_2 scrubbing, and their degradation products, are often corrosive. Their corrosivity depends on CO_2 loading, concentration, chemical speciation, metallurgy, and local conditions. Corrosion can be greatly impacted by the presence of heat-stable salts and the products of corrosion and solvent degradation. Corrosion is often controlled through the use of corrosion inhibitors, which can, in turn, influence solvent degradation rates. Corrosion concerns directly impact capital cost through the selection of corrosion-resistant materials of construction, and operating cost through the cost of inhibitors, increased solvent degradation rates, and higher system maintenance costs.

Chemical and Physical Properties. The chemical and thermodynamic characteristics of a solvent certainly help to determine its performance with respect to issues such as CO_2 removal, energy requirements, degradation, and corrosion, but they also directly impact a variety of factors such as operability, reliability, and EH&S. A solvent that has hazardous characteristics (toxicity, flammability, etc.) can clearly present environmental and safety risks. Addressing these risks may, in turn, result in difficult solvent handling operations, complicated automated control systems, and special requirements for the disposal of waste materials, all of which increase cost. Solvent physical properties also strongly influence the design and performance of a CO_2 scrubbing system. Solvent viscosity impacts the mass transfer performance of the absorber, and surface tension can impact the wettability of packing surfaces and the foaming tendencies of a solvent. Viscosity, density, and heat capacity all impact the performance of process heat exchangers.

2.4 B&W's Solvent Development Approach

Over the past several years, significant B&W resources and funding have been devoted to the search for a superior solvent-based CO_2 scrubbing process. As suggested by the discussion of the previous section, much of this work has focused on the development of a superior solvent formulation. A variety of tools and methodologies had to be put in place as critical enablers for this development effort. The rationale for selecting the needed tools can be illustrated by considering, for example, the kind of information needed to develop a conceptual design for an absorber vessel. This information is illustrated in Figure 2.5. The items shown in red suggest the types of tools and methods required to complete the design.



$$N(z) = K_G \cdot A_{eff} \cdot (p_{CO2} - p^*_{CO2})$$

Local conditions at z

- N(z) = Flux of CO_2
- K_G = Mass transfer coefficient
  - *Wetted-wall column*
- A_{eff} = Gas-liquid contact area
  - *Physical or CFD model*
- P^*_{CO2} = Equilibrium partial pressure
  - *Laboratory VLE data*

Entire column

- $\int N(z)\, dz$
  - *Simulation model*
- Model Validation!
  - *Pilot and demo plant data*

Figure 2.5 Design Tools

The rate of CO_2 absorption, or flux *N*, can be expressed as the product of an overall mass transfer coefficient, K_G, the effective gas-liquid contact area, A_{eff}, and the driving force for mass transfer expressed as the difference between the actual gas-phase partial pressure of CO_2 , p_{CO2}, and the partial pressure of CO_2 that would be required to bring the gas phase into equilibrium with the bulk liquid, p^*_{CO2}. Key information on the fundamental characteristics of a solvent can be generated in laboratory-scale equipment. This information is generated for conditions at a particular point in the absorber (or regenerator). By generating information over a wide range of conditions, a computer simulation model can then be used to predict the overall performance of the process. The model predictions must, of course, be verified at every step of the way using representative data from pilot-plant and demonstration facilities.

Many of the tools and methods suggested by Figure 2.5 have been put in place at B&W's Research Center in Barberton, Ohio. Great care has been taken to validate and benchmark the tools, all of which have been or are planned to be used during this project. These include:

Wetted-Wall Column (WWC). B&W's laboratory-scale WWC, illustrated in Figure 2.6, is used to provide fundamental mass transfer and VLE information which can be used to better assess the potential performance of the solvent. It is also possible to estimate the enthalpy of absorption using VLE data generated from the WWC for developmental solvents where such information is not available elsewhere.

Figure 2.6 B&W's Wetted-Wall Column

Process Simulator. B&W's bench-scale process simulator, illustrated in Figure 2.7, is a fully-integrated CO_2 scrubbing process, albeit at very small scale. The unit contains most of the equipment that would be used at larger scale, including the absorber column at left, the regenerator column at right, and the electrically-heated reboiler at lower right in the photograph. The unit operates on synthetic flue gas and is designed to capture about a kilogram of CO_2 per hour. It provides the first chance to look at the performance of a new solvent in a fully-integrated process, facilitates parametric studies of the important independent process variables, and provides data for computer simulation model validation.

Figure 2.7 B&W's Process Simulator

Laboratory Corrosion Techniques. B&W has extensive knowledge and capabilities related to the corrosion of metals in a wide variety of environments. Electrochemical tests are conducted using a standard bench-top electrochemical test cell to facilitate a rapid determination of corrosivity. Weight loss tests are also conducted in the laboratory by subjecting test specimens to a carefully controlled corrosive environment. The mass loss of the specimens provides a representative corrosion rate.

Regenerable Solvent Pilot Plant. B&W's CO_2 scrubbing pilot plant, shown in Figure 2.8, provides high quality, quantitative, performance data representative of full-scale equipment. The pilot plant operates on approximately 3,100 lbs/hr of flue gas, or 7 tons/day of captured CO_2. It can be operated on coal flue gas generated by B&W's Small Boiler Simulator, or in recirculation mode using a synthetic mixture of nitrogen and CO_2. Key performance parameters like regeneration energy and CO_2 removal rate are compared among candidate solvents. Other operational issues including solubility, volatility and viscosity of solvents are also evaluated during pilot plant testing.

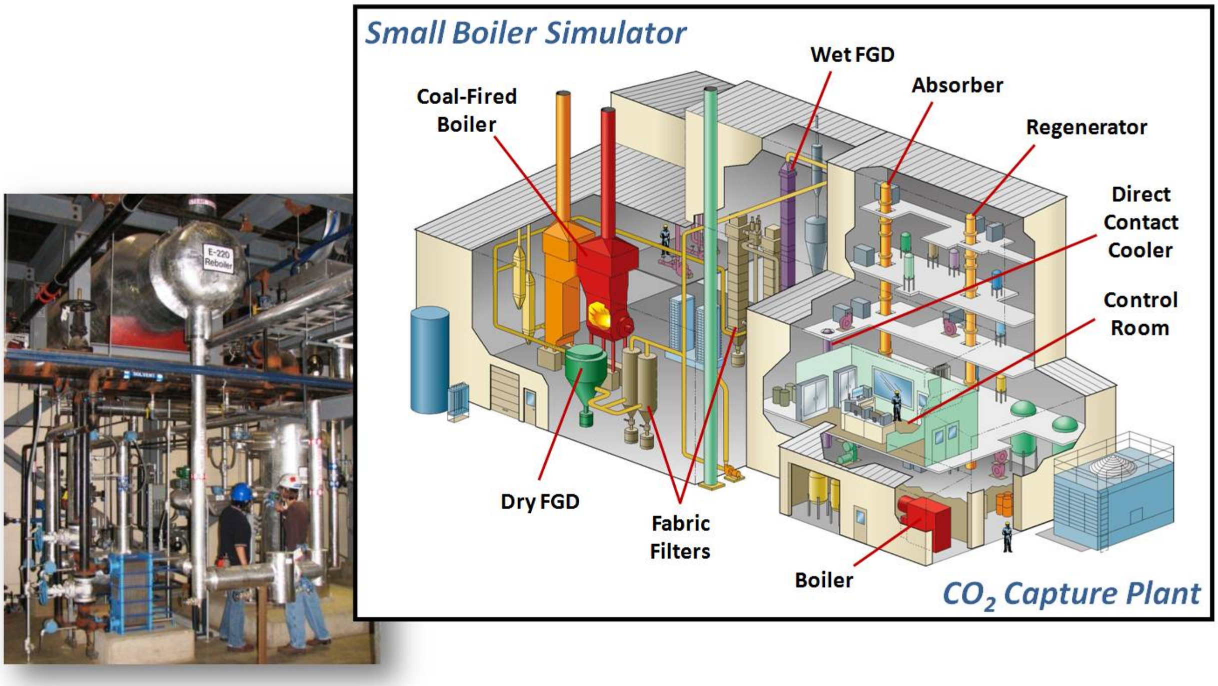


Figure 2.8 B&W's 7 ton/day CO_2 Scrubbing Pilot Plant

Computer Process Simulation. B&W semi-empirical and Aspen Plus® rate-based computer simulation models are used to support experimental work and to make performance predictions. Modeling of the CO_2 scrubbing process is quite difficult in that it comprises a multi-component, multi-phase system with mass transfer accompanied by chemical reaction. It is further complicated by the fact that at the concentrations of interest, the solvent (electrolyte) solutions can exhibit highly non-ideal behavior. Considerable effort has been required to validate the models against experimental results.

2.5 Results of Prior Work by B&W

Using these validated tools, B&W conducted an intensive 5-year development effort aimed at the development of a superior, proprietary, B&W CO_2 scrubbing process for *near-term commercial application*. The overall effort was aimed at finding a better solvent, improving process design, making better use of heat sources within the power plant, and reducing the cost of CO_2 compression. Identification of a superior solvent formulation was a critical enabling component of the development effort. Solvent development activities, shown in Figure 2.9, carried solvent candidates from discovery through initial screening, laboratory-scale characterization, bench-scale process studies, process simulation modeling, pilot-plant studies, and detailed technical and economic evaluation.

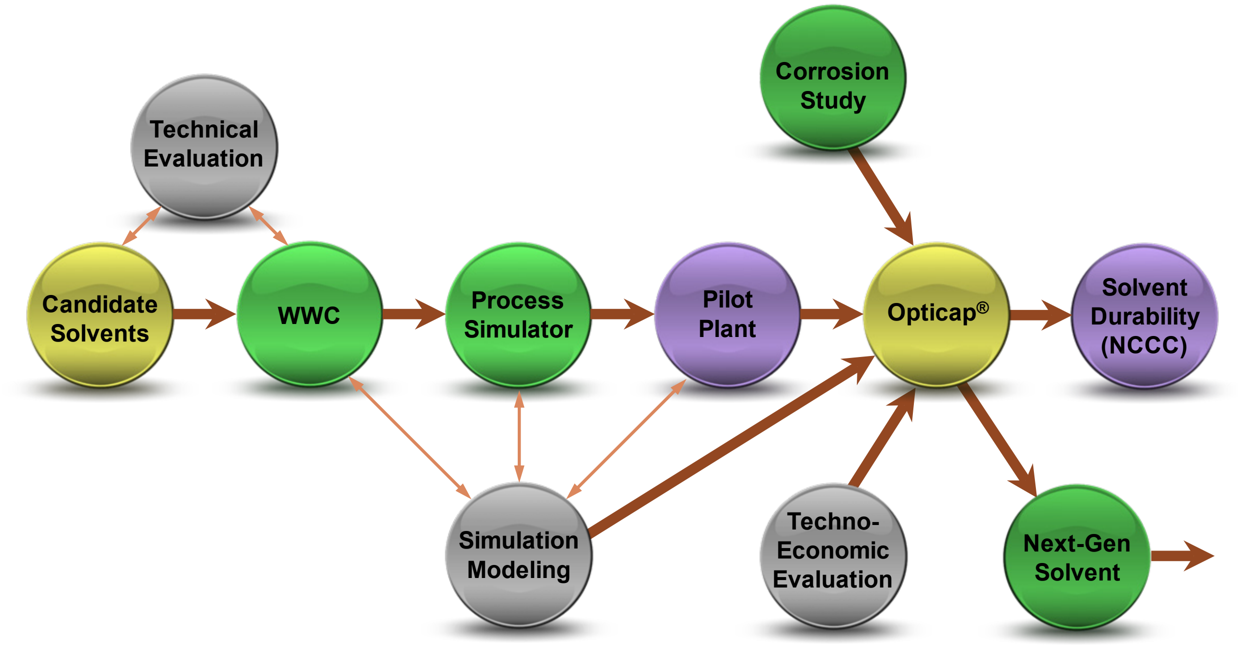


Figure 2.9 B&W's Regenerable Solvent Development Program
(color key: gold-decisions, silver-analyses, green-lab studies, purple-pilot tests)

The many solvents initially considered were systematically reduced in number as the evaluations proceeded from the laboratory to pilot plant scale. Solvent selection was primarily focused on formulations that optimally balanced the competing characteristics of low heat of reaction, high CO_2 carrying capacity, and high absorption rates (fast kinetics and high rates of mass transfer at the gas-liquid interface), although other aspects of solvent performance (volatility, degradation, corrosion, toxicity, price, etc) were taken into account where such information was available. The benchmark solvent was 30 wt% MEA, which yields relatively high absorption rates and adequate CO_2 carrying capacity, but also has a high heat of reaction and less-than-ideal volatility, corrosion and degradation characteristics. Ultimately, the best candidates were rated according to a variety of technical, economic and commercial considerations, and a final selection was made.

This solvent development work culminated in the selection of a proprietary solvent formulation known as OptiCap®. Successful durability testing of the OptiCap solvent was then conducted under commercially-representative conditions at the U.S. Department of Energy's National Carbon Capture Center (NCCC) located at Southern Company's Plant Gaston in Wilsonville, Alabama.

In parallel with its OptiCap development work, also as illustrated in Figure 2.9, B&W has, and continues to identify, evaluate, and develop advanced CO_2 capture systems for coal-fired power plants. These activities include technologies such as oxy-coal combustion, chemical looping, and advanced post-combustion systems based on solid sorbents, membranes, developmental solvents such as ionic liquids, catalytic systems employing small-molecule carbonic anhydrase mimics, and a next-generation concentrated PZ-based solvent. This latter effort is the subject of the project described, herein.

3.0 SELECTION OF INITIAL CANDIDATE FORMULATIONS

3.1 Rationale

Viewed from high level, this project is entirely about the identification, development, and validation of a concentrated piperazine-based solvent formulation that globally optimizes the technical, economic, and environmental performance of a CO_2 scrubbing system as applied to a coal-fired utility boiler. The central role played by the solvent was discussed at some length in the previous section. Figure 3.1 is intended to illustrate the point in a somewhat more detailed fashion. The figure indicates how a wide variety variables and design features might be used to impact the performance of the capture process. Their impacts are grouped according to four major performance factors including capital cost, operating cost, reliability, and environmental, health and safety (EH&S), and are further subdivided according to major system performance parameters. Factors that are strongly related to the properties of the solvent are identified with an asterisk. While not intended to be an exhaustive list, the figure clearly illustrates the impact solvent selection has on system performance.

Figure 3.1 also provides a good jumping off point for thinking about the daunting task of selecting a solvent formulation that globally optimizes system performance over this large number of factors. The early stages of a solvent selection program are particularly challenging since initial candidate selections must typically be made without the benefit of good fundamental solvent property data. Without such data, it is extremely difficult to even roughly estimate the performance of a given candidate. This closely approximates the state of affairs during the Budget Period 1 project work described, herein.

Of course the solvent selection work being conducted under this project ***did not*** start from a clean sheet of paper. Years of development work at B&W had already narrowed the field to a family of solvent formulations comprising blends containing piperazine in concentrations above about 14 wt%. Results of the earlier work therefore provided a foundation upon which to build. For example, it had been demonstrated at pilot scale that some blends of concentrated PZ with other amines performed better than concentrated PZ, alone, with respect to absorption rate, reboiler heat duty, and solubility. Further, a 40.8 wt% PZ solvent formulation had been well characterized by B&W through extensive testing at the laboratory, bench, and pilot scales supplemented by comprehensive rate-based computer simulation modeling.

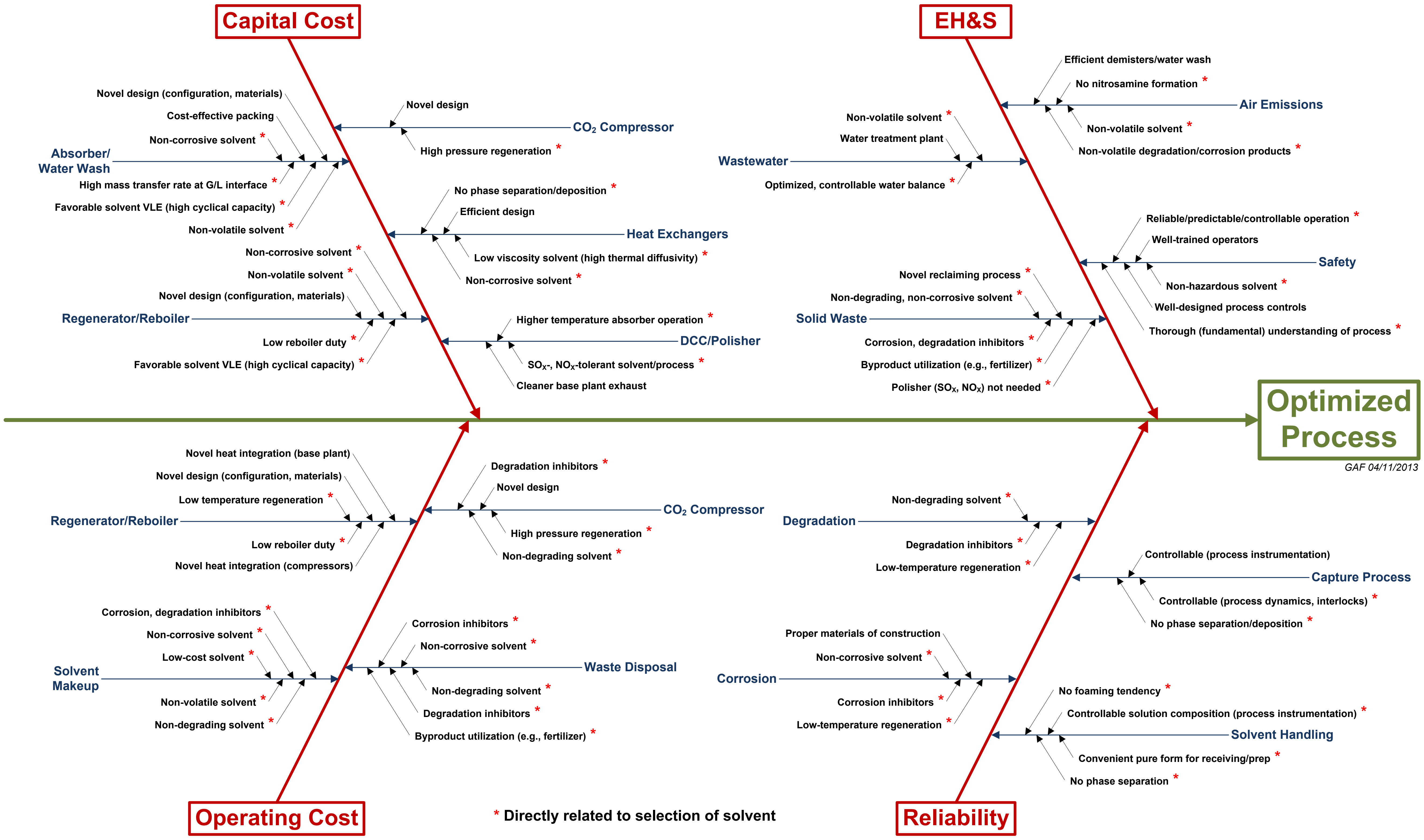


Figure 3.1 Solvent Selection Is Key to a Globally Optimized Capture Process

In light of the extensive database available for a 40.8 wt% PZ solvent formulation, this formulation has served as the prototype, or baseline, formulation throughout the Budget Period 1 work. It provides extremely high rates of absorption, reasonable CO_2 carrying capacity, low regeneration energy due to favorable thermodynamic characteristics, relatively low volatility, and reduced CO_2 compression costs provided by regeneration at high pressure enabled by the good resistance to thermal oxidative degradation exhibited by 40.8 wt% PZ. These important quantitative measures of performance were therefore used as selection criteria for the evaluation of candidate formulations of new PZ-based solvents.

The 40.8 wt% PZ formulation also exhibits a variety of less-than-desirable performance characteristics. While not representing “fatal flaws”, these negative characteristics naturally served to establish initial performance goals for an improved PZ-based formulation. For example, piperazine and its reaction products with CO_2 have limited solubility. Piperazine hexahydrate and protonated piperazine carbamate monohydrate may precipitate from the solvent solution if CO_2 loadings are allowed to get too low or too high, respectively. This significantly limits the CO_2 loading range permissible which, in turn, limits the solvent’s CO_2 carrying capacity. Operation at or near saturation can also impact the operability and reliability of the system if troublesome deposits tend to form during normal operation, or during system transients. The price of PZ is higher than that of MEA, although this cost might be offset by the lower rates of degradation and evaporation exhibited by 40.8 wt% PZ. PZ is somewhat less biodegradable than MEA, and is harder to handle due to its higher freezing temperature. Finally, the performance of concentrated PZ solvents is simply not as well studied or as well understood as that of more conventional solvents such as MEA. These and other factors provided performance enhancement goals for the selection of an optimal solvent formulation.

3.2 Downselection Methodology

The identification and selection of promising solvent formulation candidates during Budget Period 1 of this project was planned and orchestrated, and final selections were made, under Task 2: Engineering Analysis. This work was facilitated by performance predictions provided by work under Task 3: Performance Calculations and limited laboratory screening studies conducted under Task 4: Laboratory Data. The overall approach was to develop a “long list” of candidate formulations through a process of discovery which was then trimmed to a list of about 12 promising candidates through an initial evaluation methodology. These 12 candidates were then subjected to a more detailed evaluation taking advantage of performance predictions and laboratory results provided by Tasks 3 and 4. Finally, on the basis of this more detailed evaluation, the four most promising candidate solvent formulations were selected to carry forward.

The activities supporting the Budget Period 1 solvent evaluation studies are summarized in Figure 3.2. The tasks under which each of the various activities was carried out are indicated by superscripts in the figure. B&W's extensive experience gleaned from 5 years of previous solvent evaluation work greatly facilitated the process.

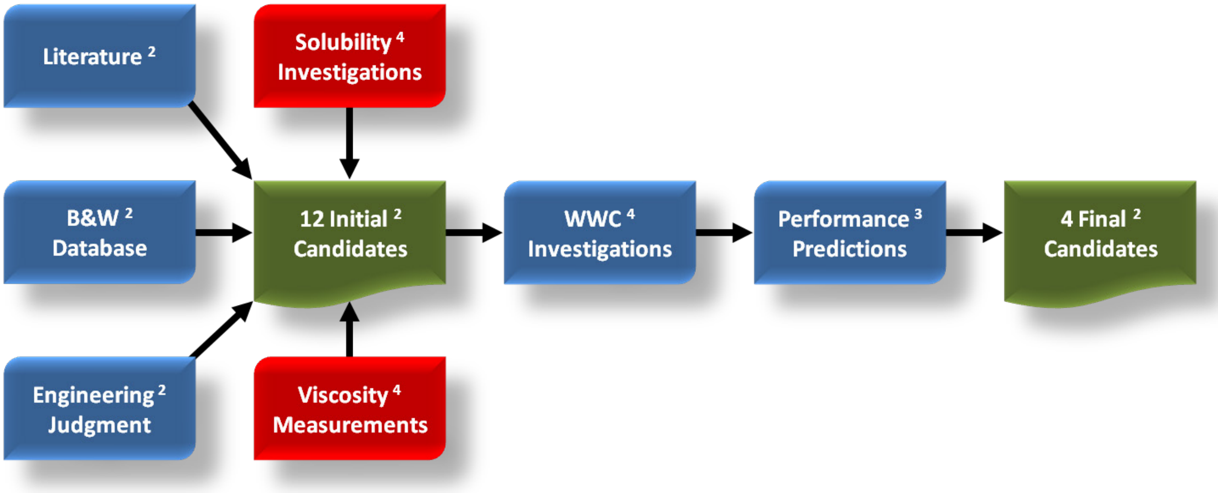


Figure 3.2 Overview of Budget Period 1 Solvent Selection Activities

A "long list" of potential PZ-based formulations was developed based on literature review, previous B&W solvent work, and brainstorming activities. These formulations were then judged according their expected performance related to factors such as: heat of absorption, cyclic capacity, absorption rate, toxicity, solubility, degradation, volatility, corrosivity, viscosity, foaming tendency, surface tension, and raw material cost. Table 3.1 illustrates B&W's assessment of the relative importance of these various factors in determining the performance of a commercial CO_2 scrubbing system. While very qualitative and subjective, factors identified as potential "show-stoppers" are items for which no engineering work-around is likely.

During the Budget Period 1 work, expected performance was not considered in an absolute sense, but rather was judged against the performance of the baseline solvent formulation, 40.8 wt% PZ. It should also be recognized that quantitative property and performance information on these developmental formulations was, in general, not available at this early stage of the work. Many of the decisions made during this evaluation were, of necessity, of a very qualitative, "gut feel" nature.

Table 3.1 Evaluation of Solvent Properties

Property	Importance	Potential Show-Stopper
Heat of absorption	10	Yes
Capacity	10	Maybe
Absorption Rate	10	Yes
Toxicity	6	Yes
Solubility	6	Maybe
Degradation	6	Yes
Volatility	6	Maybe
Corrosivity	6	Maybe
Viscosity	4	Yes
Foaming	4	Maybe
Surface tension	4	Maybe
Cost	2	Maybe

The original project plans called for the “long list” of discovered solvents to be trimmed by this methodology to 12 initial candidates using only *existing* B&W data, literature data, and engineering analysis. It soon became apparent, however, that existing information and theoretical considerations were not sufficient to make the needed judgments for innovative, never-been-tested, solvent formulations. Additional, unplanned, laboratory characterization tests, shown in red blocks in Figure 3.2, were therefore conducted to provide the needed insights.

The additional testing comprised preliminary solubility and viscosity characterization of select candidate formulations. Solubility studies involved measurements aimed at verifying that a particular formulation could actually be made in the laboratory, and that the formulation did not exhibit an unworkable solubility window in the presence of CO_2.

A high solvent viscosity can increase pumping costs, negatively impact the performance of process heat exchangers, and, most importantly, reduce the rate of mass transfer in the absorber. Based on previous B&W experience at the bench and pilot scales, a formulation with viscosity greater than about 10 cP under absorber conditions (roughly 40-50 C) was deemed unacceptable.

3.3 The “Long List” of Candidate Formulations

A “long list” of 55 potential PZ-based formulations, shown in Table 3.2, was developed based on literature review, previous B&W solvent work, and brainstorming activities. The candidate formulations are grouped according to the following types of formulations:

Single Amine. The only single-amine solutions included are aqueous solutions of concentrated PZ. This was done to establish baseline data for concentrated PZ against which the performance of other candidates could be compared.

Amine Blend. These blends contain concentrated PZ in combination with one or more additional amines. The second amine is typically a tertiary or hindered amine. These blends are primarily intended to widen the solubility operating window (relative to 40.8 wt% PZ) and reduce regeneration energy (by increasing capacity and optimizing the heat of absorption). However, such blends obviously may have different performance characteristics across the full spectrum of factors (e.g., degradation, corrosion, volatility, price, etc.)

Amine/Amino Acid Salt. A relatively large number of blends of concentrated PZ with amino acids are included. The principal anticipated benefits of using amino acids are their natural resistance to degradation and, when used in neutralized salt form, their very low volatility. Amino acids can be neutralized with either inorganic or organic bases to form dissolved salts in aqueous solution. However, the use of inorganic bases such as potassium or sodium hydroxide is complicated by the limited solubility of the resulting salts. All work in this study focused on the neutralization of the amino acid with an amine, resulting in the formation of an amine/amino acid salt (AAAS).

Two basic approaches to the formulation of AAAS solutions were investigated. The first comprised the straightforward neutralization of the amino acid with PZ through the preparation of an equimolar solution. Since PZ is a diamine, both the anion and cation of the resulting AAAS are theoretically capable of reacting with CO_2. An example of this type of AAAS is shown in the table as PZ/Sar, in this case representing an equimolar solution of piperazine with the amino acid sarcosine. In one instance a mixture of two amino acids, Arg and Sar, is neutralized with equimolar PZ. Several samples of amino acids neutralized with MEA are also included. The purpose of these solutions is described in Section 3.4.

The second approach involved the neutralization of the amino acid with an amine, typically a diamine, followed by the addition of PZ. The solutions can be thought of as AAAS solutions *promoted* with PZ. An example of such a formulation is shown in the table as PZ/(Sar/PZ), representing an AAAS solution of piperazine and sarcosine promoted with piperazine.

Table 3.2 "Long List" of Candidate Formulations

Type	Formulation	Concentration *wt%*
Amine	PZ	40
	PZ	45
Amine Blend	PZ/DEEA	21/29
	PZ/2-PE/DMAE	12/7/30
Carbonate	K_2CO_3	20
	PZ/ Na_2CO_3	14/20
	PZ/ $(NH_4)_2CO_3$	14/20
	PZ/ K_2CO_3	13.8/22.14
	MAPA/ K_2CO_3	14/22
PZ / Organic	PZ/Sulfolane	40/5
	PZ/Sulfolane	40/10
	PZ/Sulfolane	40/15
	PZ/Sulfolane	40/20
	PZ/Sulfolane	40/30
	PZ/Methanol	40/2
	PZ/Ethanol	40/2
	PZ/Propanol	40/2
	PZ/Butanol	40/1
	PZ/Butanol	40/2
	PZ/Butanol	40/5
	PZ/Arg/Sulfolane	14.3/29.3/5
Amine Amino Acid Salt (AAAS)	MEA/Arg	7.4/20
	MEA/Pro	14.5/27.2
	MEA/Sar	15.2/22.6
	MEA/Tau	14/28.6
	PZ/(Arg/MAPA)	20/(20/10)
	PZ/(Arg/PZ)	20/(20/10)
	PZ/(Arg/Sar)	16/(25/3.6)
	PZ/(Sar/DMAPA)	20/(14/16)
	PZ/(SarMAPA)	20/(15/15)
	PZ/(Sar/MAPA)	20/(20/20)
	PZ/(Sar/PZ)	20/(15/15)
	PZ/(Dmg/DMAPA)	20/(30)
	PZ/(Dmg/MAPA)	20/(30)
	PZ/(Dmg/PZ)	20/(30)
	PZ/Dmg	20/23.9
	PZ/Arg	4/15
	PZ/Arg	9.9/19.6
	PZ/Arg	14/29
	PZ/His	15/27
	PZ/Lys	14.5/25
	PZ/Lys	16/26
	PZ/Lys	18.4/31.4
	PZ/Pro	19.2/25.7
	PZ/Pro	21/29
	PZ/Pro	22/29
	PZ/Pro	32/42
	PZ/Sar	20.3/21.1
	PZ/Sar	25/25
	PZ/Sar	26.5/27.7
	PZ/Tau	6.2/9
	PZ/Tau	12/17.8
	PZ/Tau	18.8/27
	PZ/Tau	21/30
	PZ/Tyr	13.7/29

Inorganic Salt. The carbonate salts of sodium and potassium have long been used commercially for the capture of CO_2. It was seen in the last section that these solvents are best suited to pressure-swing applications, and exhibit slow rates of reaction with CO_2. A promoter like PZ or a catalyst is often added to improve the reaction rate. The performance of carbonate systems is also constrained by the solubility of the carbonate and bicarbonate species. Carbonates in combination with concentrated PZ were primarily of interest in this project because they are non-volatile, non-degrading, safe, and inexpensive. The challenge was to find a blend of concentrated PZ with a carbonate salt that would provide a wider solubility window, higher capacity, and lower regeneration energy (by increasing capacity and optimizing heat of absorption).

Organic Additive. Another approach taken in an attempt to widen the solubility operating window of concentrated PZ was to add an organic compound that modified the solubility of either the piperazine hexahydrate (lean precipitate) or the protonated piperazine carbamate monohydrate (rich precipitate), or both.

3.4 Solvent Solubility Characterization Testing

3.4.1 Rationale

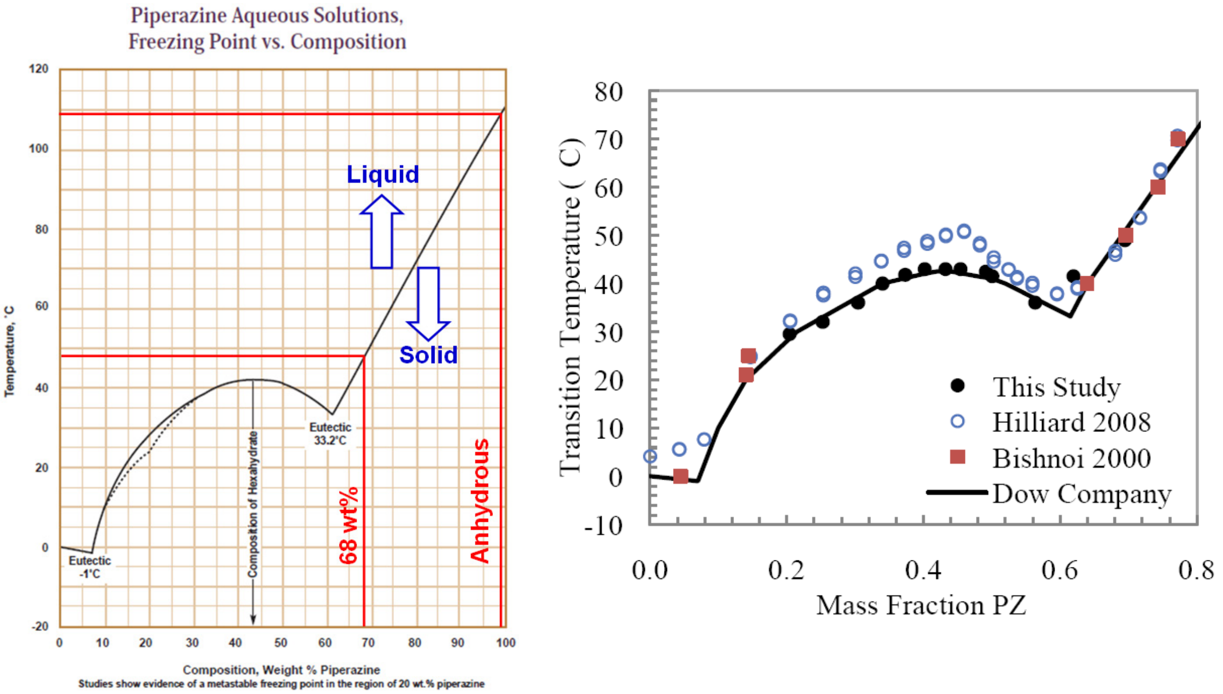
No laboratory solubility studies were planned to be done during Budget Period 1. However, during the process of selecting the 12 initial candidate formulations it quickly became apparent that existing data and information did not provide sufficient insight into the solubility behavior of the proposed formulations. Preliminary laboratory solubility characterization testing was therefore carried out to provide meaningful solubility data upon which informed decisions could be made. It should be noted that the preliminary solubility characterization testing described in the following sections was not intended to provide precise, fundamental, thermodynamic property data. Rather, the testing was very exploratory in nature, designed to identify solvent formulations whose solubility behavior under CO_2 scrubbing conditions might compare favorably with that of 40.8 wt% PZ.

The Behavior of Concentrated Piperazine (Baseline Formulation)

Piperazine can be commercially obtained as pure, anhydrous flakes or as a 68 wt% PZ aqueous solution. Both of these forms are solid under typical room temperature conditions. The solubility of piperazine in water is dependent upon concentration and temperature according to Figure 3.3. Dilution below 15 wt% PZ is required to ensure a clear liquid solution at room temperature. The relatively common use of PZ as a promoter in blended carbon capture solutions (for example: K_2CO_3/PZ or AMP/PZ) generally avoids solubility issues because the PZ component is present at concentrations below 10 wt%. In general higher concentrations of PZ have been avoided to preclude susceptibility to precipitation of solid species.

In 2007, Professor Gary Rochelle's research group at the University of Texas at Austin determined that the solubility behavior of concentrated PZ is strongly dependent on its CO_2 content[1]. This innovative observation added another dimension to the PZ solubility picture, as indicated in Figure 3.4. The figure illustrates the impact of CO_2 loading on the solubility behavior of two solutions of concentrated PZ:

- 8 molal PZ, equivalent to about 40.8 wt% PZ, and
- 10molal PZ, equivalent to about 46wt% PZ.



(a) Source: The Dow Chemical Company, "Ethyleneamines," August 2001. http://www.dow.com/amines/pdfs/108-01347.pdf

(b) Source: S.A. Freeman et al., "Carbon Dioxide Capture with Concentrated, Aqueous Piperazine," Energy Procedia 1 (2009) 1489–1496; GHGT-9, Washington, D.C.

Figure 3.3 Aqueous Piperazine Solubility

As indicated in the figure, wherein the clear solutions occupy the the central region of the graph between the saturation lines, piperazine hexahydrate ($PZ \cdot 6H_2O$) precipitates when the CO_2 loading is too lean, whereas a nearly saturated rich CO_2 loading condition produces a

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[1] Rochelle, G.T., et al., United States Patent 7,938,887 B2, May 10, 2011.

protonated piperazine carbamate monohydrate ($H^+PZCOO^-{\cdot}H_2O$) precipitate. From a process point of view, this creates a restricted CO_2 loading range over which the scrubbing process can be operated if solid precipitation or troublesome deposition is to be avoided. As temperature is increased the solubility of each of these solid species increases.

As precipitation, or solidification, proceeds there is a partitioning of PZ, H_2O, and CO_2 between the solid and liquid phases based on thermodynamic equilibrium. Observationally, a lean-loaded solution exhibiting solids, such as that shown in Figure 3.5, tends to remain somewhat fluid. The rod-shaped solids form a slurry which will flow under shear. Not surprisingly, this fluidity decreases as the fraction of solids increases. Conversely, crystals formed in a rich-loaded solution tend to be hard and immobile. The crystals form with a clear transparent color and agglomerate as they grow. It is also obvious from the photos that there is a distinct difference in the density of the two types of crystals. Crystals ($PZ{\cdot}6H_2O$) originating in a lean solution are less dense than the liquid and float, as shown in Figure 3.5. Crystals formed in a rich solution ($H^+PZCOO^-{\cdot}H_2O$) are more dense than the liquid and sink to the bottom, as shown in Figure 3.6.

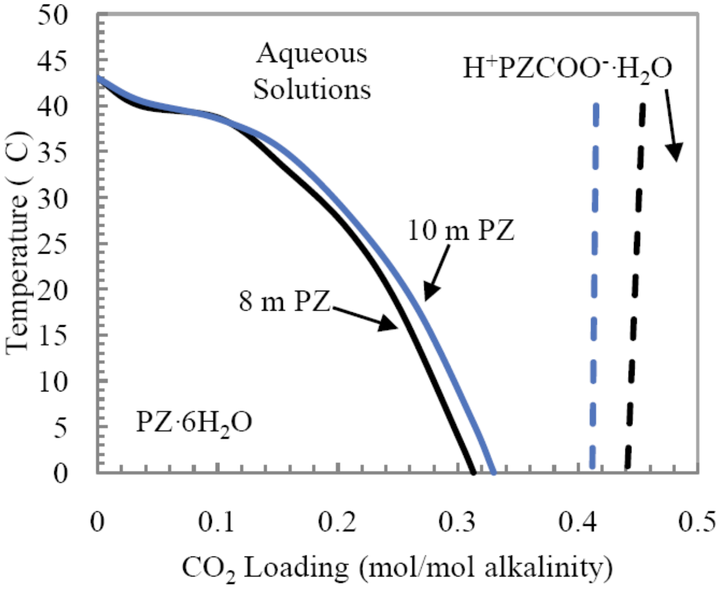


Figure 3.4 PZ Solubility Versus Temperature and CO_2 Loading

Source: S.A. Freeman et al., “Carbon dioxide capture with concentrated, aqueous piperazine,” Energy Procedia 1 (2009) 1489–1496; GHGT-9, Washington, D.C.

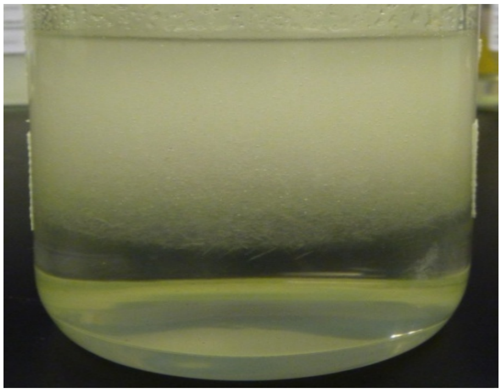


Figure 3.5 Lean PZ Solution

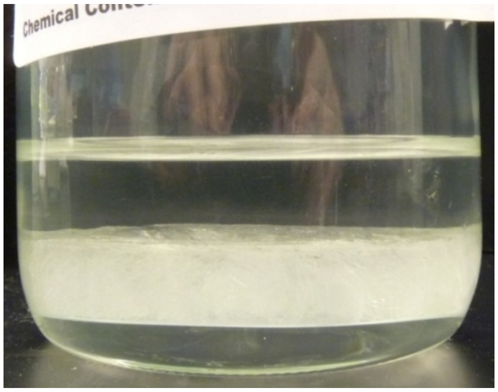


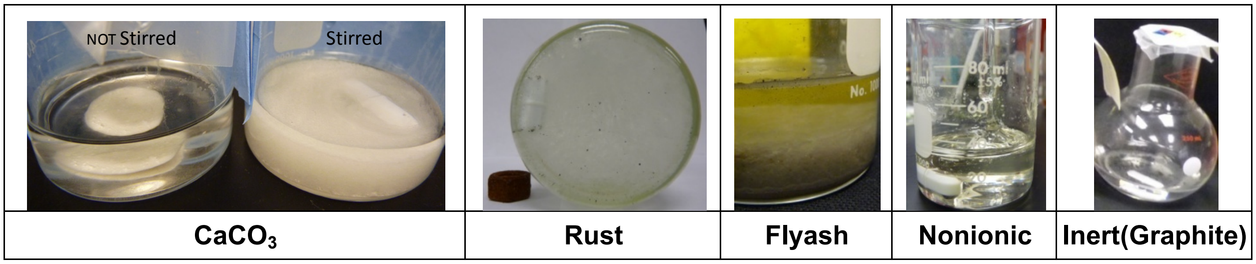
Figure 3.6 Rich PZ Solution

While solid piperazine hexahydrate readily and predictably forms under the expected conditions of concentration, temperature and CO_2 loading, the formation of solid $H^+PZCOO^- \cdot H_2O$ under rich CO_2 loading conditions is much less predictable. It has been observed on many occasions that PZ solutions with rich CO_2 loadings well beyond the solubility limits indicated in Figure 3.4 can remain as clear, supersaturated solutions for extended periods – up to at least 6 months on some occasions. The crystallization behavior of these relatively large-molecule crystals is apparently kinetically controlled, and the process by which the molecules become sufficiently well organized to form crystals can be quite slow.

The phenomenon of crystallization is complicated and proceeds in a step-wise manner. Nucleation is the first step in the process and comprises the formation of small crystals, or nuclei, that are large enough to be thermodynamically likely to grow rather than re-dissolve. Nucleation is often associated with the presence of impurities or surfaces upon which the molecules of the solute can solidify. The following step is crystal growth wherein the nuclei grow as additional solute molecules are added to the crystal. Due to their commercial importance, crystallization phenomena have been extensively studied, and a detailed theoretical framework has evolved. It is nevertheless difficult or impossible to make a priori predictions of the rates of crystal nucleation and growth in many situations, especially for large molecular crystals like $H^+PZCOO^- \cdot H_2O$.

From an experimental point of view, another significant complication is the tendency of $H^+PZCOO^- \cdot H_2O$ solutions to remain in a supersaturated state for extended periods. It is not possible to generate good solubility data if unsaturated, saturated, and supersaturated solutions behave identically (no precipitation). This issue has resulted in significant laboratory trial and error work to find ways to ensure that supersaturated solutions crystallize reliably, and in manageably short times.

The general approach that has been most useful is to provide artificial nucleation sites to the solution through the addition of trace amounts of various impurities. Small amounts of impurities can profoundly impact the nucleation rate, and may also enhance or inhibit rate of crystal growth. Thus the outcome of experiments with impurity addition is complex and unpredictable[1]. Both to facilitate meaningful solubility experiments and to gain some insight into the impacts of impurities likely to be encountered in commercial coal-fired systems, several types of impurities were investigated. As illustrated in Figure 3.7, solids such as limestone, iron oxide, coal flyash, nonionic substances such as sucrose, relatively inert substances such as graphite, and others were investigated. Interestingly, and somewhat surprisingly, most of these solids were ineffective in causing crystallization to occur, even in significantly supersaturated rich PZ solutions.



$CaCO_3$ **Rust** **Flyash** **Nonionic** **Inert(Graphite)**

Figure 3.7 Contaminant Screening Study Examples

The most reliable way found to cause a supersaturated solution to crystallize was to add a seed crystal of the expected solid, itself. Figure 3.8 is a photograph of crystals of $H^+PZCOO^-\cdot H_2O$ used to "seed" solutions suspected of being saturated or supersaturated with $H^+PZCOO^-\cdot H_2O$. The seed crystal thus provides a tailor-made nucleation site for the $H^+PZCOO^-\cdot H_2O$ and crystal growth generally occurs rapidly and continues until the liquid phase solute concentration drops to saturation[2]. This method was adopted for use in most of the solubility studies described in the following sections.

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[1] Myserson, A.S., Handbook of Industrial Crystallization, Butterworth-Heinemann, Boston, MA, (1993).

[2] Whitten, K.W., R.E. Davis, and M.L. Peck, General Chemistry with Qualitative Analysis (Fifth Edition), Saunders College Publishing, Fort Worth, TX, pp 507-508, (1996).

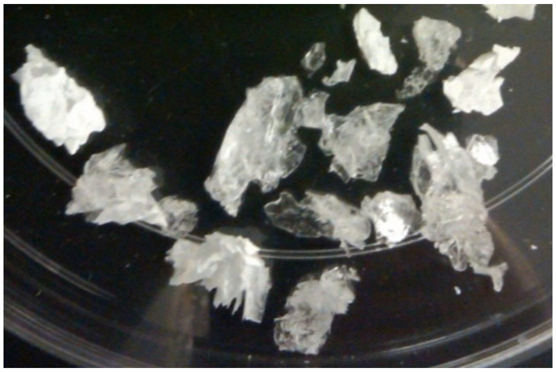


Figure 3.8 Magnified Crystals from Rich PZ Solution

3.4.2 Methods

General chemistry laboratory techniques were used to conduct scoping experiments and to determine preliminary solubility characteristics of candidate formulations. Leveraging prior in-house knowledge, initial assessments using laboratory glassware and minimal volume quantities (<300 ml) offered insight into the tendency of the solutions to precipitate solids. Select formulations were evaluated on molar concentration of constituents and CO_2 loading. Solutions were gravimetrically prepared at room temperature using stock chemicals and high-purity water. The neat solutions were visually assessed for solubility during preparation, both immediately following mixing and after some time had elapsed. This represents the extreme lean loading condition, no CO_2 at all. Then, CO_2 was gravimetrically reacted with the solvent using a gas washing bottle as shown in Figure 3.9 to achieve a target CO_2 loading condition. Solubility observations were again conducted during the CO_2 sparging process as well as after the exothermic heat of solution had subsided.

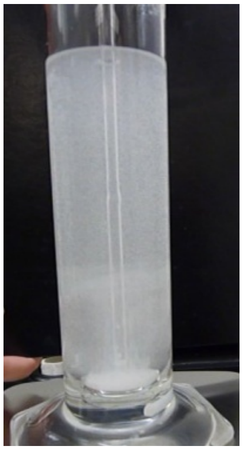


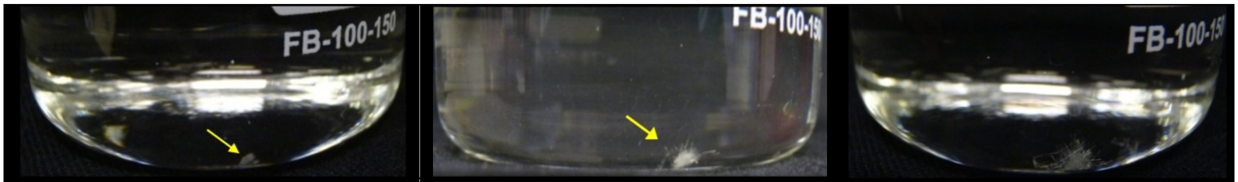
Figure 3.9 Gravimetric Loading of Solvent with CO_2

In the instances where the components appeared to be completely dissolved (clear solution), it was necessary to add a seed crystal of the expected compound to ensure that the solution was not in a state of supersaturation. Seed crystals of $H^+PZCOO^- \cdot H_2O$ used for this purpose were generated from a rich CO_2 loaded concentrated PZ solution, separated using filter paper, and stored in a sealed sample jar. As a seed crystal is added to a supersaturated solution, as demonstrated using a 150 ml glass beaker in Figure 3.10, crystal growth generally proceeds rapidly as illustrated in Figure 3.11.

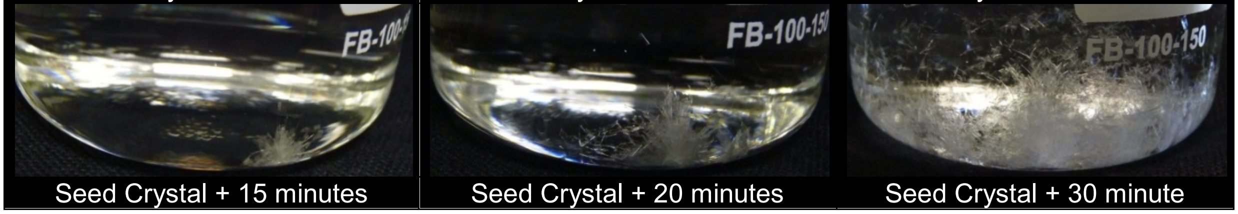
Both quantitative and qualitative observations were carefully recorded throughout the studies. A lab notebook and photographs documented solution characteristics throughout including: solution color and clarity, the presence of solids, the nature and relative density of the solids, etc.

Solutions that contained solids were heated on a hot plate using a water bath, and the solution temperature was monitored with a thermometer. An approximate saturation temperature was thus obtained by increasing the heat input and observing dissolution. This facilitated a comparison of the solubility behavior of a candidate formulation against that of a 40.8 wt% PZ solution.

Figure 3.10 Doping of Solution with Seed Crystal



Seed Crystal + 1 minute Seed Crystal + 5 minutes Seed Crystal + 10 minutes



Seed Crystal + 15 minutes Seed Crystal + 20 minutes Seed Crystal + 30 minute

Figure 3.11 Crystal Growth in Rich PZ After Seeding

3.4.3 Results

Summary

Several candidate formulations of concentrated PZ solvents containing carbonates, other amines, and salts of amino acids, were investigated to establish a *very preliminary* understanding of their solubility behavior. Also evaluated were organic additives specifically designed to improve the solubility of PZ and its carbamates. Carbonate salts and the salts of amino acids, of interest primarily for reasons other than solubility improvement, tended to exhibit limited solubility under relevant CO_2 scrubbing conditions, adding a layer of complication to the already complicated solubility behavior of PZ itself. Judgments made about the suitability (with respect to solubility) of the various candidate formulations characterized in the laboratory are summarized in Table 3.3. Observations made concerning the possible solubility operating window are also summarized in the table. Eight candidate formulations were eliminated from consideration based on their solubility characteristics, alone. Several other candidates exhibited what was considered to be only marginally acceptable solubility characteristics.

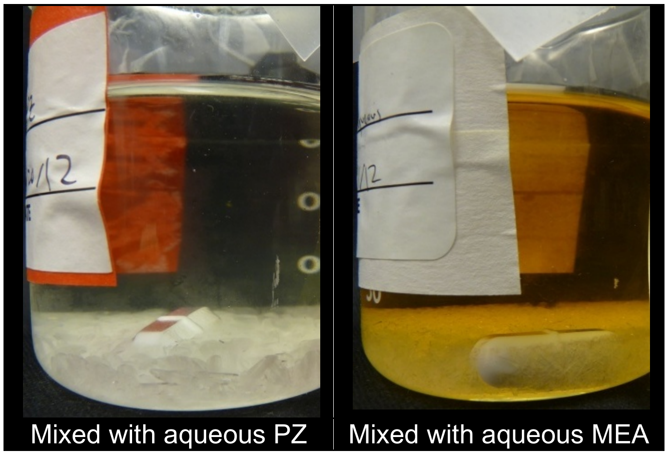
Table 3.3 Results of Laboratory Solubility Studies

Type	Formulation	Concentration wt%	CO_2 Loadings Tested mole CO_2/mole alkalinity	Initial Solubility Assessment	Notes on Observed Solubility Window
Amine	PZ	40	0, 0.20, 0.27, 0.31, 0.34, 0.38,	**Accept**	20 C, 0.25-0.44; 40-60 C, 0.07-0.44
	PZ	45	0, 0.3	**Accept**	20 C, 0.26-0.41; 40-60 C, 0.07-0.41
Amine Blend	PZ/DEEA	21/29	0, 0.2, 0.4, 0.5	**Accept**	40-60 C, 0.00-0.50
	PZ/2-PE/DMAE	12/7/30	0, 0.20, 0.30, 0.40, 0.45	**Accept**	20-60 C, 0.0-0.5
Amine Amino Acid Salt (AAAS)	MEA/Arg	7.4/20	0	**Marginal**	not an issue > 40 C
	MEA/Pro	14.5/27.2	0	**Accept**	not an issue
	MEA/Sar	15.2/22.6	0	**Accept**	not an issue
	MEA/Tau	14/28.6	0	**Reject**	
	PZ/(Arg/MAPA)	20/(20/10)	0, 0.25	**Accept**	20-60 C, >0.25
	PZ/(Arg/PZ)	20/(20/10)	0, 0.25	**Accept**	40-60 C, >0.25
	PZ/(Arg/Sar)	16/(25/3.6)	0, 0.191	**Accept**	20-60 C, >0.19
	PZ/(Sar/DMAPA)	20/(14/16)	0, 0.45	**Accept**	20-60 C, <0.45
	PZ/(SarMAPA)	20/(15/15)	0, 0.25, 0.30, 0.40, 0.45	**Accept**	20-60 C, 0.0-0.45
	PZ/(Sar/MAPA)	20/(20/20)	0, 0.20	**Accept**	60 C, >0.2
	PZ/(Sar/PZ)	20/(15/15)	0, 0.25, 0.30, 0.40, 0.45	**Accept**	40-60 C, 0.25-0.45
	PZ/Arg	4/15	0	**Accept**	similar (better) to PZ/Arg 14/29
	PZ/Arg	9.9/19.6	0	**Accept**	similar (better) to PZ/Arg 14/29
	PZ/Arg	14/29	0, 0.10, 0.6, 0.215, 0.25, 0.30, 0.35, 0.40, 0.45, 0.52	**Accept**	40-60 C, 0.25-0.52
	PZ/His	15/27	0, 0.13, 0.30	**Reject**	
	PZ/Lys	14.5/25	0, 0.56	**Accept**	20 C, <0.56; 40 C, >0.00
	PZ/Lys	16/26	0, 0.10, 0.35	**Accept**	20-60 C, 0.1-0.35
	PZ/Lys	18.4/31.4	0, 0.30	**Marginal**	20 C, >0.30
	PZ/Pro	19.2/25.7	0, 0.49	**Marginal**	similar (better) to PZ/Pro 21/29
	PZ/Pro	21/29	0, 0.35	**Marginal**	40-60 C, 0.35
	PZ/Pro	22/29	0, 0.32	**Marginal**	similar to PZ/Pro 21/29
	PZ/Pro	32/42	0	**Marginal**	similar (worse) to PZ/Pro 21/29
	PZ/Sar	20.3/21.1	0, 0.38, 0.485	**Accept**	20 C, 0.38-0.49
	PZ/Sar	25/25	0, 0.25, 0.30, 0.40, 0.45	**Accept**	20-60 C, 0.25-0.45
	PZ/Sar	26.5/27.7	0, 0.30	**Accept**	20 C, 0.30
	PZ/Tau	6.2/9	0	**Accept**	not an issue
	PZ/Tau	12/17.8	0, 0.45	**Reject**	
	PZ/Tau	18.8/27	0	**Reject**	
	PZ/Tau	21/30	0, 0.30	**Reject**	
	PZ/Tyr	13.7/29	0, 0.33	**Reject**	
Carbonate	K_2CO_3	20	0	**Accept**	not an issue
	PZ/ K_2CO_3	13.8/22.14	0, 0.35, 0.40, 0.50	**Reject**	
	MAPA/ K_2CO_3	14/22	0, 0.10, 0.15, 0.22, 0.40, 0.45, 0.50	**Accept**	20-60 C, 0.10-0.40
PZ / Organic	PZ/Sulfolane	40/5	0, 0.035, 0.06, 0.085, 0.098, 0.112, 0.12, 0.126, 0.15, 0.20, 0.25, 0.31, 0.38, 0.40, 0.42, 0.45, 0.495	**Accept**	20 C, 0.12-0.42
	PZ/Sulfolane	40/10	0, 0.027, 0.051, 0.074, 0.088, 0.10, 0.20, 0.25, 0.31, 0.38, 0.42	**Accept**	20 C, 0.10-0.42
	PZ/Sulfolane	40/15	0, 0.42	**Accept**	20 C, <0.42
	PZ/Sulfolane	40/20	0, 0.42	**Accept**	20 C, <0.42
	PZ/Sulfolane	40/30	0, 0.112, 0.19	**Accept**	20 C, >0.19
	PZ/Butanol	40/1	0	**Accept**	same as 40 wt% PZ
	PZ/Butanol	40/2	0, 0.42	**Accept**	same as 40 wt% PZ
	PZ/Butanol	40/5	0, 0.42	**Accept**	same as 40 wt% PZ, slightly slower rate of rich precipitate crystallization
	PZ/Arg/Sulfolane	14.3/29.3/5	0	**Reject**	

Discussion of Solubility Investigations

Amino Acid Salts. Seven amino acids (AA) were experimentally evaluated to provide information on how AA blending might affect the performance of concentrated PZ solvents. Simple mixing experiments were organized and performed to determine the potential for solubility issues with equimolar AA/PZ solutions. The first set of experiments fixed the molar alkalinity of each AA-PZ solution at 8 $mol_{alk}/kg\ H_2O$ (8 molal, or 8m). This value was selected based on a minimum expected molar alkalinity of solvents to remain competitive with 40.8 wt% PZ, itself. For reference, a 40.8 wt% PZ solution contains 15.5 $mol_{alk}/kg\ H_2O$, while a 30 wt% MEA solution contains 7 $mol_{alk}/kg\ H_2O$. Some of the resulting AA/PZ solutions appeared to have undissolved PZ while others appeared to have undissolved AA.

To verify that undissolved PZ was indeed the suspected species present in some of the solutions, follow-up testing was conducted with equimolar AA-MEA solutions. The same AA concentrations were used as those of the earlier PZ set. As expected the MEA solutions mimicking the PZ solutions where undissolved PZ was suspected exhibited no solid phase (MEA being more soluble than PZ). Further, the PZ-based solutions that were believed to have undissolved AA also had undissolved crystals in the corresponding MEA solutions. An example of the same AA crystals appearing in both aqueous PZ and MEA solutions is shown in Figure 3.12.


Mixed with aqueous PZ

Mixed with aqueous MEA

Figure 3.12 Amino Acid Crystals in Both PZ and MEA solutions

The third set of AA experiments was done with solutions that were prepared by initially adding AA to water (without PZ) until the solubility limit of the AA was reached, then PZ was added in an amount equimolar with the AA. Of these solutions, half had solids present. One AA solution actually had two types of solids present: one floating at the top of the solution which appeared to be PZ flakes and the other sinking to the bottom. This behavior is illustrated in Figure 3.13.

Figure 3.13 Equimolar AA-PZ Blend with Two Types of Solids Present

Several samples with undissolved AA crystals were slowly heated to determine an approximate dissolution temperature. These experiments suggested that the dissolution temperature in the PZ solutions is significantly reduced over the expected value in pure water. The dissolution temperatures were around 40C indicating that the formulations could potentially be used with caution in a CO_2 scrubbing process.

Of course these neat solution solubility studies do not provide a complete picture. Just as CO_2 has a significant impact on concentrated PZ solubility in aqueous solutions, it also influences the solubility behavior of AA/PZ blends. Accordingly, these same AA/PZ mixtures were reacted with CO_2 to observe any changes in solubility behavior. The addition of CO_2 both to a moderate loading of α = 0.3 mol CO_2/mol$_{alk}$ and to a typical rich CO_2 loading of α > 0.4 mol CO_2/mol$_{alk}$ revealed that several of the AA/PZ solutions have promise in terms of solubility characteristics. However, several other AA/PZ blends were subsequently eliminated due to an unmanageable presence of solids; an extreme example of which is given in Figure 3.14.

Potassium Carbonate. Inorganic carbonate salts such as potassium carbonate (K_2CO_3) have long been used commercially for the capture of CO_2 and other acid gases – typically in a pressure-swing scrubbing process. Due to the relatively slow kinetics of solvents such as potassium carbonate, a catalyst or promoter is often used to enhance the CO_2 absorption rate. One common promoter used for this purpose is PZ. For this application PZ is usually present in solution at concentrations less than 10 wt%.

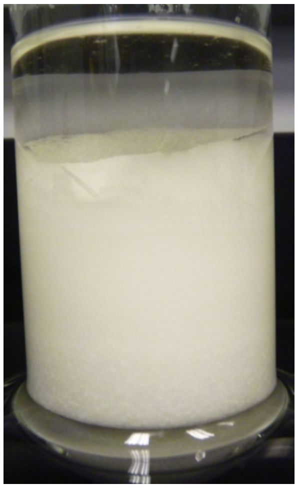
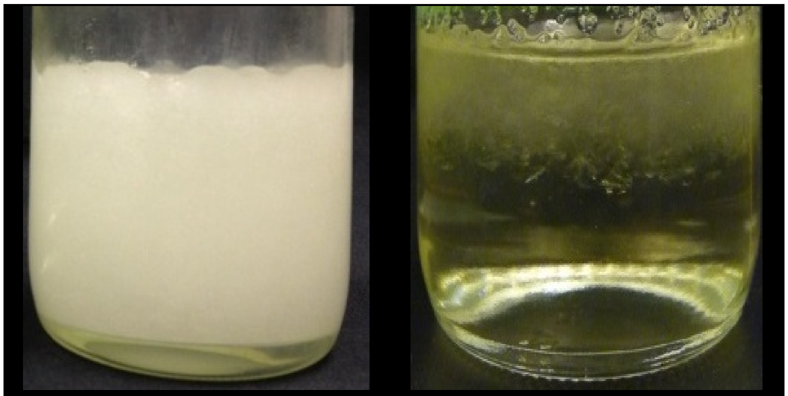


Figure 3.14 Rejected AA-PZ-CO_2 Blend

In contrast to the promoter role for PZ, solutions of interest in this study were targeted at K_2CO_3/PZ blends where the PZ concentration is significantly above 14 wt%. A significant number of laboratory mixing tests were done to identify workable blends of concentrated PZ with K_2CO_3. However, all of the blends tested exhibited troublesome solubility behavior across a range of CO_2 loading conditions. Even in the best blends the resulting solubility window was so narrow that the working capacity for CO_2 capture would be unacceptably low. Consequently, further investigation of K_2CO_3/PZ blends was not indicated.

Organic Additives. Another approach aimed specifically at broadening the solubility window of concentrated PZ solvents was also investigated. Here the additives are not used for their reactivity with CO_2 such as amines, carbonates, or amino acids. Instead, the compounds tested were intended to improve the solubility of PZ and/or its carbamate in aqueous solution. Two organic compounds were selected for testing. Again, the intent was to expand the solubility window without losing the performance benefits of PZ.

Sulfolane was investigated at various concentrations while holding PZ concentration at 40.8 wt%. Five blends were tested up to an evenly split partition of sulfolane and water. CO_2 addition across the spectrum of lean to rich loadings was investigated for each solution. Favorable indications were observed showing a widening of the solubility window. While solids were not completely eliminated, their solubility and fluidity was improved, as illustrated in Figure 3.15. Two promising formulations were selected for further evaluation. For the PZ/Sulfolane (40 wt%/5 wt%) formulation, the lean loading solubility limit appeared to be reduced relative to that of 40.8 wt% PZ. Based on these very preliminary trials, the resulting wider solubility window should increase CO_2 working capacity and improve process operating reliability.

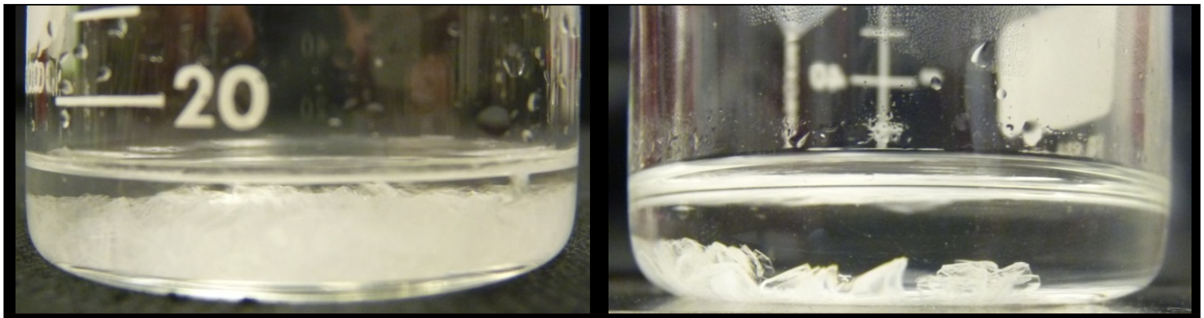


40wt% PZ
No CO_2 Loading

40wt% PZ with organic additive
No CO_2 loading

Figure 3.15 Impact of Organic Additive on PZ Solubility

Butanol was also investigated as a possible additive at three concentrations, again holding the PZ concentration constant at 40.8 wt%. In the usual fashion, neat solutions were evaluated first, then CO_2 was added to determine if any noticeable changes in solubility were realized. Neat solutions at room temperature did not exhibit any marked improvement in solubility. At the rich CO_2 loading condition of α = 0.42 mol CO_2/mol_{alk}, the 2 wt% butanol solution appeared nearly identical to the baseline 40.8 wt% PZ aqueous solution. Some minor improvement was observed with the 5 wt% butanol solution, as shown in Figure 3.16. The solutions were not considered promising enough to warrant further investigation.



With 2% organic alcohol
Rich CO_2 Loading
α = 0.42 mol CO_2/mol_{alk}

With 5% organic alcohol
Rich CO_2 Loading
α = 0.42 mol CO_2/mol_{alk}

Figure 3.16 Impact of Organic Alcohol Additive Under Rich Conditions

3.5 Solvent Viscosity Characterization Testing

3.5.1 Rationale

The viscosity of a CO_2 scrubbing solvent can impact system performance in a variety of ways. A highly viscous solvent may result in

- Low mass transfer rates in the absorber and regenerator,
- Low heat transfer rates in the cross heat exchanger and other heat transfer equipment, and
- High pumping power requirements.

These impacts of solvent viscosity have been clearly seen in previous bench- and pilot-scale testing of CO_2 scrubbing systems at B&W. Absorber performance has been seen to be surprisingly sensitive to even small changes in temperature due to its impact on solution viscosity. Through such testing it has been determined that solvent viscosity under absorber conditions (roughly 40-50 C) should be below about 10 centipoises (cP) – certainly below 20 cP.

The viscosity behavior of candidate concentrated PZ formulations is complicated and depends on component type and concentration, CO_2 loading, and temperature. As with solubility behavior, it is difficult to accurately predict solution viscosity *a priori*. So although no viscosity testing was originally planned for Budget Period 1, it was deemed necessary to make viscosity measurements to ensure that the selected candidates exhibited acceptable viscosity characteristics. *This was not intended to be an exhaustive study, it was simply meant to facilitate the screening process.*

3.5.2 Methods

Visual inspection by pouring and/or agitation alone was not sufficient for assessing solution viscosity. A simple bench-top method was therefore used to quantify the viscosity of candidate formulations. A size 150 calibrated Cannon-Fenske Routine Viscometer, shown in Figure 3.17, with a range of 7-35 centistokes (cSt) was used to determine kinematic viscosity. The glassware comprises two tubes: the tube with the capillary (1) and the venting tube (2) in the image. By passing the test liquid through the reservoir (3), upper timing mark (4), lower timing mark (5), pre-run sphere (6), capillary (7), and measuring sphere (8) an elapsed time is recorded. The liquid efflux time was measured in seconds for a 6.2 ml charge volume. Calibration data and constants at 40 C and 22 C were provided by the manufacturer for the purpose of calculating viscosity.

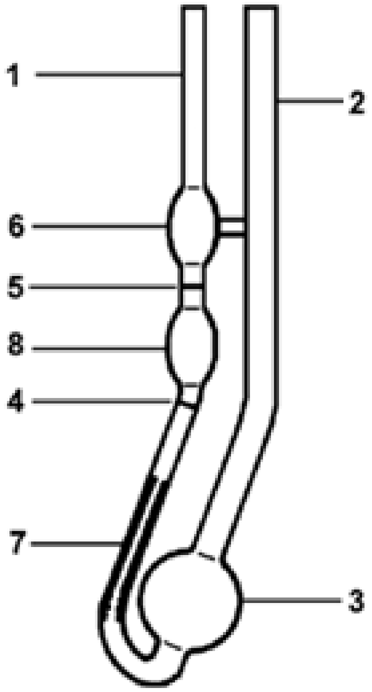


Figure 3.17 Cannon-Fenske Routine Viscometer

3.5.3 Results

Summary

A glass capillary viscometer was used to make preliminary measurements of the kinematic viscosity of several candidate solvent formulations at 20 and 40 C and various CO_2 loadings. Approximately 50 tests were conducted, the results of which are summarized in Table 3.4. Using B&W's "rule of thumb", six candidates with dynamic viscosities greater than about 10 cP at absorber conditions (about 40 C) were eliminated from further consideration (highlighted in red in Table 3.4). Several other candidates exhibited marginally acceptable viscosity characteristics (highlighted in yellow in Table 3.4).

Table 3.4 Results of Laboratory Viscosity Investigations

(Green: Accepted; Yellow: Marginal; Red: Rejected)

Formulation	CO_2 loading	Trial 1			Trial 2			Trial 3			Trial 4			Trial 5		
		Time *seconds*	Temp *C*	Viscosity *mm^2/s*	Time *seconds*	Temp *C*	Viscosity *mm^2/s*	Time *seconds*	Temp *C*	Viscosity *mm^2/s*	Time *seconds*	Temp *C*	Viscosity *mm^2/s*	Time *seconds*	Temp *C*	Viscosity *mm^2/s*
40PZ	0.2	168	44	5.81	173	43	5.98	179	42	6.19	185	41	6.39	192	40	6.64
	0.3	193	44	6.67	201	42.5	6.95	209	41.5	7.22	221	40	7.64			
	0.38	241	42	8.33												
	0.3	415	20	14.34	446	20	15.41	438	20	15.14						
45PZ	0.3	322	43.5	11.13	348	41.5	12.03									
14PZ/29Arg	0.45	226	44	7.81	236	42.5	8.16	246	41	8.50						
	0.519	251	43.5	8.67	261	42	9.02									
16PZ/32Arg	0.307	341	42.5	11.78	367	41	12.68									
16PZ/25Arg4Sar	0.191	208	43.5	7.19	216	42.5	7.46	230	40.5	7.95						
20PZ/20Arg10MAPA	0.25	1444	20	49.90	1374	20	47.49									
20PZ/20Arg10PZ	0.25	1449	20	50.08												
14PZ/25Lys	0.557	186	44	6.43	190	43	6.57									
16PZ/26Lys	0.35	201	45	6.95	211	43	7.29	219	42	7.57						
18PZ/31Lys	0.294	448	43.5	15.48	489	41	16.90									
20PZ/27Pro	0.487	202	40.5	6.98	203	40	7.02									
22PZ/29Pro	0.319	261	44	9.02	277	43	9.57									
20PZ/15Sar15MAPA	0.25	891	20	30.79	895	20	30.93	890	20	30.76						
	0.45	1245	21.5	43.03												
23PZ/23Sar	0.485	190	42	6.57	378	20	13.06	383	20	13.24	188	42	6.50			
25PZ/25Sar	0.25	510	20	17.63	603	20	20.84	563	20	19.46						
	0.235	246	42	8.50	235	43	8.12									
27PZ/27Sar	0.303	342	45	11.82	365	43	12.61	388	41	13.41						
20PZ/15Sar15PZ	0.25	768	20	26.54	859	20	29.69	757	20	26.16						
40PZ/5Sulf	0.15	541	20	18.70	240	38	8.29									
	0.45	701	20	24.23	722	20	24.95	278	44.5	9.61	295	42.5	10.20	311	41	10.75
40PZ/10Sulf	0.2	482	20	16.66	198	39	6.84									

Discussion of Viscosity Investigations

Kinematic viscosity is plotted as a function of CO_2 loading in Figure 3.18 for the candidate formulations tested. The relationship between kinematic and dynamic viscosity is given by:

$$v = \frac{\mu}{\rho}$$

where v is the kinematic viscosity, μ is the dynamic viscosity, and ρ is the fluid density. Since the densities of the formulations of interest are near that of water (~1 gm/cm^3) the values for kinematic viscosity in cSt shown in the figure are very nearly equal to the dynamic viscosity expressed in cP. As mentioned, above, formulations with viscosities much above 10 cP were eliminated from further consideration.

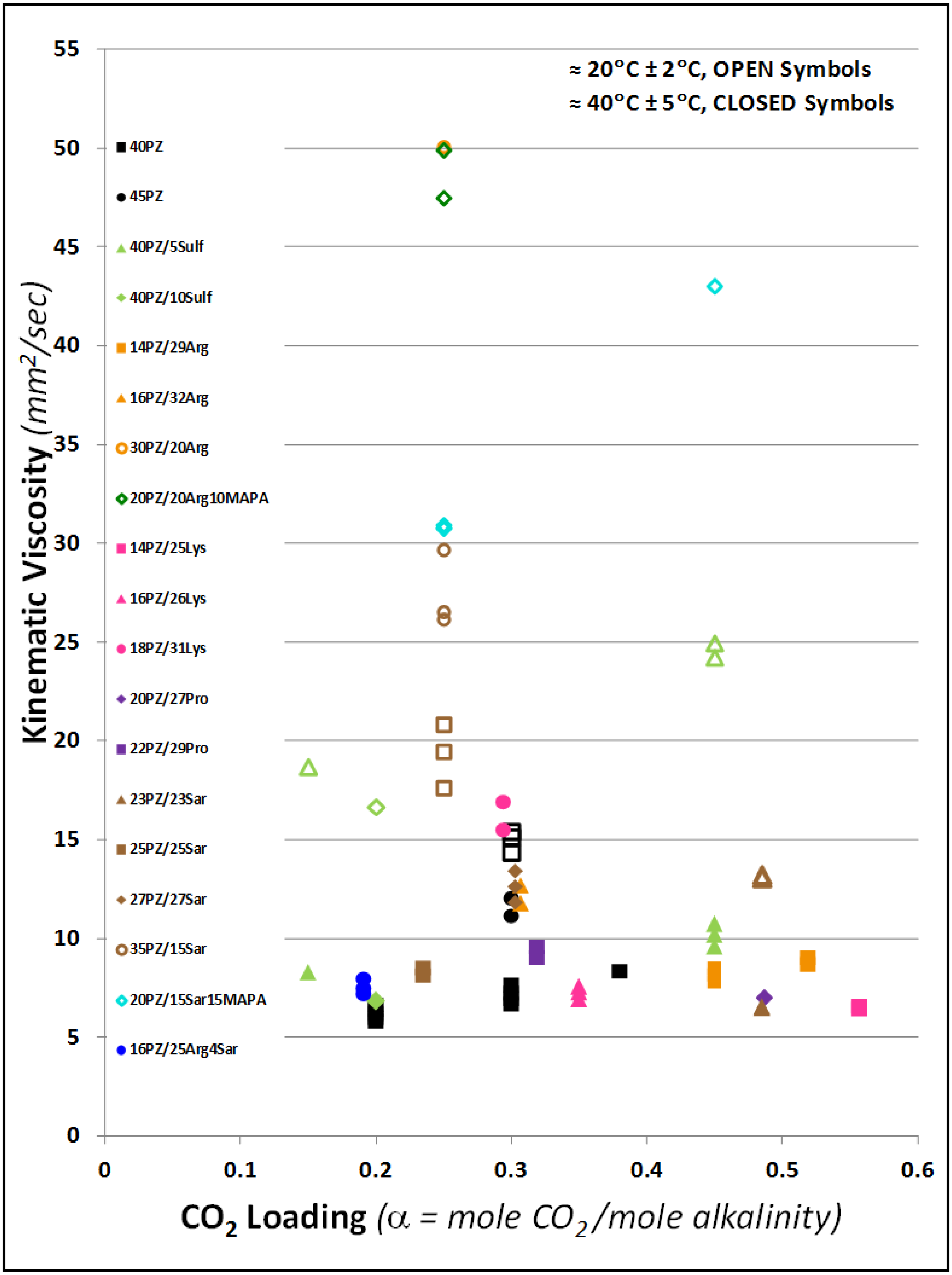


Figure 3.18 Viscosity Screening Results

3.6 Initial Candidates Selected

Using the screening methodology described, above, augmented by the results of the solubility and viscosity laboratory characterization tests, 14 unique formulations of concentrated PZ with other components were selected as the initial solvent formulation candidates. The selected formulations are shown in green in Table 3.5. Also shown in the table are the primary reasons for the elimination of the rejected candidates (shown in red in Table 3.5).

Table 3.5 Summary of Initial Selection Decisions/Rationale

Type	Formulation	Concentration wt%	Initial Evaluation / Disposition
Amine	PZ	40	**Selected for WWC testing. (baseline solvent)**
	PZ	45	**Eliminated: high viscosity.**
Amine Blend	PZ/DEEA	21/29	**Selected for WWC testing.**
	PZ/2-PE/DMAE	12/7/30	**Selected for WWC testing.**
Amine Amino Acid Salt (AAAS)	MEA/Arg	7.4/20	**Eliminated: too slow (not PZ-based), poor solubility.**
	MEA/Pro	14.5/27.2	**Eliminated: too slow (not PZ-based), high cost (Pro).**
	MEA/Sar	15.2/22.6	**Eliminated: too slow (not PZ-based).**
	MEA/Tau	14/28.6	**Eliminated: too slow (not PZ-based), poor solubility.**
	PZ/(Arg/MAPA)	20/(20/10)	**Eliminated: high viscosity.**
	PZ/(Arg/PZ)	20/(20/10)	**Eliminated: high viscosity.**
	PZ/(Arg/Sar)	16/(25/3.6)	**Eliminated: PZ/Arg and PZ/Sar more attractive.**
	PZ/(Sar/DMAPA)	20/(14/16)	**Selected for WWC testing.**
	PZ/(SarMAPA)	20/(15/15)	**Selected for WWC testing (marginal viscosity @ 20 C).**
	PZ/(Sar/MAPA)	20/(20/20)	**Selected for WWC testing.**
	PZ/(Sar/PZ)	20/(15/15)	**Selected for WWC testing (marginal viscosity @ 20 C).**
	PZ/(Dmg/DMAPA)	20/(30)	**Eliminated: high cost (Dmg).**
	PZ/(Dmg/MAPA)	20/(30)	**Eliminated: high cost (Dmg).**
	PZ/(Dmg/PZ)	20/(30)	**Eliminated: high cost (Dmg).**
	PZ/Dmg	20/23.9	**Eliminated: high cost (Dmg).**
	PZ/Arg	4/15	**Eliminated: 14/29 blend more attractive (faster,higher capacity).**
	PZ/Arg	9.9/19.6	**Eliminated: 14/29 blend more attractive (faster,higher capacity).**
	PZ/Arg	14/29	**Selected for WWC testing.**
	PZ/His	15/27	**Eliminated: poor solubility, high cost (His).**
	PZ/Lys	14.5/25	**Eliminated: 16/26 blend more attractive (faster,higher capacity), marginal cost (Lys).**
	PZ/Lys	16/26	**Selected for WWC testing.**
	PZ/Lys	18.4/31.4	**Eliminated: high viscosity, marginal cost (Lys).**
	PZ/Pro	19.2/25.7	**Eliminated: poor solubility, high cost (Pro).**
	PZ/Pro	21/29	**Selected for WWC testing.**
	PZ/Pro	22/29	**Eliminated: poor solubility, high cost (Pro).**
	PZ/Pro	32/42	**Eliminated: poor solubility, high cost (Pro).**
	PZ/Sar	20.3/21.1	**Eliminated: 25/25 blend more attractive (faster,higher capacity).**
	PZ/Sar	25/25	**Selected for WWC testing.**
	PZ/Sar	26.5/27.7	**Eliminated: high viscosity.**
	PZ/Tau	6.2/9	**Eliminated: Low concentration (too slow, low capacity).**
	PZ/Tau	12/17.8	**Eliminated: poor solubility.**
	PZ/Tau	18.8/27	**Eliminated: poor solubility.**
	PZ/Tau	21/30	**Eliminated: poor solubility.**
	PZ/Tyr	13.7/29	**Eliminated: poor solubility.**
Carbonate	K_2CO_3	20	**Eliminated: too slow, low capacity.**
	PZ/ Na_2CO_3	14/20	**Eliminated: $NaHCO_3$ less soluble than $KHCO_3$.**
	PZ/ $(NH_4)_2CO_3$	14/20	**Eliminated: volatility (NH_3).**
	PZ/ K_2CO_3	13.8/22.14	**Eliminated: poor solubility.**
	MAPA/ K_2CO_3	14/22	**Selected for WWC testing.**
PZ / Organic	PZ/Sulfolane	40/5	**Selected for WWC testing.**
	PZ/Sulfolane	40/10	**Selected for WWC testing.**
	PZ/Sulfolane	40/15	**Eliminated: volatility (Sulfolane odor), no advantage over 40/5 blend.**
	PZ/Sulfolane	40/20	**Eliminated: volatility (Sulfolane odor), no advantage over 40/5 blend.**
	PZ/Sulfolane	40/30	**Eliminated: volatility (Sulfolane odor), no advantage over 40/5 blend.**
	PZ/Methanol	40/2	**Eliminated: volatility of methanol.**
	PZ/Ethanol	40/2	**Eliminated: volatility of ethanol.**
	PZ/Propanol	40/2	**Eliminated: volatility of propanol.**
	PZ/Butanol	40/1	**Eliminated: solubility same as 40 wt% PZ, volatility of butanol.**
	PZ/Butanol	40/2	**Eliminated: solubility same as 40 wt% PZ, volatility of butanol.**
	PZ/Butanol	40/5	**Eliminated: solubility same as 40 wt% PZ, volatility of butanol.**
	PZ/Arg/Sulfolane	14.3/29.3/5	**Eliminated: no advantage over PZ/Sulfolane blends.**

4.0 SELECTION OF FINAL CANDIDATE FORMULATIONS

4.1 Final Downselection Methodology

The 14 initial candidate formulations were subsequently evaluated in more detail to arrive at a list of four final candidate formulations, as illustrated in Figure 4.1 (shown earlier). As a reminder, the tasks under which each of the various activities was carried out are indicated by superscripts in the figure. The initial candidates were evaluated using WWC results and B&W Semi-Empirical Model performance predictions provided by Tasks 4 and 3, respectively. Finally, on the basis of this more detailed evaluation, the four most promising candidate solvent formulations were selected to carry forward.

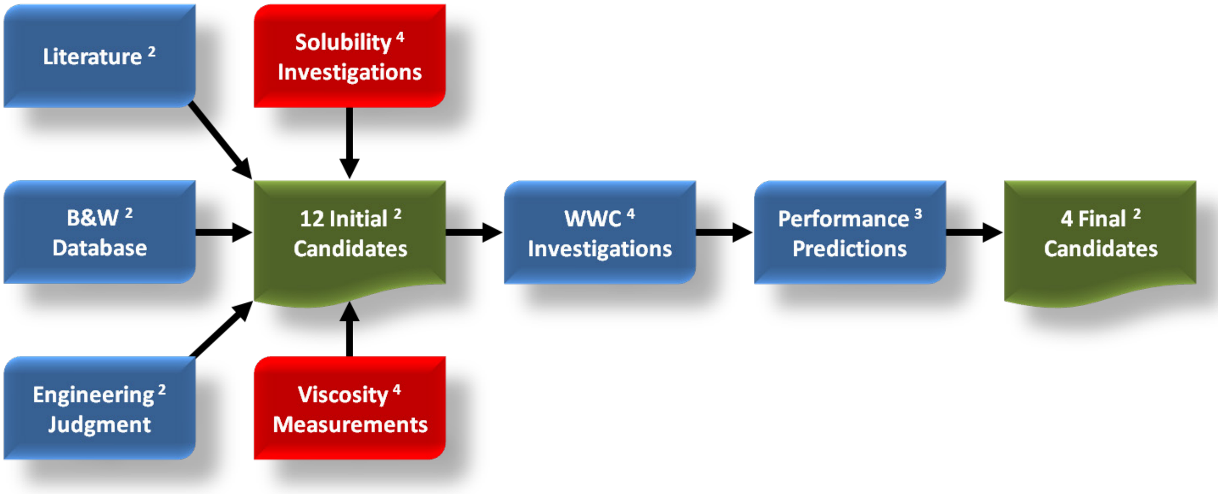


Figure 4.1 Overview of Budget Period 1 Solvent Selection Activities

4.2 Wetted-Wall Column Investigations

4.2.1 Rationale

B&W's wetted-wall column (WWC) was used to collect CO_2 absorption rate and solubility data on candidate solvent formulations using experimental protocols previously established and validated by B&W. The WWC is a differential reactor capable of providing mass transfer rates and VLE data on a specific solvent. From the outset it was recognized that such measurements were crucial to the proper selection of candidate solvent formulations, and WWC characterization testing was therefore included in the original project plan.

Some of the most important advantages of 40.8 wt% PZ include high absorption rates, low regeneration energy, and good capacity. Any candidate solvent formulation must maintain these benefits. The data obtained using the WWC can be used to estimate these key performance parameters, thereby facilitating a meaningful selection process. CO_2 absorption rate, or flux, and equilibrium CO_2 solubility data were measured at different temperatures under various CO_2 loading conditions using the WWC. These data were then used to make preliminary performance predictions, as described in the following section, which in turn were used to support the candidate selection methodology.

4.2.2 Methods

B&W's WWC, shown in Figure 4.2, is constructed of stainless steel and has a diameter of 1.27 cm (0.5 in). The hydraulic diameter and height of the gas-liquid reaction zone (annulus) are 0.43 cm and 9.13 cm, respectively. The column assembly resides in a bath of circulating silicon oil, the temperature of which is maintained by a temperature controller with an accuracy of ±0.1 C. Solvent solutions are circulated through the column at a constant rate of $3x10^{-6}$ m^3/s (180 ml/min) using a digitally-controlled pump.

Nitrogen and carbon dioxide are introduced to the system through two separate mass flow controllers. The desired concentration of CO_2 is achieved by varying the flow rate of these two gas species, while keeping the total gas flow rate the same. The WWC was operated near atmospheric pressure for all experiments in this study. Gas flow rate is kept at 4 standard liters per minute. The gas mixture is heated and saturated with water vapor under temperature-controlled conditions, and then flows to the column. The gas mixture flows counter-currently past the thin solvent film on the column and then to a gas analysis system. Water vapor in the outlet gas is removed in a condenser and the CO_2 concentration is measured by a CO_2 analyzer. Changing the inlet CO_2 concentration allows testing under both absorption and desorption conditions.

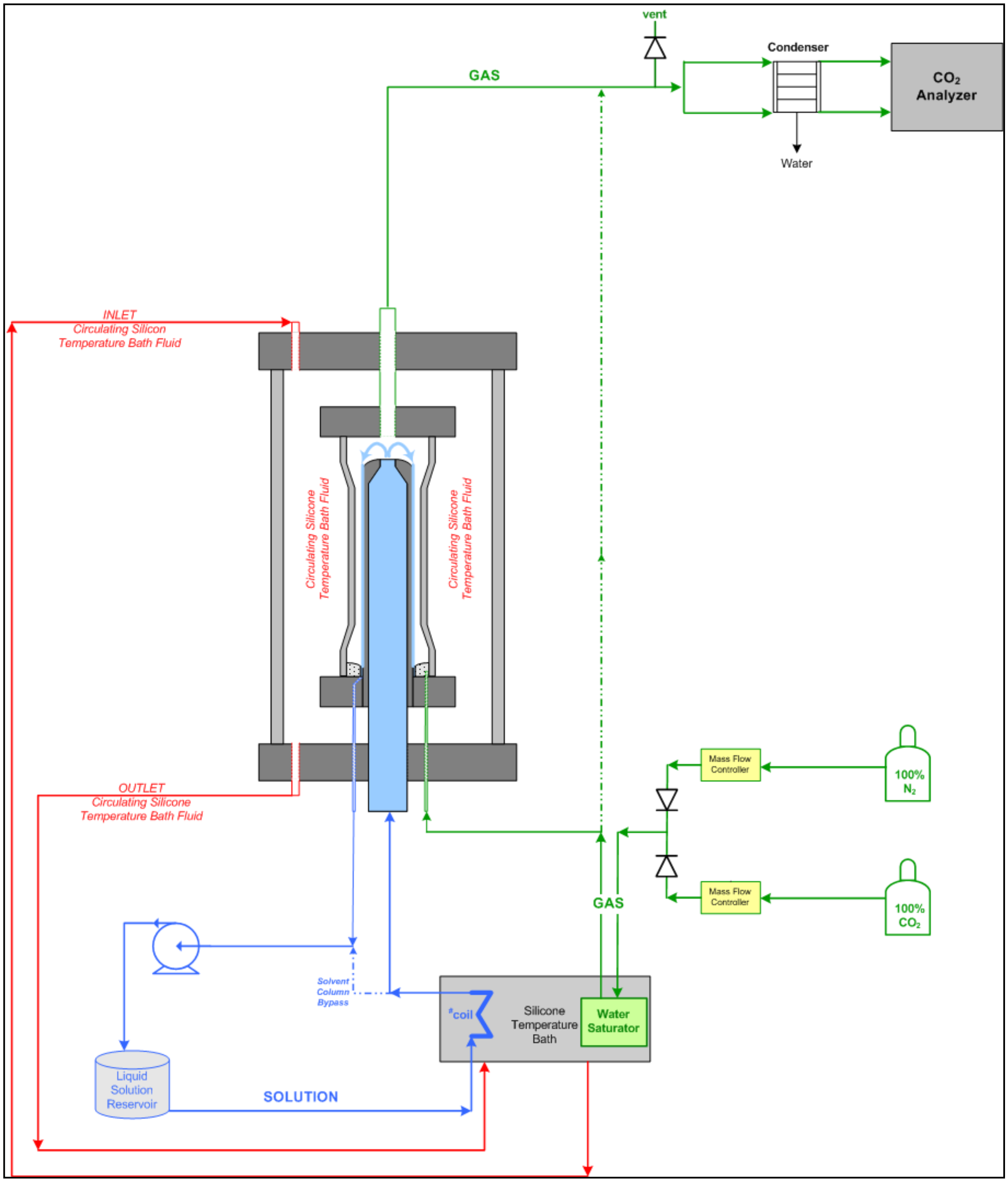


Figure 4.2 Schematic of WWC Apparatus

The liquid film mass transfer coefficient, k'_g, as well as the equilibrium partial pressure of CO_2, p_{CO2}^*, is obtained from each WWC test, as described below. Other important parameters such as heat of absorption and CO_2 working capacity can also be derived from these experimental data. Preliminary solvent formulation performance can then be estimated with in-house semi-empirical models.

Testing Procedures. Candidate solvents at specified concentrations are tested in the WWC at three different loadings, typically 0.2, 0.4 and 0.6 mol CO_2/mol$_{alk}$. Solutions are prepared gravimetrically by mixing pure chemical with distilled water to the desired concentration. Pure carbon dioxide gas is bubbled into the solution to get the desired CO_2 loading condition. Each solvent concentration/loading combination is then transferred into the WWC apparatus and tested.

An experimental test matrix is developed for each test condition with a total of six data points to be completed for each experiment. Three of these are absorption points and three are desorption points. To get these values, the solution inside the WWC is contacted with various concentrations of the carbon dioxide and nitrogen gas mixture. The resulting gas streams are analyzed for carbon dioxide content. The flux for each absorption/desorption point is then calculated from the difference in partial pressure at each point and plotted versus the CO_2 partial pressure of that point, as can be seen in Figure 4.3. The slope of the line is the K_G (overall mass transfer coefficient) value for the solution at that concentration, loading, and temperature. The x-intercept of this line yields the equilibrium partial pressure of that particular solvent mixture. The equilibrium partial pressure is the partial pressure at which the solution neither absorbs or desorbs and is different for each solvent, concentration, loading and temperature combination.

The general equation used to describe the absorption rate, or flux of CO_2, is: .

$$N = K_G \left(p_{CO2} - p^*_{CO2}\right) \qquad (4\text{-}1)$$

Where N is the flux of CO_2 moving across the gas-liquid interface, K_G is the overall mass transfer coefficient, p_{CO2} is the gas-phase CO_2 partial pressure, and p^*_{CO2} is the partial pressure of CO_2 that would be in equilibrium with the bulk liquid phase. As can be seen from Figure 4.3, the slope of the fitted line is K_G and the interception of fitted line with the x-axis is p^*_{CO2}.

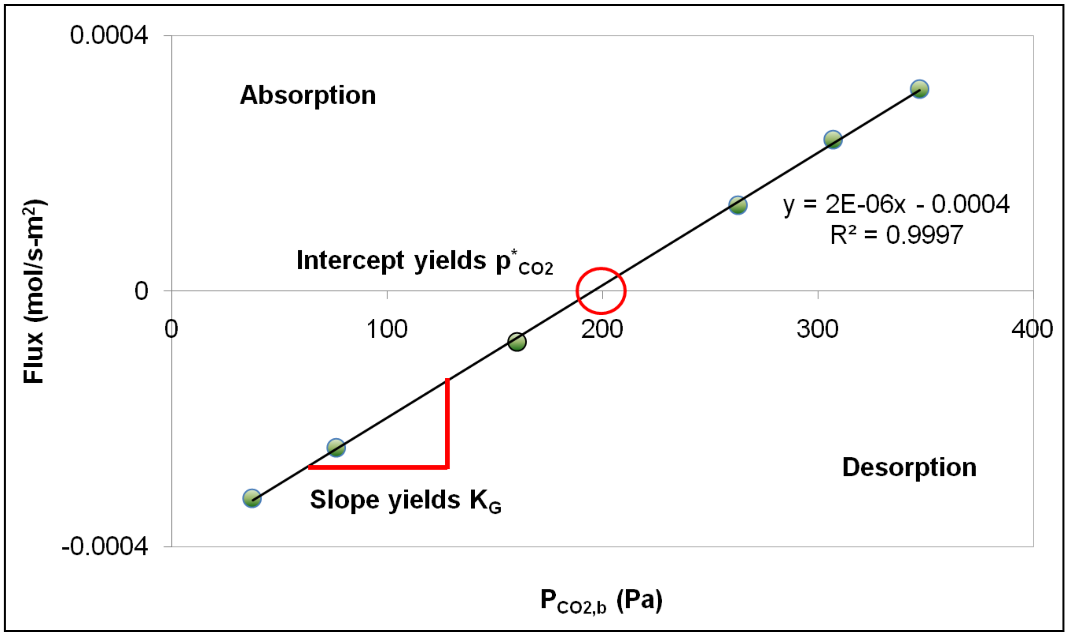


Figure 4.3 Flux Versus Driving Force

Theoretical Considerations

For CO_2 absorption with amine, the mass transfer process comprises three series resistances: the gas film resistance R_g, the reaction film resistance R_{rxn}, and the liquid film resistance R_{Leq}.:

$$R = R_g + \mathrm{R_{rxn}} + \mathrm{R_{Leq}} \tag{4-2}$$

or, expressed in terms of conductances:

$$\frac{1}{K_G} = \frac{1}{k_g} + \frac{H_{CO2}}{Ek_l^0} + \frac{1}{k_{l,prod}}\frac{\Delta P_{CO2}^*}{\Delta[CO_2]_T} \tag{4-3}$$

Where K_G is the overall mass transfer coefficient, k_g is the gas film mass transfer coefficient, H_{CO2} is the Henry's constant for CO_2 in amine solution, E is the enhancement factor, k_l^0 is the liquid phase mass transfer coefficient of CO_2, and $k_{l,prod}$ is the liquid phase mass transfer coefficient of the reaction product. The k_l^0 used in this study was calculated from the correlation developed by Pacheco[1].

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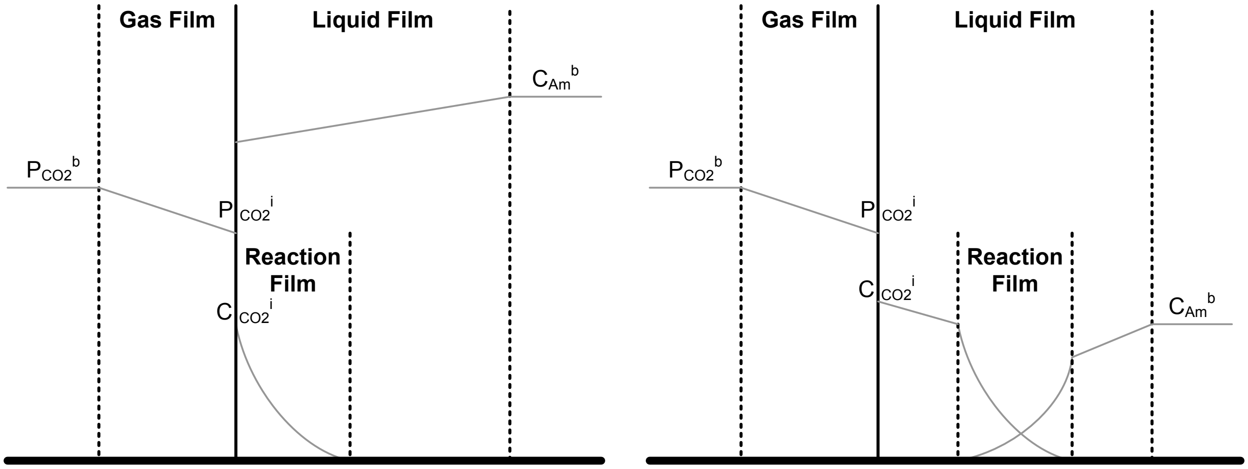
[1] Pacheco, M.A., Mass Transfer, Kinetics, and Rate-Based Modeling of Reactive Absorption, Doctoral Thesis, University of Texas at Austin, p. 318, (1998).

When the purpose of a WWC experiment is to derive chemical reaction kinetics, it is critical to ensure that the experiment is carried out in the pseudo first order (PFO) regime. In this regime, the free amine concentration is much higher than the CO_2 concentration, so the free amine concentration remains mostly constant at the gas-liquid interface and throughout the reaction film. The reaction starts at the gas-liquid interface and completes within the reaction film, as shown in Schematic A of Figure 4.4. This eliminates the mass transfer resistance caused by the reactant diffusion through the liquid film, which would be more pronounced if the free amine concentration were lower (shown in Schematic B of Figure 4.4).



A. Pseudo-first order reaction (high C_{Am}^b)

B. Fast second order reaction (low C_{Am}^b)

C_{Am}^b	Amine concentration in bulk liquid phase	C_{CO2}^i	CO_2 concentration at the gas-liquid interface
P_{CO2}^b	Partial pressure of CO_2 in the bulk gas phase	P_{CO2}^i	Partial pressure of CO_2 at the gas-liquid interface

Figure 4.4 Interface Behavior for the Liquid-Phase Reaction (Two-Film Theory)

Since the concentration or partial pressure of CO_2 is low compared to that of free amine, the amount of reaction product produced in the reaction film provides negligible mass transfer resistance. So the third term in (4-3), which accounts for the diffusion resistance of reactants and products, can be neglected. Mass transfer resistance due to reaction kinetics, shown in the second term of (4-3), can be calculated directly from experimental data, since the first term is addressed through a correlation specific to the WWC device and the third term can be neglected under the PFO regime. This kinetic resistance is also considered representative of the total liquid film resistance.

When the PFO assumption applies, the enhancement factor, *E,* is considered to be equal to the Hatta number, *Ha*, which is defined as:

$$Ha = \sqrt{M} = \frac{\sqrt{k_2[Am]D_{CO2}}}{k_l^0} \tag{4-4}$$

Where *M* is a dimensionless number, D_{CO2} is the diffusion coefficient of CO_2 in the amine solution, [Am] is the free amine concentration, and k_2 is the second order reaction rate constant. Substituting (4-4) into (4-3) and considering the PFO assumption yields:

$$\frac{1}{K_G} = \frac{1}{k_g} + \frac{H_{CO2}}{\sqrt{k_2[Am]D_{CO2}}} \tag{4-5}$$

To simplify (4-5), the liquid film resistance is often shown as $1/k_g'$:

$$\frac{1}{K_G} = \frac{1}{k_g} + \frac{1}{k_g'} \tag{4-6}$$

To determine whether the experimental conditions satisfy the PFO assumptions, the relative magnitude of the Hatta number is compared to the infinite enhancement factor E_i, which is defined by penetration theory as:

$$E_i = \sqrt{\frac{D_{CO2}}{D_{am}}}\left(1 + \frac{D_{am}}{D_{CO2}}\frac{[Am]RT}{\gamma_{am} m_{CO2} P_{CO2}^{b}}\right) \tag{4-7}$$

Where D_{am} is the diffusion coefficient of amine in solution, γ_{am} is the stoichiometry for the amine reaction, m_{CO2} is the distribution coefficient of CO_2, and $P_{CO2}{}^{b}$ is the bulk phase CO_2 partial pressure. The general rule used in this study was that E_i/Ha must be greater than 10 to ensure the PFO condition.

The overall mass transfer coefficient K_G can be obtained from CO_2 absorption and desorption experiments in the WWC. To determine the liquid film mass transfer coefficient, k_g', the gas film mass transfer coefficient, k_g, must be known – see (4-6). The gas film mass transfer coefficient, k_g, was determined by the analytical correlation proposed by Hobler[1] for short columns:

$$Sh = A\left(ReSc\frac{d}{h}\right)^B \tag{4-8}$$

The Sherwood number, Reynolds number, and Schmidt number are defined as:

$$Sh = \frac{RTdk_g}{D_{CO2}} \tag{4-9}$$

$$Re = \frac{du\rho}{\mu} \tag{4-10}$$

$$Sc = \frac{\mu}{\rho D_{CO2}} \tag{4-11}$$

Where R is the gas constant, T is the temperature, d is the hydraulic diameter of the annulus (0.43 cm), h is the height of the WWC (9.13 cm), D_{CO2} is the diffusion coefficient of CO_2 in the gas phase, u is the gas velocity, ρ is the gas density, and μ is the gas dynamic viscosity. These dimensionless numbers can be calculated under specific experiment conditions and the constants A and B can then be regressed according to (4-8). Once A and B are obtained, by solving (4-8), (4-9), (4-10), and (4-11), the resulting correlation can be used to predict k_g,:

$$k_g = A\left(\frac{D_{CO2}}{RTd}\right)\left(\frac{ud^2}{hD_{CO2}}\right)^B \tag{4-12}$$

Pacheco[2] used CO_2 absorption into 2 M MEA to determine the correlation of k_g, while Bishnoi[3] used a 0.1 M sodium hydroxide (NaOH) solution to absorb SO_2. In this study, a 1.7 M PZ solution was used to absorb CO_2 due to its fast reaction rate with CO_2. The experimental conditions included three gas flow rates (2, 3, and 4 standard liters per minute), two solvent temperatures (40ºC and 60ºC), and CO_2 partial pressures ranging from 25-600 Pa. A total of 22

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[1] Hobler, T., Mass Transfer and Absorbers, Oxford: Pergamon Press, (1966).

[2] Pacheco, M.A., Mass Transfer, Kinetics, and Rate-Based Modeling of Reactive Absorption, Doctoral Thesis, University of Texas at Austin, p. 318, (1998).

[3] Bishnoi, S., Carbon Dioxide Absorption and Solution Equilibrium in Piperazine Activated Methyldiethanolamine, Doctoral Thesis, University of Texas at Austin, p. 219, (2000).

data points were regressed and constants *A* and *B* were determined to be 1.05 and 0.724, respectively. All 22 data points used in the regression were collected under conditions where the mass transfer was at least 50% gas film controlled; this ensured accuracy of the regressed parameters. The average absolute relative deviation between the experimental and model results for k_g was approximately 4.8%.

4.2.3 Results

Summary

The 14 solvent formulations selected during the initial evaluation were subsequently characterized using the WWC. Several of the candidate formulations exhibited CO_2 absorption rates comparable to that of 40.8 wt% PZ, the baseline solvent for this study. Three solvents that exhibited impressive CO_2 absorption rates were PZ/2-PE/DMAE (12/7/30), PZ/Sulfolane (40/5) and PZ/Sulfolane (40/10). As anticipated, none of the candidate formulations exhibited absorption rates measurably higher than that of 40.8 wt% PZ.

CO_2 cyclical or working capacity was estimated using VLE data obtained from the WWC at different CO_2 loadings. Several of the candidate formulations exhibited higher theoretical maximum capacities than that of 40.8 wt% PZ. These included PZ/2-PE/DMAE (12/7/30), PZ/DEEA (21/29), PZ/Sulfolane (40/5), and PZ/Sulfolane (40/10).

During WWC testing, six of the 14 initial candidates were found to exhibit characteristics which made them noncompetitive and were eliminated from further consideration (highlighted in red in Table 4.1). In general, once a formulation was determined to be noncompetitive WWC testing was stopped. The primary observations that resulted in the elimination of the various solvent formulations are also listed in the table. Overall, WWC testing resulted in eight candidate formulations (highlighted in green in Table 4.1) being carried forward into the performance prediction (modeling) evaluation conducted under Task 3.

Table 4.1 Summary of WWC Evaluations

Type	Formulation	Concentration *wt%*	WWC Evaluation / Disposition
Amine	PZ	40	**Selected for Semi-Empirical Model evaluation.**
Amine Blend	PZ/DEEA	21/29	**Selected for Semi-Empirical Model evaluation.**
	PZ/2-PE/DMAE	12/7/30	**Selected for Semi-Empirical Model evaluation.**
Amine Amino Acid Salt (AAAS)	PZ/(Sar/DMAPA)	20/(14/16)	Eliminated: slow, not competitive.
	PZ/(SarMAPA)	20/(15/15)	**Selected for Semi-Empirical Model evaluation.**
	PZ/(Sar/MAPA)	20/(20/20)	Eliminated: high viscosity.
	PZ/(Sar/PZ)	20/(15/15)	**Selected for Semi-Empirical Model evaluation.**
	PZ/Arg	14/29	**Selected for Semi-Empirical Model evaluation.**
	PZ/Lys	16/26	Eliminated: marginal viscosity, high cost, poor VLE.
	PZ/Pro	21/29	Eliminated: marginal viscosity, high cost, poor VLE.
	PZ/Sar	25/25	**Selected for Semi-Empirical Model evaluation.**
Carbonate	MAPA/ K_2CO_3	14/22	Eliminated: slow, poor VLE.
PZ / Organic	PZ/Sulfolane	40/5	**Selected for Semi-Empirical Model evaluation.**
	PZ/Sulfolane	40/10	Eliminated: somewhat lower capacity than 40/5 blend.

Discussion of WWC Investigations

A total of fourteen solvent formulations were evaluated using the WWC during Budget Period 1. These solvents are listed in Table 4.2. In general, five different categories of solvent formulations were studied: single amines, amine blends, amine/amino acid salts, inorganic salts, and organic additives.

Table 4.2 Solvents Tested in the WWC

Solvent		Concentration (wt%)
Single Amine	PZ	40
Amine Blend	PZ/DEEA	21/29
	PZ/2-PE/DMAE	12/7/30
Amine/Amino Acid Salt	PZ/SarDMAPA	20/30
	PZ/SarMAPA	20/30
	PZ/SarMAPA	20/40
	PZ/SarPZ	20/30
	LysPZ	42
	ArgPZ	43
	ProPZ	50
	SarPZ	50
Inorganic Salt	MAPA/ K_2CO_3	14/22
Organic Additive	PZ/Sulfolane	40/5
	PZ/Sulfolane	40/10

Absorption Rate. Figure 4.5 contains a plot of WWC absorption rate data obtained at 40 C for the candidate solvent formulations. Figure 4.6 contains a similar plot of absorption rates for the candidate formulations at 60 C. The equilibrium partial pressure of CO_2, p^*_{CO2}, which corresponds to different CO_2 loading conditions is plotted on the x-axis. The liquid film mass transfer coefficient, k_g', is plotted on the y-axis. A higher value for k_g' indicates higher absorption rates and generally faster reaction kinetics, and is primarily a function of CO_2 loading. For a given solvent, the higher the CO_2 loading, the smaller the k_g' value will be.

Solvents with faster reaction kinetics generally show consistently strong k_g' throughout the entire loading range. CO_2 absorption reaction kinetics are generally considered more important in the rich loading range than in the lean loading range, mainly because CO_2 loading has a significant impact on absorption rate. Comparison of k_g' at a CO_2 equilibrium partial pressure of 5,000 Pa is therefore used to rank candidate solvents with respect to absorption rate. A vertical line indicating the point at which the CO_2 loading corresponds to an equilibrium partial pressure of 5,000 Pa is shown in both Figure 4.5 and Figure 4.6.

Figure 4.5 illustrates that several of the candidate formulations evaluated exhibit absorption rates comparable to that of 40.8 wt% PZ, the baseline solvent of this study. In particular, PZ/2-PE/DMAE (12%/7%/30%) and PZ/Sulfolane (40%/5% and 40%/10%) are solvents that exhibit impressive CO_2 absorption rates. Also as anticipated, none of the candidate formulations exhibited absorption rates measurably higher than that of 40.8 wt% PZ.

Quantitative absorption rate and VLE data obtained during WWC testing at 40 and 60 C are also summarized in tabular form in Table 4.3 and Table 4.4, respectively.

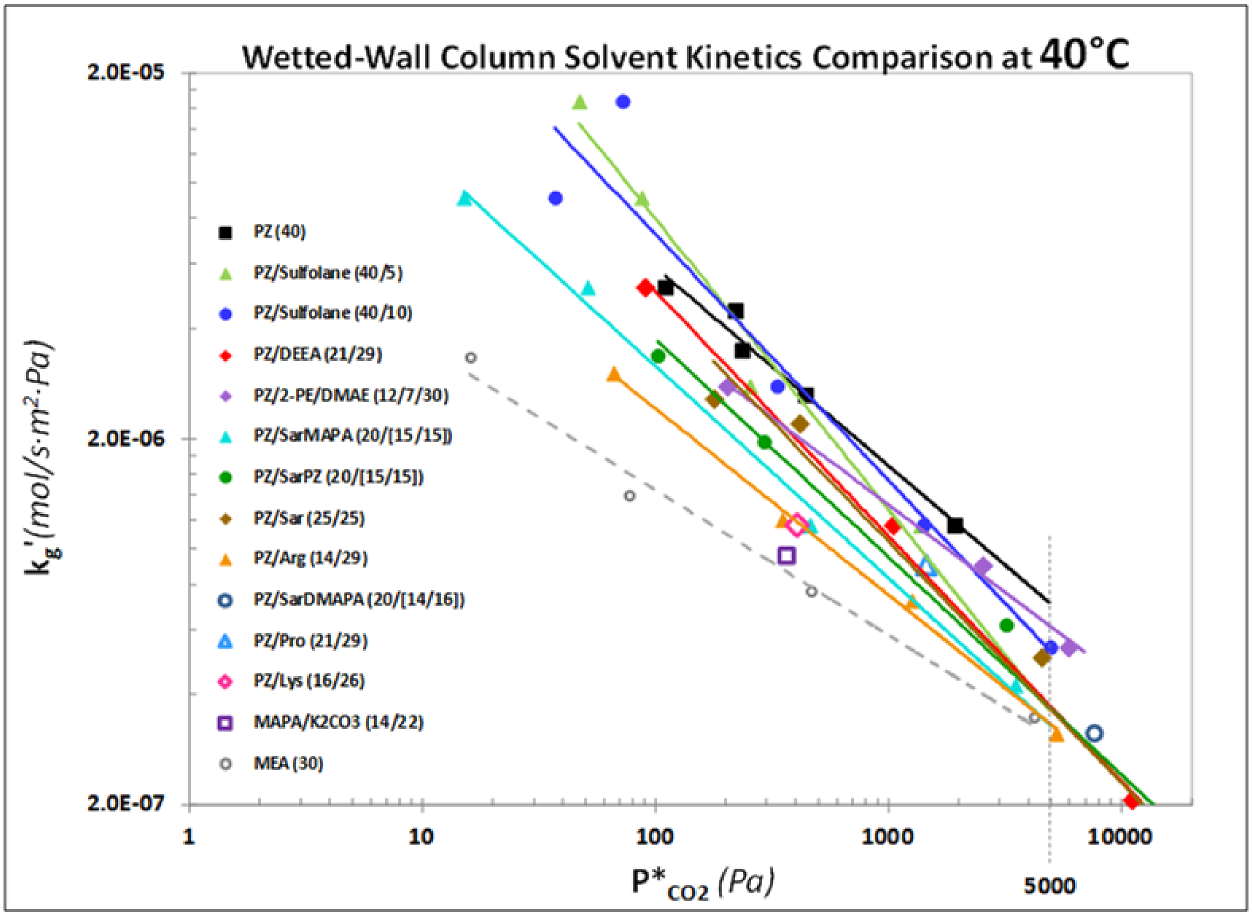


Figure 4.5 Solvent Absorption Rate Comparison at 40 C

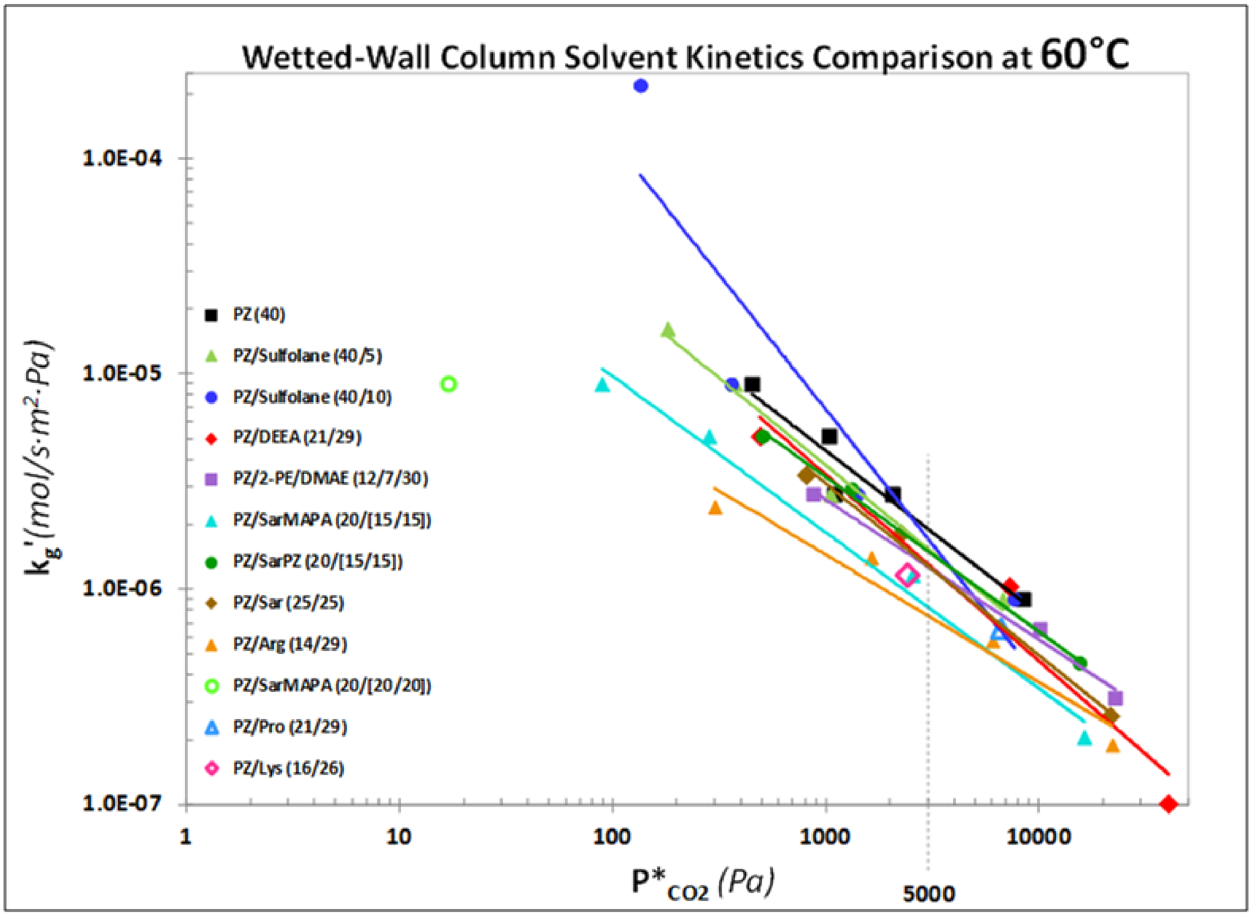


Figure 4.6 Solvent Absorption Rate Comparison at 60 C

Table 4.3 Summary of k_g' and VLE Results from WWC (40 C)

α	p*	k_g'	α	p*	k_g'
(mol CO_2/mol alk)	*(Pa)*	*(mol/s·m^2·Pa)*	*(mol CO_2/mol alk)*	*(Pa)*	*(mol/s·m^2·Pa)*
MEA (30)			**PZ/DEEA (21/29)**		
0.252	*16*	*3.34E-06*	0.20	90	5.18E-06
0.351	*77*	*1.40E-06*	0.40	1,045	1.16E-06
0.432	*465*	*7.66E-07*	0.50	11,090	2.06E-07
0.496	*4,216*	*3.47E-07*	**PZ/2-PE/DMAE (12/7/30)**		
PZ (40)			0.20	203	2.78E-06
0.27	110	5.18E-06	0.40	2,540	9.01E-07
0.31	220	4.47E-06	0.45	5,925	5.38E-07
0.31	235	3.48E-06	**PZ/SarPZ (20/[15/15])**		
0.34	440	2.63E-06	0.25	102	3.37E-06
0.38	1,920	1.16E-06	0.30	292	1.96E-06
PZ/Sulfolane (40/5)			0.4	3,200	6.19E-07
0.20	47	1.67E-05	0.45	24,600	1.20E-07
0.25	87	9.10E-06	**PZ/Arg (14/29)**		
0.31	254	2.78E-06	0.25	66	3.02E-06
0.38	1,375	1.16E-06	0.35	350	1.20E-06
PZ/Sulfolane (40/10)			0.40	1,260	7.21E-07
0.20	37	9.10E-06	0.45	5,250	3.13E-07
0.25	72	1.67E-05	**PZ/Sar (25/25)**		
0.31	332	2.78E-06	0.25	178	2.57E-06
0.38	1,410	1.16E-06	0.30	415	2.20E-06
0.42	4,955	5.38E-07	0.40	4,540	5.05E-07
PZ/SarMAPA (20/[15/15])			0.45	30,200	9.16E-08
0.25	15	9.10E-06	**PZ/SarDMAPA (20/[14/16])**		
0.30	51	5.18E-06	0.45	7,650	3.13E-07
0.40	460	1.16E-06	**PZ/Lys (16/26)**		
0.45	3,500	4.24E-07	0.35	405	1.16E-06
MAPA/K_2CO_3 (14/22)			**PZ/Pro (21/29)**		
0.40	365	9.56E-07	0.35	1,450	9.01E-07

Table 4.4 Summary of k_g' and VLE Results from WWC (60 C)

α (mol CO_2/mol alk)	p* (Pa)	k_g' (mol/s·m^2·Pa)
PZ (40)		
0.27	450	8.95E-06
0.31	1,035	5.13E-06
0.31	1,100	2.76E-06
0.34	2,050	2.76E-06
0.38	8,400	8.99E-07
PZ/Sulfolane (40/5)		
0.20	181	1.62E-05
0.25	375	8.95E-06
0.31	1,051	2.76E-06
0.38	6,770	8.99E-07
PZ/Sulfolane (40/10)		
0.20	135	2.18E-04
0.25	360	8.95E-06
0.31	1,410	2.76E-06
0.38	7,660	8.99E-07
PZ/SarMAPA (20/[15/15])		
0.25	89	8.95E-06
0.30	283	5.13E-06
0.40	2,550	1.16E-06
0.45	16,300	2.06E-07
PZ/SarMAPA (20/[20/20])		
0.20	17	8.95E-06
PZ/Pro (21/29)		
0.35	6,650	6.54E-07
PZ/DEEA (21/29)		
0.20	491	5.13E-06
0.40	7,260	1.03E-06
0.50	40,425	1.01E-07
PZ/2-PE/DMAE (12/7/30)		
0.20	873	2.76E-06
0.40	10,115	6.54E-07
0.45	22,730	3.13E-07
PZ/SarPZ (20/[15/15])		
0.25	505	5.13E-06
0.30	1,320	2.92E-06
0.40	15,500	4.54E-07
PZ/Arg (14/29)		
0.25	302	2.41E-06
0.35	1,635	1.40E-06
0.40	6,060	5.74E-07
0.45	22,100	1.89E-07
PZ/Sar (25/25)		
0.25	810	3.39E-06
0.30	2,245	1.81E-06
0.40	21,550	2.58E-07
PZ/Lys (16/26)		
0.35	2,420	1.16E-06

CO_2 Cyclical Capacity. CO_2 cyclical or carrying capacity can be estimated using the VLE data obtained from the WWC at different loadings. The rich loading of each tested candidate solvent was fixed at that which would yield an equilibrium partial pressure of CO_2 equal to 5000 Pa at 40 C. CO_2 capacity was then estimated with various lean loadings corresponding to different equilibrium partial pressures of CO_2, as plotted in Figure 4.7. The results also summarized in Table 4.5. The smaller the equilibrium partial pressure of CO_2, the leaner the loading will be. CO_2 capacity estimated with the smallest equilibrium partial pressure corresponding to each solvent is the theoretical maximum capacity for that specific solvent, *not necessarily the optimum lean loading for that solvent in an actual commercial process*. Several of the candidate formulations exhibited higher theoretical maximum capacities than that of 40.8 wt% PZ. These included PZ/2-PE/DMAE (12/7/30), PZ/DEEA (21/29), PZ/Sulfolane (40/5), and PZ/Sulfolane (40/10).

Capacity and VLE results obtained from WWC testing at 40 C are also summarized in tabular form in Table 4.5.

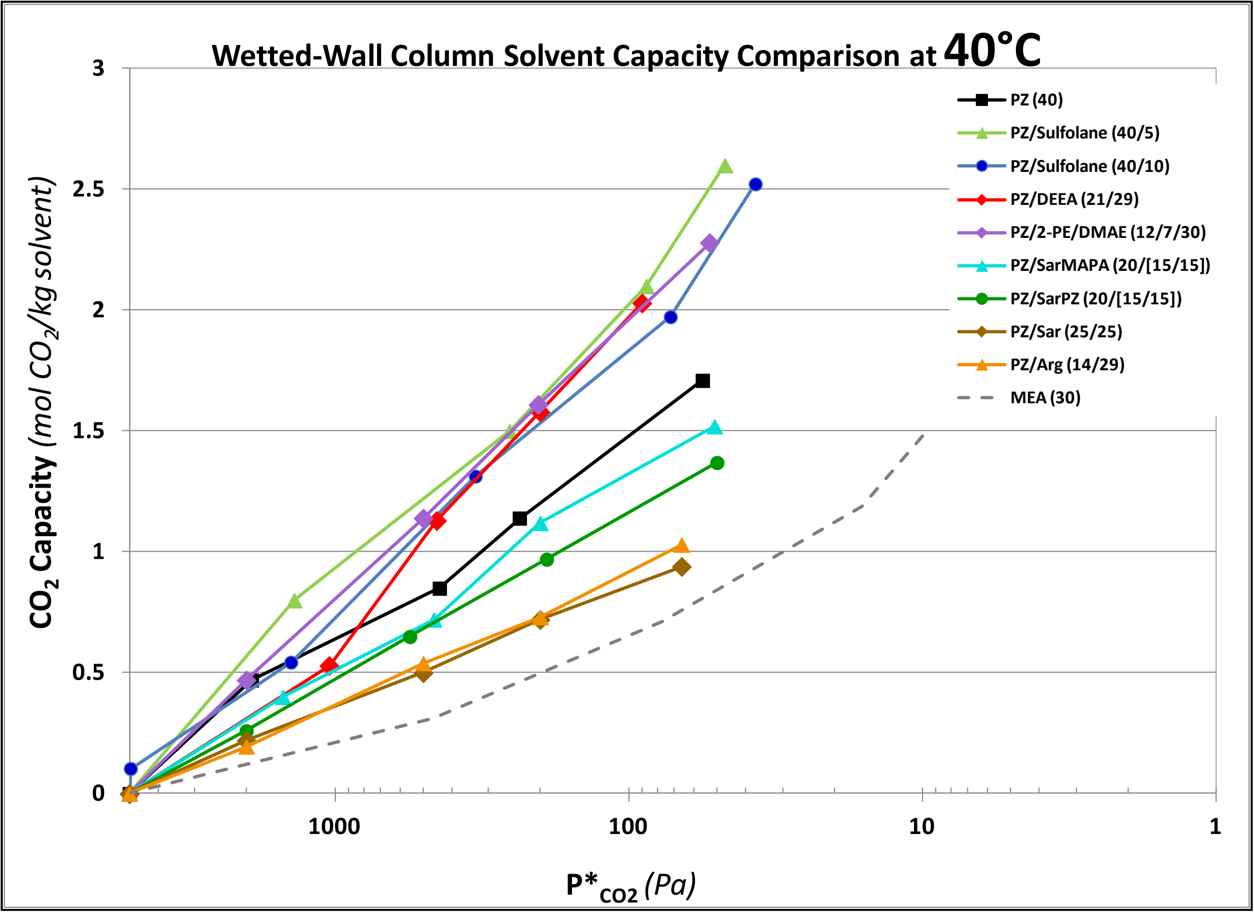


Figure 4.7 Solvent Cyclical CO_2 Capacity Comparison at 40 C

Table 4.5 Summary of Cyclical Capacity and VLE Results from WWC (40 C)

α	p*	CO_2 Capacity
(mol CO_2/mol alk)	*(Pa)*	*(mol CO_2/kg solution)*
MEA (30)		
0.194	10	*1.48*
0.252	*16*	*1.19*
0.351	*77*	*0.71*
0.432	*465*	*0.31*
0.496	*5,000*	0
PZ (40)		
0.25	56	*1.71*
0.31	235	*1.14*
0.34	440	*0.85*
0.38	1,920	*0.47*
0.43	5,000	0
PZ/Sulfolane (40/5)		
0.20	47	*2.6*
0.25	87	*2.1*
0.31	254	*1.5*
0.38	1,375	*0.8*
0.46	5,000	0
PZ/Sulfolane (40/10)		
0.20	37	*2.52*
0.25	72	*1.97*
0.31	332	*1.31*
0.38	1,410	*0.54*
0.42	4,955	*0.10*
0.43	5,000	0
PZ/SarMAPA (20/[15/15])		
0.30	51	*1.52*
0.35	200	*1.12*
0.40	460	*0.72*
0.44	1,500	*0.4*
0.49	5,000	0

α	p*	CO_2 Capacity
(mol CO_2/mol alk)	*(Pa)*	*(mol CO_2/kg solution)*
PZ/DEEA (21/29)		
0.20	90	*2.03*
0.26	200	*1.58*
0.32	450	*1.13*
0.40	1,045	*0.53*
0.47	5,000	0
0.50	11,090	*n/a*
PZ/2-PE/DMAE (12/7/30)		
0.10	53	*2.28*
0.20	203	*1.61*
0.27	500	*1.14*
0.37	2,000	*0.47*
0.44	5,000	0
0.45	5,925	n/a
PZ/SarPZ (20/[15/15])		
0.23	50	*1.37*
0.28	190	*0.97*
0.32	555	*0.65*
0.37	2,000	*0.26*
0.4	5,000	0
0.45	24,600	n/a
PZ/Arg (14/29)		
0.25	66	*1.03*
0.31	200	*0.73*
0.35	500	*0.54*
0.42	2,000	0.195
0.46	5,000	0
0.45	5,250	n/a
PZ/Sar (25/25)		
0.22	66	*0.94*
0.26	200	*0.72*
0.30	500	*0.5*
0.35	2,000	*0.22*
0.39	5,000	0
0.45	30,200	n/a

4.3 Performance Predictions

4.3.1 Rationale

As described in Section 3, process performance predictions are needed to properly interpret the implications of the WWC results. WWC results do not directly provide information on regeneration energy requirements, for example, but it would be unreasonable to select candidate solvent formulations without considering this major performance factor. While performance predictions could have been made using a more rigorous modeling approach, the value of constructing detailed models at such an early stage in solvent development work had been shown to be minimal during earlier B&W work. A more efficient methodology was therefore developed based on a semi-empirical approach to performance prediction. A protocol for solvent screening using the semi-empirical model was subsequently established and validated against both more-rigorous Aspen Plus® rate-based simulation models and performance data from pilot-plant testing. This existing semi-empirical modeling methodology was used to support the solvent selection work during Budget Period 1. Aspen Plus® rate-based simulation models were to be developed in later stages of the project based on detailed solvent characterization testing.

4.3.2 Methodology

A rate-based semi-empirical model was previously developed by B&W to support the early stages of solvent evaluation. It is primarily used to predict optimal lean and rich loadings, solvent CO_2 working capacity (based on the optimal rich and lean loadings), absorber column liquid to gas mass flow ratio (L/G), required absorber packing height to achieve 90% CO_2 removal, heat of reaction for CO_2 absorption (ΔH_{abs}), and reboiler heat duty for each of the candidate formulations on the basis of preliminary laboratory data generated with the WWC. Some key features of the model include:

- 500 MW_e power plant
- CO_2 recovery rate is 90%
- Flue gas mass flow rate of 5,310,000 lbs/hr
- 12 vol% CO_2 (wet) in flue gas
- Flue gas pressure is 1.04 bars
- Structured packing is assumed
- Approach temperature for cross heat exchanger is 10 C
- Absorber diameter is kept the same *for all solvents*

Optimum rich loading may be estimated by comparing estimated reboiler heat duty and absorber packing height under different rich loading conditions with lean loading fixed. With this pre-determined optimum rich loading, regeneration energy and packing height under different lean loading conditions may be compared, and the optimum lean loading can be estimated.

4.3.3 Results

Summary

The semi-empirical, rate-based model was used to estimate key performance parameters for the promising solvent formulation candidates. Only limited WWC experimental data is required to develop such a semi-empirical model for a specific solvent, which greatly enhanced the efficiency of the solvent evaluation and selection tasks. As described in the previous section, seven of the fourteen candidates carried through WWC testing were deemed of sufficient promise to warrant semi-empirical model evaluation. Both 40.8 wt% PZ (8m PZ), the baseline PZ-based formulation, and 30 wt% MEA, a widely-used acid gas removal solvent, were also included in the study for comparison purposes. Semi-empirical model studies were thus conducted on the following nine solvent formulations:

- 30 wt% MEA
- 40.8 wt% PZ
- 29 wt% DEEA / 21 wt% PZ
- 30 wt% DMAE / 7 wt% 2-PE / 12 wt% PZ
- 30 wt% SarMAPA / 20 wt% PZ
- 30 wt% SarPZ / 20 wt% PZ
- 5 wt% Sulf / 40.8 wt% PZ
- 43 wt% ArgPZ
- 50 wt% SarPZ

The B&W semi-empirical model was used to estimate optimal lean and rich loadings, solvent CO_2 working capacity (based on the optimal rich and lean loadings), absorber column liquid to gas mass flow ratio (L/G), required absorber packing height to achieve 90% CO_2 removal, heat of reaction for CO_2 absorption (ΔH_{abs}), and reboiler heat duty for each of the candidate formulations. This information, summarized in Table 4.6, was used to select the final candidate formulations under Task 2. The selections were primarily made on the basis of reboiler heat duty and cyclical, or working, capacity, since these two performance factors tend to encompass the net influences of the remaining factors. The four selected formulations, highlighted in green in Table 4.6, include:

- 29 wt% DEEA/21 wt% PZ
- 30 wt% DMAE/7 wt% 2-PE/12 wt% PZ
- 5 wt% Sulf/40.8 wt% PZ
- 30 wt% SarMAPA/20 wt% PZ

The selection of the first three candidates on list was straightforward due to their low estimated reboiler heat duty requirements. Two of the formulations, 30 DMAE/7 2-PE/12 PZ and 5 Sulf/40.8 PZ, outperform MEA by almost 30%. Further, the working capacity of the 5 Sulf/40.8 PZ formulation is over 100% higher than that of 30 MEA. Reboiler heat duty requirements for SarMAPA/PZ and SarPZ/PZ were quite similar to one another, however. The SarMAPA/PZ formulation was ultimately chosen as the fourth candidate due to its higher working capacity and slightly faster absorption rate.

Table 4.6 Summary of Performance Prediction Results and Selection

(Baseline solvents: Yellow; Selected solvents: Green; Rejected solvents: Red)

Formulation	α_{Lean}	α_{Rich}	Cyclical Capacity (mol CO_2/ kg solvent)	Absorber L/G (mass/mass)	Packing Height for 90% CO_2 Removal (ft)	Average Heat of Absorption, ΔH_{abs} (kJ/mol)	Reboiler Heat Duty (Btu/lb CO_2)
30 MEA	0.25	0.50	1.2	3.0	40	82.0	1,794
40.8 PZ	0.24	0.43	1.8	2.1	16	63.1	1,393
29 DEEA 21 PZ	0.18	0.47	2.2	1.7	33	71.2	1,411
30 DMAE 7 2PE 12 PZ	0.10	0.44	2.3	1.6	41	60.5	1,300
30 SarMAPA 20 PZ	0.28	0.49	1.7	2.2	40	73.1	1,504
30 SarPZ 20 PZ	0.23	0.40	1.4	2.7	49	67.7	1,493
5 Sulf 40 PZ	0.20	0.46	2.6	1.4	16	63.1	1,335
43 ArgPZ	0.24	0.46	1.1	3.4	26	65.8	1,541
50 SarPZ	0.21	0.39	1.0	3.6	17	68.8	1,593

Discussion of Performance Prediction (Modeling) Investigations

B&W's semi-empirical, rate-based model was used to estimate key performance parameters for the promising solvent formulation candidates.

Heat of Absorption. The heat of absorption of CO_2 is roughly estimated in the semi-empirical model by numerically differentiating VLE data generated in the WWC in conjunction with the Van't Hoff equation:

$$\frac{d(\ln\ p^*_{CO2})}{d\left(\frac{1}{T}\right)} = -\frac{\Delta H_{abs}}{R} \tag{4-13}$$

where R is the gas constant. The heat needed to reverse this reaction in the regenerator directly contributes to the energy required for regeneration, or reboiler heat duty.

Reboiler Heat Duty. Reboiler heat duty represents a key performance factor predicted by the semi-empirical model. As seen earlier, the steam required for solvent regeneration greatly impacts the levelized cost of electricity by reducing the amount electricity produced by the power plant. In a retrofit situation, the extraction of such a large amount of steam from the turbine cycle can be unworkable. Large reboilers also contribute significantly to the capital cost of the process.

Estimates of reboiler heat duty for the nine solvent formulations are presented in Figure 4.8, and are normalized relative to 30 wt% MEA. Absolute results from the semi-empirical model were summarized in Table 4.6, above. The estimates for 30 wt% MEA and 40.8 wt% PZ are shown in red and green, respectively. In this figure the heat required per pound of CO_2 is shown as a percentage of that required for MEA. It can be seen that the heat required to regenerate the PZ formulation is about 18% lower than that required for MEA. This is a reasonable estimate based on B&W's previous testing and taking into account the methodology used in the semi-empirical model. By this measure, all of the candidate formulations perform significantly better than 30 wt% MEA, and several of them outperform 40.8 wt% PZ. Two of the formulations, 30 DMAE/7 2-PE/12 PZ and 5 Sulf/40.8 PZ, outperform MEA by almost 30%.

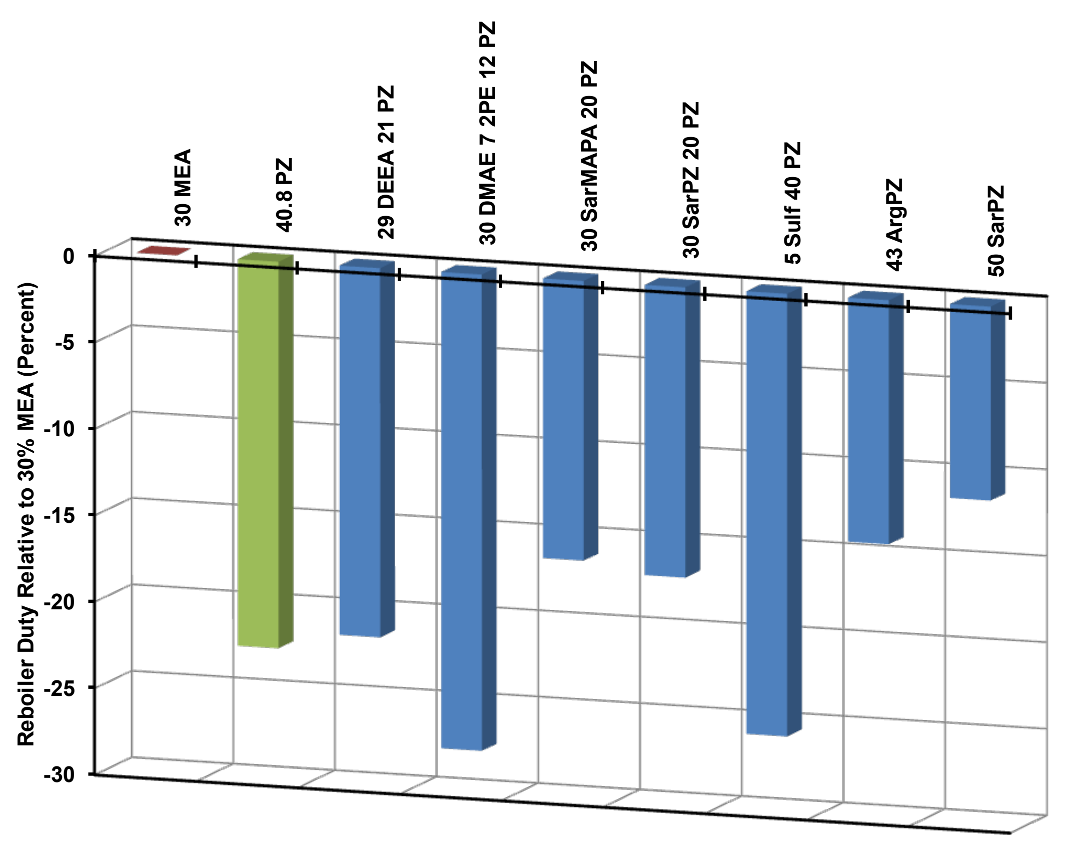


Figure 4.8 Reboiler Heat Duty Comparison

Cyclic CO_2 Working Capacity. Cyclic CO_2 working capacity represents another key performance factor estimated by the semi-empirical model used for solvent formulation evaluation. The capacity of a solvent is determined by the thermodynamic characteristics of the solvent at the relevant process operating conditions. Working capacity, set by the difference between the optimal rich and lean loadings, determines the amount of solvent that must be circulated through the process to achieve a desired CO_2 removal rate. This, in turn, impacts the size and capital cost of process equipment (e.g., absorber, regenerator, reboiler, cross heat exchanger, solvent pumps, etc.), reboiler heat duty (primarily through sensible heat requirements), and pumping power requirements.

Estimated working capacity (originally on a moles CO_2/kg solvent basis) for the nine solvent formulations are presented in Figure 4.9 and are normalized relative to 30 wt% MEA. Absolute results from the semi-empirical model were summarized in Table 4.6, above. As before, the predictions for 30 wt% MEA and 40.8 wt% PZ are shown in red and green, respectively. It can be seen that the working capacity of the PZ formulation is about 30% higher than that of MEA.

By this measure, several of the candidate formulations perform measurably better than PZ. The working capacity of the 5 Sulf/40.8 PZ formulation is over 100% higher than that of 30 wt% MEA.

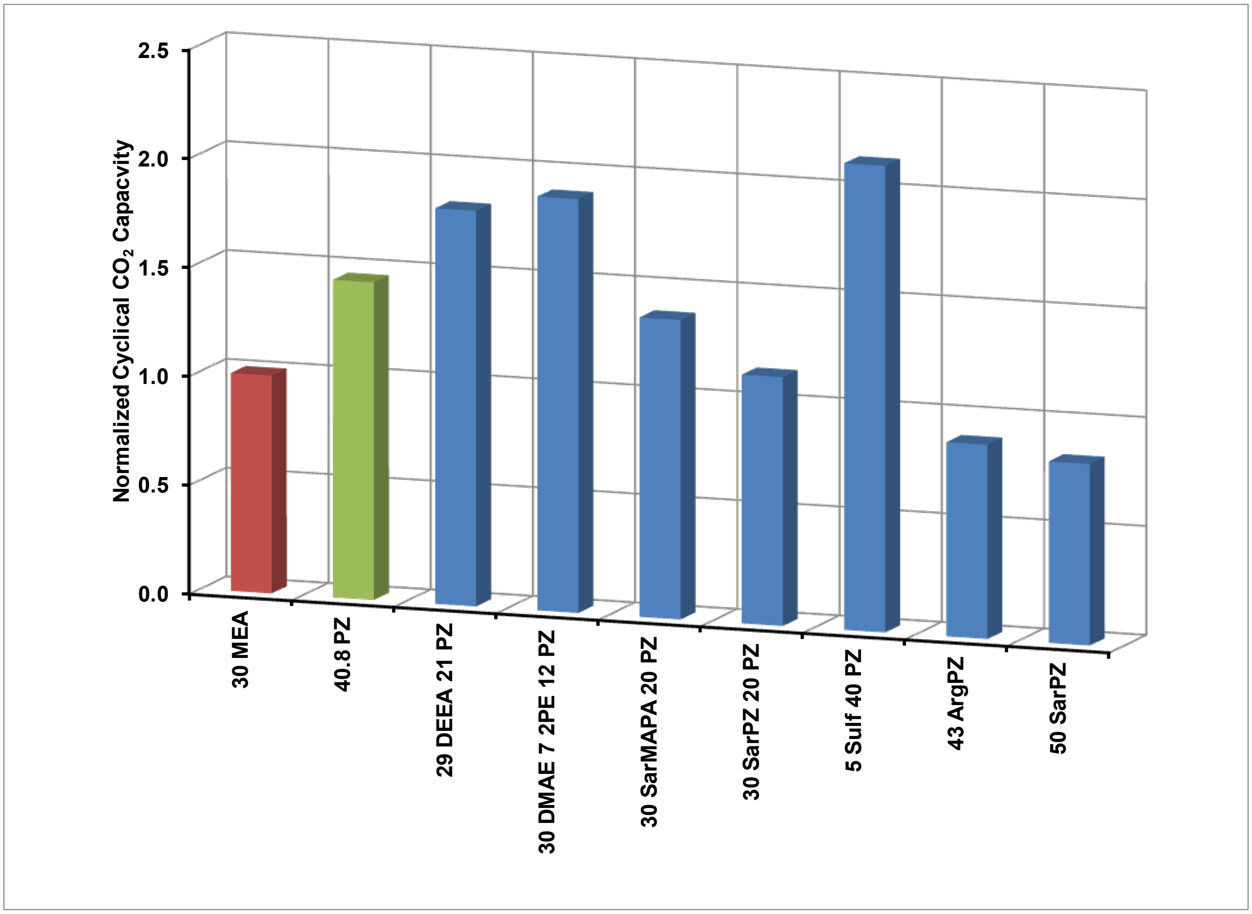


Figure 4.9 Cyclical CO_2 Capacity Comparison

Absorber Packing Height. The height of structured packing required to achieve the target CO_2 removal efficiency of 90% is a key performance factor predicted by the model. It should be kept in mind that the absorber column (packing) diameter is kept the same for all solvents in the semi-empirical model. Packing height provides an indirect measure of CO_2 absorption rate, and also provides an indication absorber capital cost.

This is not the whole story, however. Achieving the desired CO_2 removal efficiency also requires a certain amount of solvent flow to the absorber. The required flow rate is primarily determined by the solvent working capacity. From an absorber design point of view, this requirement is typically expressed as the absorber liquid-to-gas mass flow ratio, L/G. In an actual commercial absorber design, the operating L/G would affect the *diameter* of the absorber tower. Estimating absorber capital cost must therefore take into account both absorber packing height and L/G requirements estimated by the semi-empirical model.

Estimated absorber packing height and L/G requirements for the nine solvent formulations are presented in Figure 4.10, and are normalized relative to 30 wt% MEA. Absolute results from the semi-empirical model were summarized in Table 4.6, above. The estimates for 30 wt% MEA and 40.8 wt% PZ are shown in red and green, respectively. It can be seen that the PZ formulation requires only 40% of the packing height and about 60% of the L/G required for MEA, an expected result based on B&W's earlier work with PZ-based solvents. It can also be seen that most of the candidate formulations outperform PZ on one or the other of the factors, but generally not both. The 5 Sulf/40.8 PZ behaves similarly to PZ, itself.

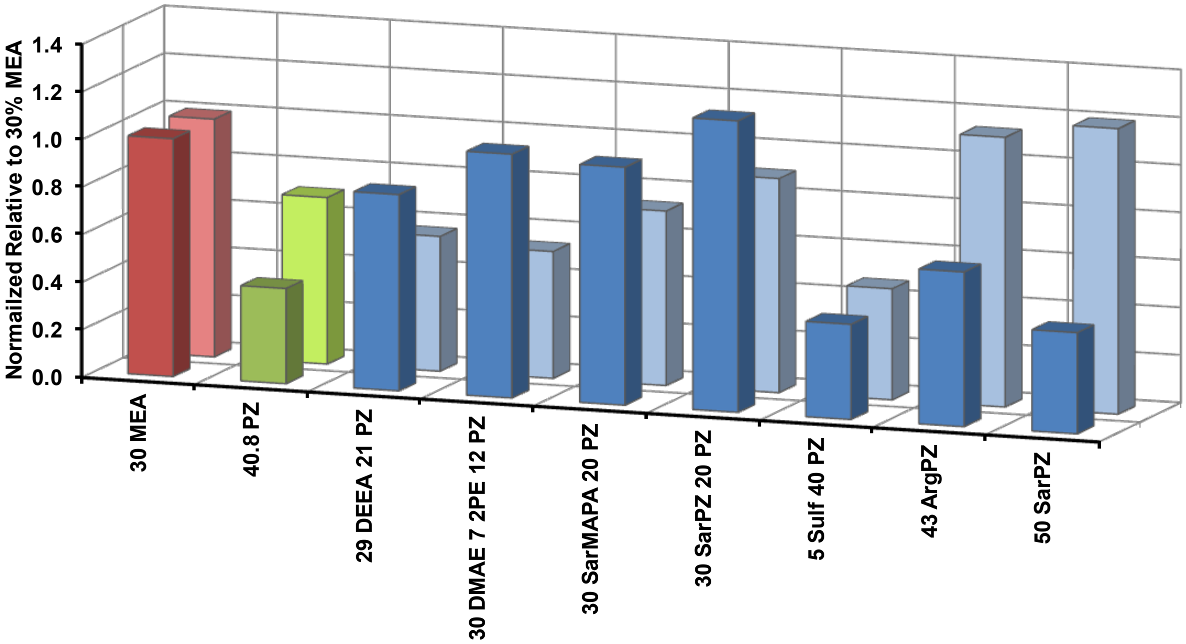


Figure 4.10 Normalized Absorber Packing Height and L/G Comparisons
(Packing height, front row; L/G, back row)

4.4 Recommended (Final) Solvent Formulations

The B&W semi-empirical model was used to estimate optimal lean and rich loadings, solvent CO_2 working capacity (based on the optimal rich and lean loadings), absorber column liquid to gas mass flow ratio (L/G), required absorber packing height to achieve 90% CO_2 removal, heat of reaction for CO_2 absorption (ΔH_{abs}), and reboiler heat duty for each of the candidate formulations. This information, summarized in Table 4.6, was used to select the final candidate formulations under Task 2. The final four candidate formulations are shown in Table 4.7. The selections were primarily made on the basis of reboiler heat duty and cyclical, or working, capacity, since these two performance factors tend to encompass the net influences of the remaining factors.

Table 4.7 Final Candidate Formulations

Category	Formulation	Composition (wt%)
Amine Blend	PZ / DEEA	21 / 29
	PZ / 2-PE / DMAE	12 / 7 / 30
Amine/Amino Acid Salt	PZ / SarMAPA	20 / 30
Organic Additive	PZ / Sulfolane	40 / 5

5.0 CONTINUOUS SOLVENT DEGRADATION SYSTEM (CSDS)

5.1 Rationale

The objective of Task 5 was to design and install a Continuous Solvent Degradation System (CSDS) to enable comprehensive investigations of the degradation characteristics of the selected solvent formulations under representative operating conditions. This testing was originally planned as part of the Budget Period 2 characterization studies, and, thus, installation of the testing apparatus required to carry out the work was included in the Budget Period 1 scope of work. For the final selection of an optimized solvent formulation in subsequent project budget periods, high quality, representative, solvent degradation data would be absolutely necessary.

Many solvents used for CO_2 scrubbing undergo irreversible chemical reactions when exposed to process conditions. The transformation of solvent components into undesirable chemical species is commonly referred to as solvent degradation. Amine solvents such as MEA or PZ chemically degrade in a variety of ways including:

- *Thermal Degradation* due to exposure to the high temperatures of the regeneration process,
- *Oxidative Degradation* due the presence of oxygen in the flue gas,
- *Carbamate Polymerization* due to the presence of CO_2, and
- *Heat-Stable Salt Formation* resulting from reactions with flue gas constituents such as SO_X, NO_X, HCl, etc.

Degradation reactions can be accelerated by the presence of degradation or corrosion products and heat-stable salts, and through the catalytic effects of various metals. Metals can be present due to the corrosion of process equipment or the presence of fly ash or limestone from the upstream power plant processes. Degradation results in the need for additional solvent makeup, and for solvent reclaiming to remove degradation products and heat-stable salts from the circulating solvent, both of which add cost and complexity to the CO_2 scrubbing process. Further, many of the possible degradation products removed by the reclaiming process are hazardous and result in a hazardous solid waste stream. Volatile degradation products can also contribute to VOC emissions at the stack. The formation and emission of nitrosamines are of particular concern

5.2 Design Basis

There are various pathways that lead to solvent degradation primarily attributable to process operating conditions and flue gas composition. Although the CO_2 scrubber is installed downstream of all other flue gas treatment processes at the power plant, and thus operates on treated flue gas, the entering gas is not pristine and contains many undesirable contaminants.

Thermal degradation is the formation of undesirable products from the decomposition or reaction of solvent species based on exposure to elevated temperatures. Regenerator operating temperatures can be in the range 100-150 C. At these temperatures, the kinetic rates of solvent degradation reactions can be substantial. Thermal degradation primarily occurs in the regenerator packing, regenerator sump, reboiler, and reclaimer.

Coal flue gas typically contains 3-8% oxygen by volume. Oxidative degradation is the result of the chemical reaction of solvent constituents with the oxygen present. Oxidation occurs primarily in the absorber packing, absorber sump, and piping leading to the cross heat exchanger. Although the flue gas typically enters the absorber at approximately 40 C, the exothermic nature of the solvent-CO_2 reaction can create higher temperatures in the absorber and downstream solvent piping. Oxygen remaining in the solvent stream downstream of the cross heat exchanger generally flashes off at the top of the regenerator and is not a factor in the regenerator.

It is well established that flue gas contaminants such as SO_2, NO_2 and HCl are completely removed in the absorber due to their relatively high reactivity. The resulting compounds do not decompose in the regeneration process and are therefore referred to as heat-stable salts. Their buildup slowly consumes the solvent, a process that must be addressed through the application of a solvent reclaiming process to partially regenerate the heat-stable salts and to remove other degradation products.

Metals present themselves in several ways: from incoming flue gas in the form of coal fly ash, from the corrosion of process equipment, or through the addition of metal-containing corrosion inhibitors. These metals can enhance the rate of solvent degradation through their catalytic activity.

The CSDS is intended to simulate these and other key features of CO_2 scrubbing processes including representative cyclical absorption and regeneration process conditions. The CSDS has been designed for continuous, unattended operation for tests lasting 100-1000 hours or more, and has been installed in an existing vented hood in B&W's CO_2 Control Laboratory. By design, it is *not* intended to replicate the entire regenerable CO_2 scrubbing process at a smaller scale. In other words, it is not a bench-scale absorption/stripping process simulator. Rather, it is designed to recreate the critical degradation-related conditions representative of an industrial CO_2 scrubbing process in a manner that can be safely operated unattended.

A batch of liquid solvent is first prepared with the desired component concentrations and a predetermined CO_2 loading. Representative concentrations of contaminants such as SO_X, NO_X, and metals are obtained through the addition of the appropriate acids or salts. The test sample is then split between separate oxidative and thermal reactors that operate in parallel. Test planning using the statistical design of experiments will be used to ensure productive and efficient investigations with the fewest number of tests.

The oxidative reactor mimics low-temperature and atmospheric-pressure absorber conditions. The solvent is charged to a 1-liter capacity glass vessel that allows for ongoing visual inspection. House supply compressed air is used as the source of gaseous O_2 to accelerate exposure compared to traditional coal-fired flue gas concentrations. This approach also minimizes gas manifold equipment and complicated instrumentation. The air flows through a high-purity water saturator before contacting the solvent using a perforated frit. Gas bubbles rise through the solvent liquid and vent via a condenser and water trap. The system is kept at the desired temperature using a constant temperature bath in the range of 40-60 C (104-140 F). Carbon dioxide may be introduced using the house supply, if necessary, to adjust CO_2 loading.

The thermal reactor simulates high-temperature regenerator conditions in the range of 100-150 C (212-302 F). Using house-supplied nitrogen, the system is kept under high pressure (typically up to 500 psig) to prevent the CO_2 from evolving. Its purpose is to subject the prepared solvent sample to representative thermal conditions, and not to regenerate the solvent. The containing 1-liter pressure vessel is jacketed and is heated using circulating oil from a constant temperature bath.

The solvent samples are switched between these oxidative and thermal reactor systems for alternating exposure to O_2 and heat. Decoupling the system is a practical simplification that provides several safety benefits by segregating the oxygen-containing and high-temperature vessels, and by reducing the complexity of high-pressure safeguards. Schematic drawings of the oxidative and thermal reactor systems are shown in Figure 5.1.

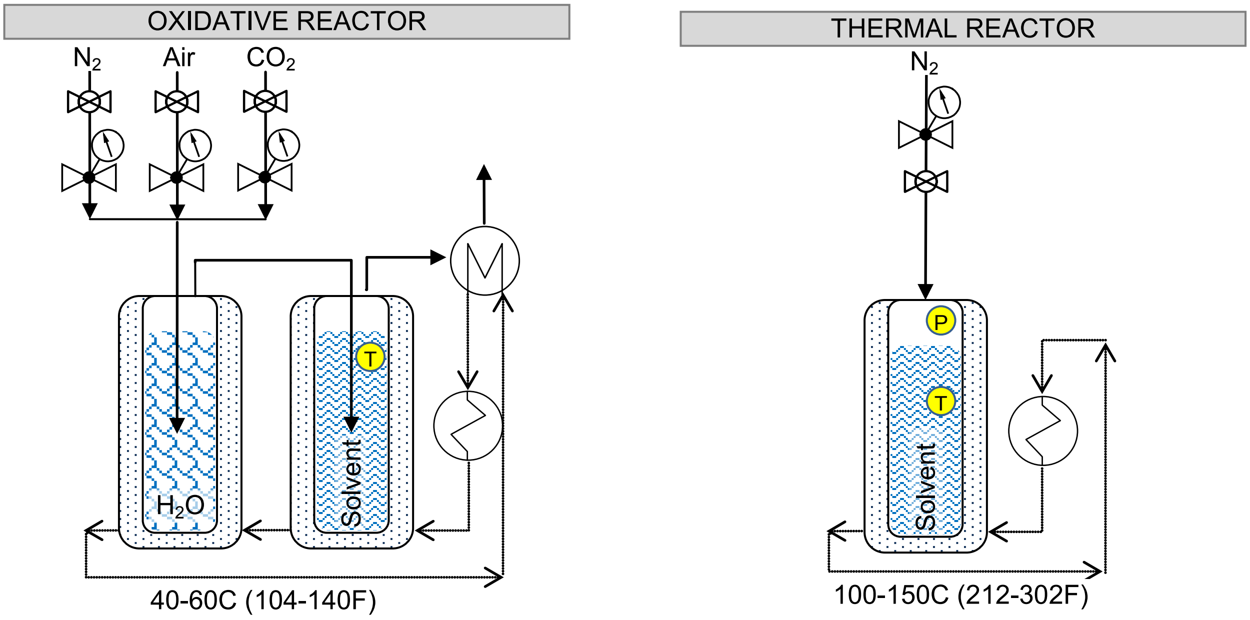


Figure 5.1 CSDS Design Concept

Specific data such as temperatures and pressures are recorded along with the logging of exposure time. Liquid samples are extracted to monitor both qualitative and quantitative changes. Analytical chemistry methods to verify solvent concentration and activity indicate if there has been any disappearance of the primary active component(s), and potentially identify the nature of any degradation product species. Other observations such as changes in color, viscosity, or phase may also suggest solvent degradation.

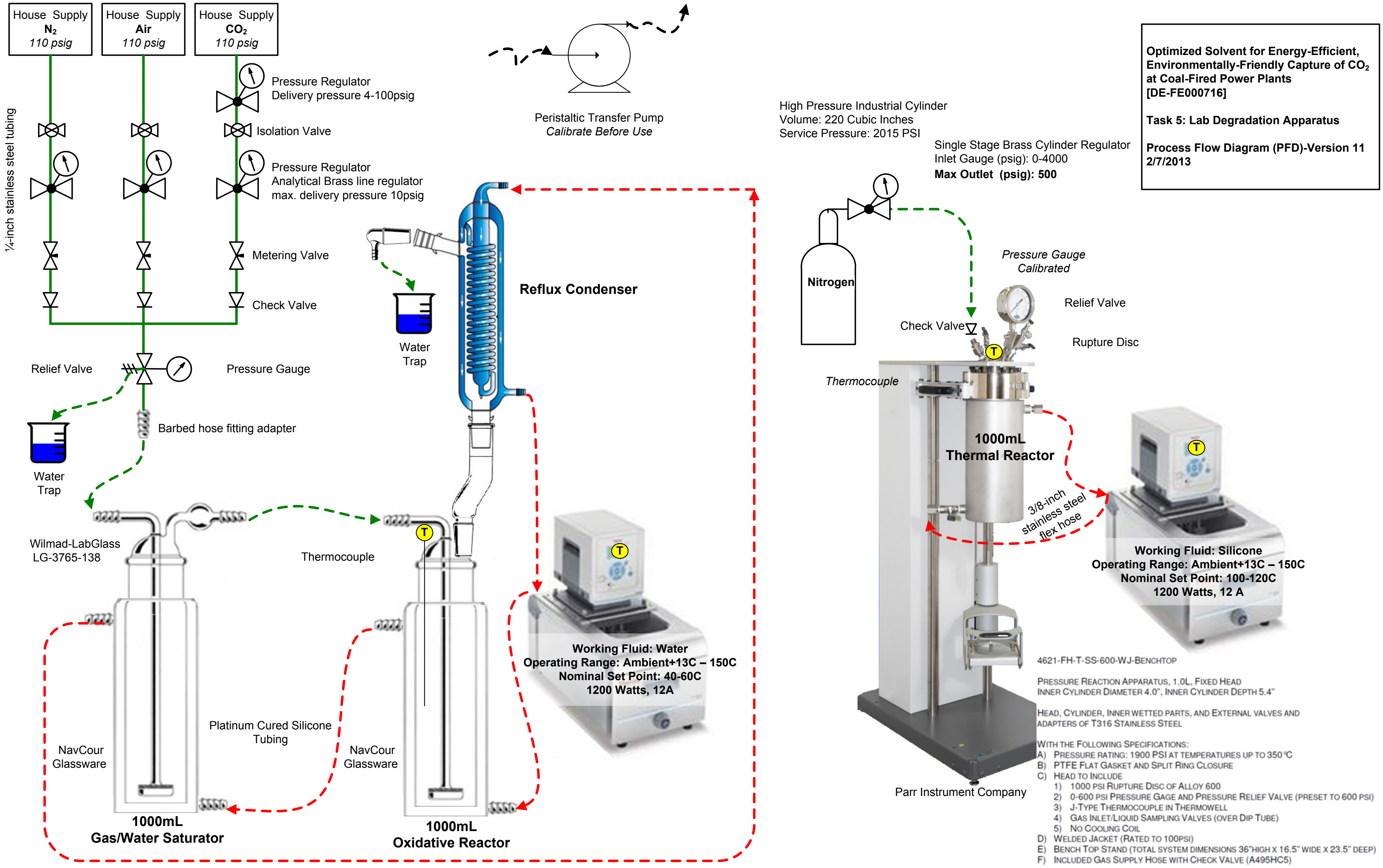
5.3 Detailed Design, Fabrication, and Installation

5.3.1 Overview

The design basis was used to develop a detailed design for the CSDS apparatus. A list of the equipment specified and subsequently procured and installed is shown in Table 5.1. A schematic drawing of the installed apparatus is shown in Figure 5.2. Compressed air, nitrogen, and CO_2 systems were already available in the lab at 110psig and were utilized.

Table 5.1 CSDS Equipment List

Oxidative Reactor Component	**Vendor**	**Quantity**
1/4-inch Stainless Steel Tubing	Swagelok Company	1
Platinum-Cured Silicone Tubing	Masterflex	1
In-Line Gas Regulator	Airgas, Inc.	3
Metering Valve	Swagelok Company	3
Check Valve	Swagelok Company	3
Relief Valve	Swagelok Company	1
Pressure Gauge	Swagelok Company	1
Hose Connector	Swagelok Company	1
Gas Washing Bottle	NavCour Glassware	2
Gas Washing Bottle Stopper Frit	NavCour Glassware	2
K-type Thermocouple	OMEGA Engineering, Inc.	1
Ring Stand	Fisher Scientific	1
Reflux Condenser	Chemglass Life Sciences	1
Glass Angle Connector	NavCour Glassware	1
Temperature Bath Circulator	ThermoFisher Scientific	1
Thermal Reactor Component	**Vendor**	**Quantity**
Pressure Vessel	Parr Instrument Company	1
Pressure Gauge	Thuemling Industrial Products	1
K-type Thermocouple	Pyromation, Inc.	1
Check Valve	Swagelok Company	1
Relief Valve	Swagelok Company	1
Rupture Disc	Fike Corporation	1
Nitrogen Gas Cylinder	Airgas, Inc.	1
Gas Cylinder Mount	Airgas, Inc.	1
Single-Stage Gas Regulator	Airgas, Inc.	1
Gas Supply Hose	Parker Hannifin Corp	1
Temperature Bath Circulator	ThermoFisher Scientific	1
3/8-inch Stainless Steel Flexible Hose	Swagelok Company	2
Tubing Insulation	Julabo	2
Silicone Oil	Dow Corning	1
Unused Ordered Parts	**Vendor**	**Quantity**
Stainless Steel Flexhose	Swagelok Company	2
Gas Cylinder Stand	Airgas, Inc.	1



Optimized Solvent for Energy-Efficient, Environmentally-Friendly Capture of CO$_2$ at Coal-Fired Power Plants
[DE-FE000716]

Task 5: Lab Degradation Apparatus

Process Flow Diagram (PFD)-Version 11
2/7/2013

4621-FH-T-SS-600-WJ-Benchtop

Pressure Reaction Apparatus, 1.0L, Fixed Head
Inner Cylinder Diameter 4.0", Inner Cylinder Depth 5.4"

Head, Cylinder, Inner wetted parts, and External valves and adapters of T316 Stainless Steel

With the Following Specifications:
A) Pressure rating: 1900 PSI at temperatures up to 350°C
B) PTFE Flat Gasket and Split Ring Closure
C) Head to Include
    1) 1000 psi Rupture Disc of Alloy 600
    2) 0-600 psi Pressure Gage and Pressure Relief Valve (preset to 600 psi)
    3) J-Type Thermocouple in Thermowell
    4) Gas Inlet/Liquid Sampling Valves (over Dip Tube)
    5) No Cooling Coil
D) Welded Jacket (Rated to 100psi)
E) Bench Top Stand (total system dimensions 36"high x 16.5" wide x 23.5" deep)
F) Included Gas Supply Hose with Check Valve (A495HC5)

Figure 5.2 CSDS Detailed Design

Prior to component procurement and assembly, a required B&W in-house Safety and Environmental Evaluations Request (SEER) was initiated. The purpose of the procedure is to ensure that new processes and equipment purchases are adequately assesses for safety, environmental and operational impacts prior to construction. The review seeks to identify all risks and establish plans for dealing with them. In addition to the potential safety hazards associated with the operation of the new equipment, the review also assessed the needs related to sample storage, waste storage and disposal, personal protective equipment, and the need for safety showers and eyewash stations. B&W's existing CO_2 Control Lab already provided many of the needed support systems and safeguards, which greatly simplified the SEER process and the design of the facility. The decision to decouple the low-temperature oxidative reactor from the high-temperature thermal reactor was primarily driven by safety considerations, especially in light of the desire to conduct long-term solvent degradation tests in an unattended mode.

One major outcome of the SEER review was a requirement to conduct a HAZOP review of the proposed CSDS. A Hazard and Operability Methodology (HAZOP) is used to identify both process hazards and operational difficulties that could potentially arise. It is a highly structured problem identification technique that comprises the analysis, for each part of the process, specific deviations (i.e., high, low, reverse) from process design conditions (i.e., pressure, temperature, flow). Credible causal factors for each scenario are identified by a small knowledgeable team and the potential consequences are identified. Safeguards are documented and recommendations for further investigation and/or action are directed. A HAZOP analysis of the CSDS was subsequently conducted, and all findings were addressed, which cleared the way for installation of the equipment.

The CSDS was subsequently installed in an existing 8-foot fume hood in the B&W CO_2 Control Laboratory (see Figure 5.3), and individual component shakedown was subsequently completed. Approximately half of the hood space is dedicated to the CSDS apparatus, itself, while the remaining bench-top provides space for solvent preparation and wet chemistry analysis activities. All work under Task 5, and indeed all work under this project, has been conducted in accordance with the B&W Research Center Standard Practice Quality Assurance (QA) Manual which is compliant to ISO-9001:2008. All equipment has been installed; and the system is ready for use in subsequent project budget periods.

Figure 5.3 Installed CSDS

5.3.2 Oxidative Reactor

The oxidative reactor provides low-temperature and atmospheric-pressure absorber conditions such that saturated incoming gas contacts the solvent solution under controllable isothermal conditions in the range of 40-60 C (104-140 F). A custom 1000 ml gas washing bottle was designed in cooperation with Douglas Navalinsky, Master Glassblower, at NavCour Glassware. The clear glass bottle design is used for both the water saturator and oxidative reactor as drawn in Figure 5.4.

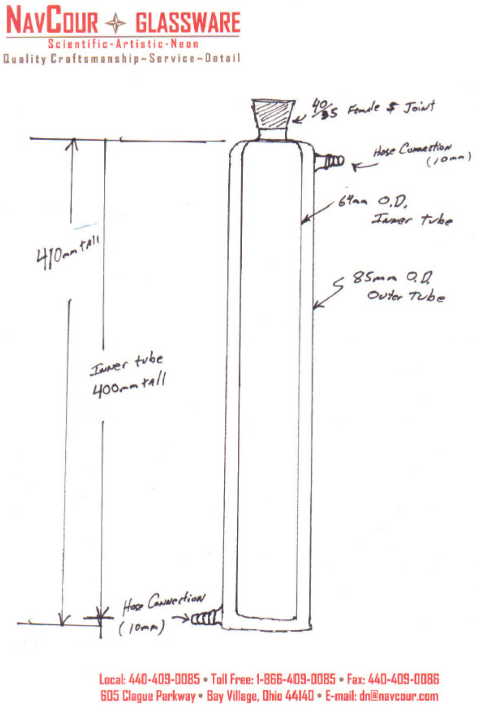


Figure 5.4 Custom Gas Washing Bottle with Jacket

A 10mm jacket surrounding the bottle facilitates water flow through the annular section. Water temperature is maintained using an external heated bath circulator. The water flow from the heated bath circulator first passes into the saturator jacket, then the oxidative reactor jacket, and finally a high-efficiency condenser before returning to the circulator for continuous recirculation. These connections are made with barbed fittings and flexible silicone tubing. The goal is to maintain the entire system at the same temperature to prevent water accumulation or loss in the solvent inventory. The saturator is charged with high-purity water and is used to saturate the incoming air at the operating temperature. The water holdup in the saturator requires intermittent monitoring and water makeup during the course of an experiment.

Approximately half of the solvent test solution is charged to the oxidative reactor. The behavior of the solvent is easily monitored with the transparent glass to observe instances of color change, level change, gas bubble movement, volatility, solids formation, etc. The oxidative reactor stopper assembly supports the porous glass distribution frit and was also customized to accommodate new penetrations as sketched in Figure 5.5. A threaded connector with o-ring was added to support the use of a thermocouple for solvent temperature monitoring. A ground-glass female standard taper fitting holds a condenser at the modified gas outlet.

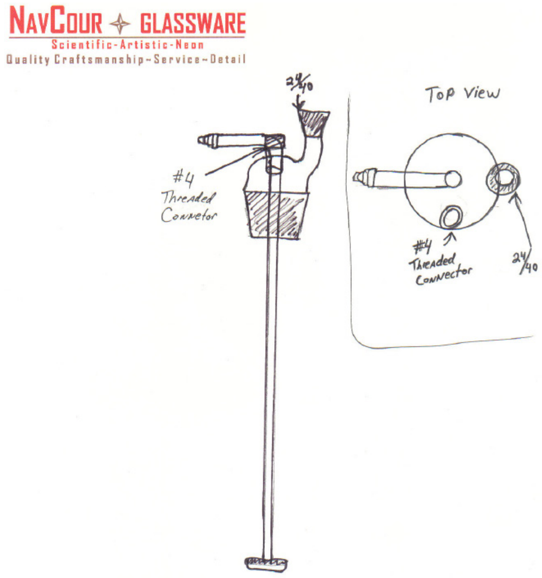


Figure 5.5 Custom Gas Washing Bottle Stopper Assembly for Oxidative Reactor

Inlet gas to the oxidative reactor is supplied using compressed air, nitrogen and CO_2, all available in the fume hood. Oxygen is the gas constituent of primary interest for test with the oxidative reactor. The use of undiluted air permits the evaluation of solvent oxidative degradation under somewhat accelerated conditions since the oxygen concentration obtained is higher than that of typical coal-fired flue gas. Nitrogen is available to dilute the air if a lower oxygen concentration is desired. Solvent CO_2 loading is set during solvent preparation and should not require the use of CO_2 in the incoming gas. However, CO_2 loading is monitored throughout a test and CO_2 can be added to the incoming gas, if needed to maintain the desired loading condition. Each of the gases can be managed with an isolation valve as well as individually adjusted with in-line regulators and metering valves. Connections are made again with barbed fittings and flexible silicone tubing.

5.3.3 Thermal Reactor

A separate thermal reactor provides the high-temperature conditions, 100-150 C (212-320 F), representative of the solvent regeneration process. Due to the high equilibrium vapor pressure of CO_2 (and water vapor) over rich solvent solutions, and the strong dependence of that pressure on temperature, a commercially-available pressure vessel from the Parr Instrument Company was selected for use as the thermal reactor. The all stainless steel design comprises three parts: the cylinder body, head, and closing mechanism. The body has a 1000 ml capacity with an inner diameter of 4 inches and depth of 5.4 inches. For safety reasons temperature is controlled using a heated silicon oil which flows through a jacket that surrounds the body, rather than through the use of an electrically-heated mantle. This approach is much less likely to overheat the sample, reduces the likelihood of hotspots, and provides for a more uniform temperature distribution. The circulating silicone oil is supplied from a heated bath circulator will. The temperature bath is programmable for set point with an accuracy of ±0.02 C in the range of 13 C above ambient to 150 C. Temperature limits can be programmed with an alarm in addition to a high-temperature cut-off. Compressed nitrogen is supplied to the sample vessel at a pressure above the saturation temperature of the solvent at the test conditions, typically ≤ 500 psig. This prevents the solvent from boiling and/or evolving CO_2. Again, the purpose of this reactor is to expose the solvent solution to reboiler/regenerator conditions, primarily a representative high temperature, NOT to regenerate the solvent in the conventional sense.

The head (or cap) of the vessel is held in a fixed position within a fixture mounted on a bench-top stand. The bench-top stand, shown in Figure 5.6, is simply a tool that facilitates ease of use. The fixed head is mounted with its attachments and the movable sample vessel is easily mated to it using the manual lift mechanism.

Figure 5.6 Parr Pressure Vessel Assembly

Four penetrations in the head allow for access to the inside of the sample vessel when closed for the following purposes:

- A *K-type thermocouple* sits in a thermowell to monitor temperature.
- A *dip tube* is used for both supplying nitrogen gas and for liquid sampling. Each function is controlled by needle valves. The gas supply hose with a check valve supplies nitrogen from a high-pressure compressed gas lecture bottle to inert the head space as well as to set the operating pressure. The liquid sampling port is capped when not in use to prevent the inadvertent release of material.

- A *rupture disc*, rated for 1000 psig, is individually connected to prevent over pressurization of the system.
- The final port serves a threefold purpose. A *calibrated pressure gauge* is used measure system pressure. A *pressure relief valve* having a set point of 600 psig is used as the primary pressure relief device. On a separate leg, normally capped, a *needle valve* can be used to vent excess pressure from the sample vessel before opening.

The exhaust streams from both the relief valve and rupture disc are routed using ½-inch tube away from the point of use and vented through the fume hood baffle.

A spilt ring device clamps the pressure vessel together by means of a stainless steel ring which has been split into two sections, as depicted in Figure 5.7. These sections slide into place from the sides and are locked together with quick-opening latches. Cap screws in the rings deliver the compressive force required to seal the vessel using the flat PTFE gasket. The cap screws are simply tightened or loosened but never completely removed from the split ring, saving time both in opening and closing the vessel and in securing the parts. The vessel can be opened and closed without disturbing any connections or fittings attached to the head.

Figure 5.7 Parr Pressure Vessel Split Ring Closure

The vessel itself is rated for 1900 psi at temperatures up to 350 C. Each vessel is hydrostatically tested with nitrogen before leaving the factory as a quality assurance standard practice. Furthermore, the Parr Instrument Company holds a Certificate of Authorization issued by the Boiler and Pressure Vessel Committee of the American Society of Mechanical Engineers (ASME) as an approved facility for manufacturing unfired pressure vessels. B&W specifically requested that this vessel be certified to ASME Code, Section VIII, Division 1 and be stamped and registered, accordingly. Due to the high pressures involved, B&W's overall approach to the design, fabrication, and installation of the thermal reactor was conservative and focused on safety of operation.

5.4 Testing Methods

5.4.1 Solvent Sample Preparation

Initial solvent preparation for degradation testing is conducted in accordance with previously established practices in B&W's CO_2 Control Lab. For each experimental investigation in the CSDS, approximately 2000 ml of solution is needed. This volume is split between the oxidative and thermal reactors; a small portion is also withheld to maintain an original sample. Solvent solutions are prepared gravimetrically using a top-loading balance by mixing pure reagent with high-purity water to the desired concentration.

A gas washing bottle is used to load the test sample with CO_2, as shown in Figure 5.8. The balance is tared and once a stable zero reading is achieved, the CO_2 flow is initiated. Nearly pure CO_2 gas is bubbled into the solution to achieve the desired loading condition. The CO_2 flows through a saturator containing high-purity water so that the bone-dry CO_2 gas does not evaporate water from the solvent solution. Gas flow continues until the desired amount of CO_2 is absorbed by the solvent solution, as determined gravimetrically by the CO_2 uptake measured directly on the balance. The flow rate of CO_2 gas is manually controlled such that the gas bubbles contacting the solvent solution are mostly absorbed. A solvent sample of known formulation and CO_2 loading is thus obtained.

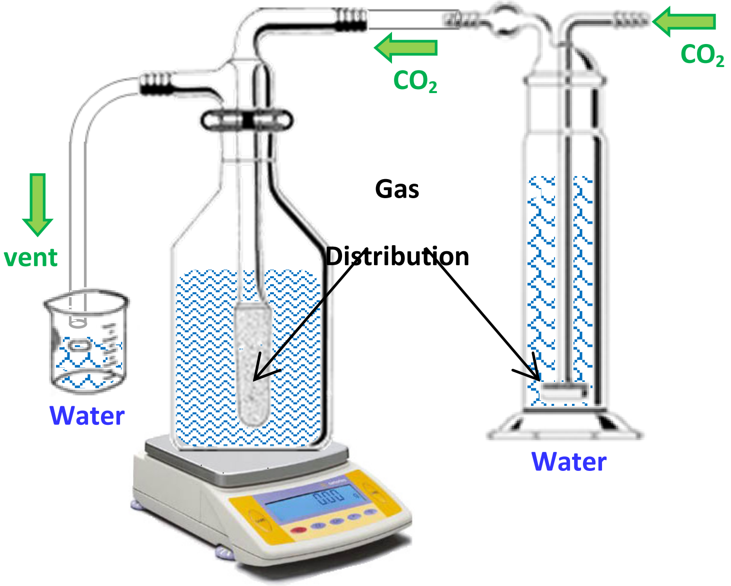


Figure 5.8 Solvent Preparation CO_2 Loading

The addition of contaminating species, such as those that might be produced when the solvent is exposed to actual flue gas, is accomplished by adding the appropriate chemical compounds to the solvent samples. Doping via chemical addition eliminates the need to supply toxic gases from compressed gas cylinders. Furthermore, steady-state concentration levels are desirable versus a continuous build-up as would occur with a flow system since blow-down would be required once some threshold limit is reached in an operating system. Metals which may enter with the flue gas stream from coal combustion or process interactions due to materials of construction can be similarly introduced. Other stabilizers such as O_2-scavenging additives, anti-foam agents, and corrosion inhibitors may also be investigated after a baseline understanding is achieved.

The divided solvent solution is periodically switched between the oxidative and thermal reactor systems for alternating exposure to oxygen and heat. The exchange is typically done after several days or weeks. The test matrix will be held constant for each of the various solvent test experiments so that direct comparisons can be deduced. Qualitative observations of changes in color, viscosity, or solubility are made during solvent transfer; photos may also be taken for documentation. Liquid solvent samples can easily be taken during these intervals and stored in amber glass colored vials for further investigation.

Analytical chemistry methods to confirm solvent concentration indicate if there has been a disappearance of the primary active component(s) and potentially identify the nature of any degradation product species. However, the purpose of this testing is not to characterize every species present but rather verify the stability of the primary active component(s) and how the innovative solvent formulations compare against PZ, alone. Simple wet chemistry titration procedures yield the total alkalinity of the solution but cannot distinguish the different contributions of multiple constituents. This is even true for neat versus degraded solutions of a single component. An external third-party analysis is required to determine speciation.

6.0 ACKNOWLEDGEMENTS

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OPTIMIZED SOLVENT FOR ENERGY-EFFICIENT, ENVIRONMENTALLY-FRIENDLY CAPTURE OF CO_2 AT COAL-FIRED POWER PLANTS

PRELIMINARY TECHNICAL AND ECONOMIC FEASIBILITY STUDY

FINAL REPORT – VOLUME 2

PERIOD OF PERFORMANCE
OCTOBER 1, 2011 TO APRIL 30, 2014

PREPARED BY:

G. A. FARTHING, JR., PRINCIPAL INVESTIGATOR
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ABSTRACT

The overall goal of this project, as originally proposed, was to *optimize* the formulation of a novel solvent as a critical enabler for the cost-effective, energy-efficient, environmentally-friendly capture of CO_2 at coal-fired utility plants. Aqueous blends of concentrated piperazine (PZ) with other compounds had been shown to exhibit high rates of CO_2 absorption, low regeneration energy, and other desirable performance characteristics during an earlier 5-year development program conducted by B&W. The specific objective of this project was to identify PZ-based solvent formulations that *globally* optimize the performance of coal-fired power plants equipped with CO_2 scrubbing systems. While previous solvent development studies have tended to focus on energy consumption and absorber size, important issues to be sure, the current work seeks to explore, understand, and optimize solvent formulation across the full gamut of issues related to commercial application of the technology: capital and operating costs, operability, reliability, environmental, health and safety (EH&S), etc. Work on the project was intended to be performed under four budget periods. The objective of the work in the first budget period has been to identify several candidate formulations of a concentrated PZ-based solvent for detailed characterization and evaluation. Work in the second budget period would generate reliable and comprehensive property and performance data for the identified formulations. Work in the third budget period would quantify the expected performance of the selected formulations in a commercial CO_2 scrubbing process. Finally, work in the fourth budget period would provide a final technology feasibility study and a preliminary technology EH&S assessment. Due to other business priorities, however, B&W has requested that this project be terminated at the end of the first budget period. This document therefore serves as the *final report* for this project. It is the second volume of the two-volume final report for Budget Period 1 and summarizes the accomplishments under Task 6 of the project, *Preliminary Technical and Economic Feasibility Study*.

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NOMENCLATURE

2-PE	2-piperidineethanol
AA	Amino acid
AAS	Amino acid salt
AAAS	Amine amino acid salt
AMP	Aminomethylpropanol
Arg	Arginine
ASME	American Society of Mechanical Engineers
B&W	Babcock & Wilcox Power Generation Group, Inc.
CSDS	Continuous Solvent Degradation Facility
DCC	Direct contact cooler
DEA	Diethanolamine
DEEA	Diethylethanolamine
DGA®	Diglycolamine®
DIPA	Diisopropanolamine
DMAE	Dimethylethanolamine
DMAPA	3-(Dimethylamino)propylamine
Dmg	Dimethylglycine
EFG+	Fluor Econamine FG Plus℠
EH&S	Environmental, health, and safety
EOR	Enhanced oil recovery
EPRI	Electric Power Research Institute
EPRI TAG	Electric Power Research Institute's Technical Assessment Guide
ESP	Electrostatic precipitator
HAZOP	Hazard and operability methodology
IECM	Integrated Environmental Control Model, Carnegie Mellon University/NETL
IGCC	Integrated gasification combined cycle
LCOE	Levelized cost of electricity
L/G	Liquid to gas flow ratio
LNB	Low-NO_X burner
LSFO	Limestone forced-oxidation
Lys	Lysine
MAPA	3-(Methylamino)propylamine
MDEA	Methyldiethanolamine

MEA	Monoethanolamine
MW_e	Electrical output in megawatts
NCCC	The National Carbon Capture Center in Wilsonville, Alabama
NGCC	Natural gas combined cycle
OFA	Over-fire air
PC4	Post-Combustion Carbon Capture Center at the NCCC
ppm	Parts per million
Pro	Proline
PSO	Pseudo first order
PSTU	Pilot Solvent Test Unit at the NCCC
PTFE	Polytetrafluoroethylene
PZ	Piperazine
Sar	Sarcosine
SCR	Selective catalytic reduction
SEER	Safety and Environmental Evaluation Request
SNCR	Selective non-catalytic reduction
Sulf	Sulfolane
Tau	Taurine
TCLP	Toxicity Characteristic Leaching Procedure
TEA	Triethanolamine
Tyr	Tyrosine
UC	University of Cincinnati
USC	Ultra-Supercritical
UT	The University of Texas at Austin
US DOE-NETL	U. S. Department of Energy National Energy Technology Laboratory
VOC	Volatile organic compound
VLE	Vapor-liquid equilibrium
WWC	Wetted-wall column
α	CO_2 loading (mol/mol_{alk})
μ	Dynamic viscosity
v	Kinematic viscosity
ρ	Density

1.0 SUMMARY OF BUDGET PERIOD 1 ACCOMPLISHMENTS

1.1 Purpose of This Report

Due to the termination of the project at the end of the first budget period, this document serves as the *final report* for this project. It is Volume 2 of the two-volume final report and summarizes the results of Budget Period 1 work completed under Task 6: Preliminary Technical and Economic Feasibility Study. Work completed under Tasks 1 through 5 is described in a separate report volume entitled "Optimized Solvent for Energy-Efficient, Environmentally-Friendly Capture of CO_2 at Coal-Fired Power Plants, Final Report – Volume 1." For completeness and continuity, however, some key results of the work under Tasks 1-5 are summarized, below.

1.2 Overview of the Technology

The capture and storage or utilization of carbon dioxide produced by coal-fired power plants is one promising approach for enabling the continued use of coal (and fossil fuels in general) in a carbon-constrained world. CO_2 scrubbing systems that employ a regenerable liquid solvent offer several potential advantages for realizing this goal. These systems are:

- Commercially available, although there is limited experience with large coal-fired applications,
- Applicable to both new and existing coal-fired power plants, unlike the integrated gasification combined cycle (IGCC) approach, and
- Applicable in either full-flow or slipstream (partial) capture scenarios, unlike both the IGCC and oxy-combustion approaches.

A schematic of a typical regenerable CO_2 scrubbing process, commonly referred to as absorption-stripping, is shown in Figure 1.1. These processes effect the removal of CO_2 from power plant exhaust gas using a wet scrubber, or absorber, similar to absorbers used to remove SO_2 from flue gases. Energy, often in the form of low-pressure steam, is used to recover the CO_2 from the solvent in the regenerator. The recovered CO_2 is dried and compressed for subsequent storage or utilization, and the regenerated solvent is pumped back to the absorber for reuse. CO_2 scrubbing systems using simple amines have been successfully applied in the petrochemical industry for decades. A major disadvantage of these systems, however, when applied to coal-fired power plants, is their high cost. It is estimated that a conventional amine-based CO_2 scrubbing process would reduce the net electrical output of the power plant by nearly one-third, and increase the cost of electricity by 60 to100%. Reducing these costs is, in the broadest sense, the rationale for the project described, herein.

1.3 Goals and Objectives of the Project

The overall goal of this project is to optimize the formulation of a novel solvent as a critical enabler for the cost-effective, energy-efficient, environmentally-friendly capture of CO_2 at coal-fired utility plants. The prototype solvent formulation is an aqueous solution of concentrated piperazine (PZ), a solvent that has been shown to exhibit high rates of CO_2 absorption, low regeneration energy, and several other desirable performance characteristics during tests conducted both by B&W and by other investigators. Through recent testing B&W has been able to further show that it is possible to modify many of the performance characteristics of a concentrated PZ solvent by adding other compounds to the formulation *while maintaining the desirable performance characteristics of the PZ solvent.*

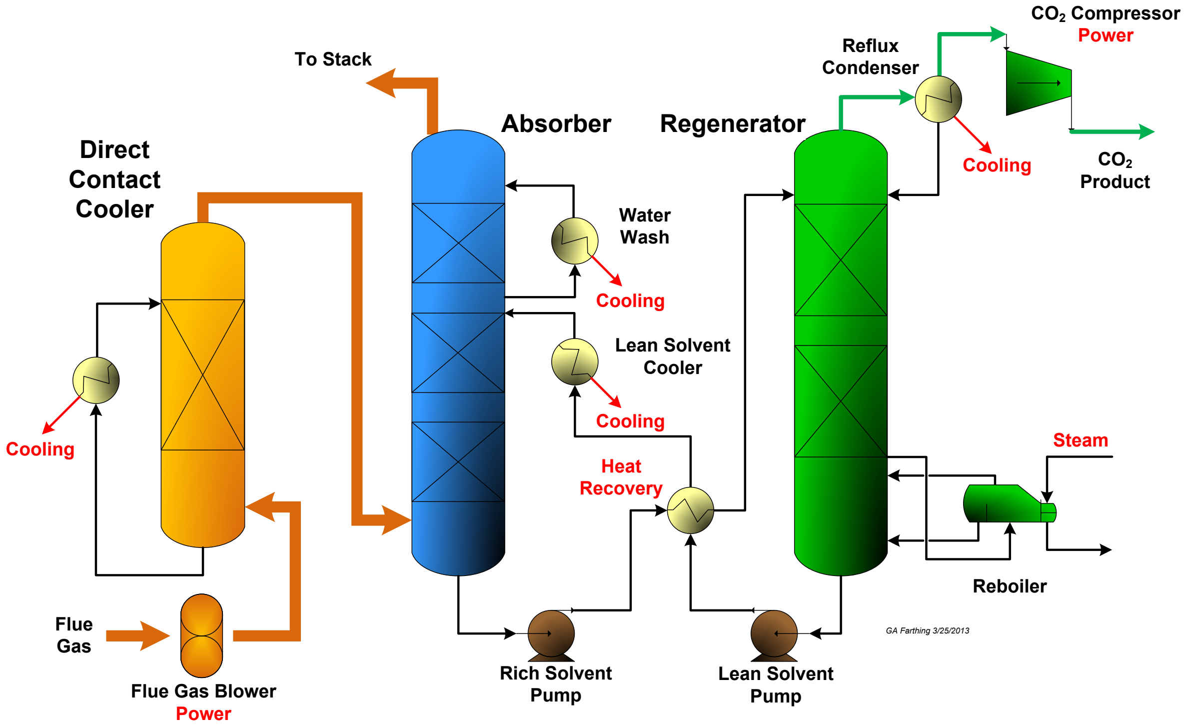

Figure 1.1 Regenerable Solvent Process

The feasibility of using solvent formulations containing high concentrations of PZ is not immediately obvious. In aqueous solution, PZ exhibits a room temperature solubility limit of about 14 wt%. Professor Gary Rochelle and his research group at the University of Texas at

Austin (UT) pointed out, however, that the solubility of PZ is strongly affected by CO_2 loading, and that clear solutions containing more than 40 wt% PZ can be prepared in the presence of CO_2. The UT team ultimately described how, through the proper control of CO_2 loading, a "solubility window" can be maintained in which an absorption/stripping process can be successfully operated[1].

Concentrated PZ provides extremely high rates of absorption, reasonably good CO_2 carrying capacity, low regeneration energy (due to favorable thermodynamic characteristics), relatively low volatility, and reduced CO_2 compression costs provided by regeneration at high pressure (enabled by PZ's good resistance to thermal degradation). A solvent comprising concentrated PZ, alone, is not a panacea, however. Solid-phase piperazine hexahydrate ($PZ\cdot 6H_2O$) and protonated piperazine carbamate monohydrate ($H^+PZCOO^-\cdot H_2O$) can precipitate from the solvent solution if CO_2 loadings are allowed to get too low or too high, respectively. This significantly limits the CO_2 loading range permissible which, in turn, limits the solvent's CO_2 carrying capacity. Operation near saturation can also impact the operability and reliability of the system if troublesome deposits tend to form during normal operation, or during system upsets. Piperazine is more expensive than the more conventional monoethanolamine (MEA) solvent, although this cost might be offset by piperazine's lower rates of degradation and evaporation. PZ is somewhat less biodegradable than MEA, and is harder to handle due to its higher freezing temperature. Finally, the performance of concentrated PZ solvents is simply not as well studied or well understood as that of more conventional solvents such as MEA.

Previous development work at B&W, in-house work conducted over several years at a cost of many millions of dollars, has quantitatively demonstrated the desirable performance characteristics of concentrated PZ-based solvents through testing programs at laboratory, bench, and pilot scales.

It is important to state that the work being conducted under this project is therefore *not* simply directed at establishing the technical feasibility of using PZ-based solvents for CO_2 scrubbing at coal-fired power plants. Rather, this project has the specific objective of identifying PZ-based solvent formulations that *globally* optimize the performance of coal power plants equipped with CO_2 scrubbing systems. While previous solvent development studies tended to focus on energy consumption and absorber size, important issues to be sure, the current work seeks to explore, understand, and optimize solvent formulation across the full gamut of issues related to

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[1] Rochelle, G.T., et al., United States Patent 7,938,887 B2, May 10, 2011.

commercial application of the technology: capital and operating costs, operability, reliability, environmental, health and safety (EH&S), etc.

The underlying premise is that solvent deficiencies such as those described above can be minimized or eliminated, and solvent advantages can be enhanced, through the novel addition of other chemical species to the basic PZ-based solvent. Formulations of interest comprise solutions containing at least 14 wt% PZ in combination with hindered amines, tertiary amines, inorganic amino acid salts, organic amino acid salts, inorganic carbonate salts, and/or other soluble organic compounds.

1.4 Project Participants

In addition to US DOE-NETL and B&W, the following organizations comprise the project team:

University of Cincinnati: Professor Stephen W. Thiel, Associate Professor, School of Energy, Environmental, Biological, and Medical Engineering, University of Cincinnati (UC), and his research team would use the facilities of their Adsorption and Ion Exchange Laboratory to provide heat capacity, vapor-liquid equilibrium, and heat of absorption data for candidate solvent formulations. These data are critical for accurate simulation model predictions. Laboratory work at the University of Cincinnati would occur during Budget Period 2 of the project.

First Energy: Ms. Eileen M. Buzzelli, Director, FE Technologies and Corporate METT, serves on the project Advisory Committee along with B&W management personnel. The Committee will meet periodically to review and advise on the commercial applicability of project plans and results.

1.5 Scope of Work

Work on the project was planned to be performed under four budget periods as illustrated in Figure 1.2. The objective of the work in the first budget period has been to identify several candidate formulations of a concentrated PZ-based solvent for detailed characterization and evaluation. The objective of work in the second budget period was to generate reliable and comprehensive property and performance data for the identified formulations. The objective of work in the third budget period was to quantify the expected performance of the candidate formulations in a representative CO_2 scrubbing process. The overall objectives of the fourth budget period were to complete a final technology feasibility study and a preliminary technology EH&S assessment. These assessments would serve to establish the feasibility of the chosen solvent formulation on economic, technical, environmental, and safety grounds. Due to other business priorities, however, B&W has requested that this project be terminated at the end of the first budget period.

The project makes extensive use of *existing* laboratory, bench, and pilot facilities at B&W's Research Center located in Barberton, Ohio. Specialized equipment for solvent development and characterization includes a wetted-wall column for solvent thermodynamic and chemical kinetics characterization, electrochemical cells for corrosion studies, a bench-scale process simulator for process optimization and operability studies, and a 7 ton/day, pilot-scale CO_2 scrubbing system for obtaining representative solvent and process performance data. A new bench-scale continuous solvent test apparatus has been constructed to characterize solvent degradation under conditions representative of a coal-fired flue gas application. Planned laboratory calorimetric work at the University of Cincinnati would provide vapor-liquid equilibrium (VLE) data, heat of absorption and heat capacity information. Experimental work has and would be supported by performance predictions using B&W's in-house semi-empirical and Aspen Plus$^{®}$ rate-based simulation computer models.

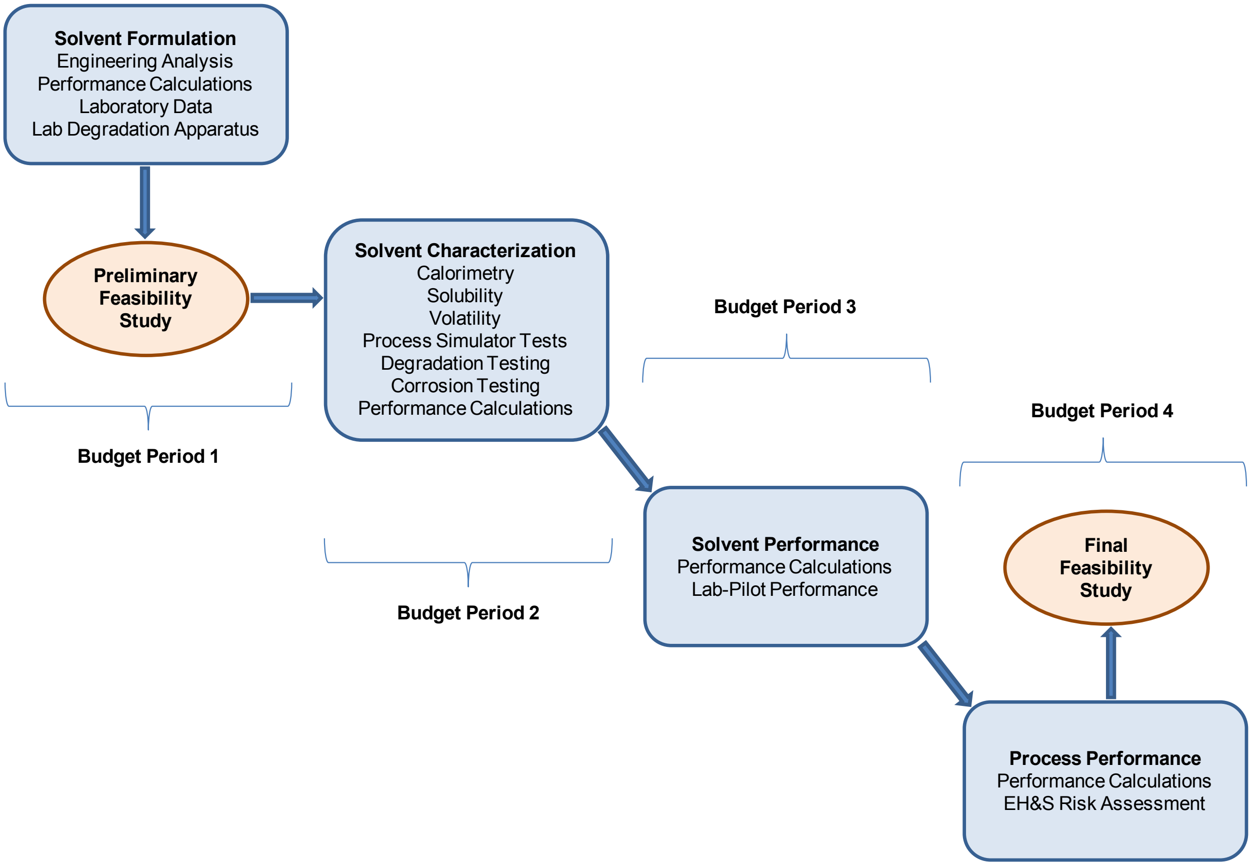
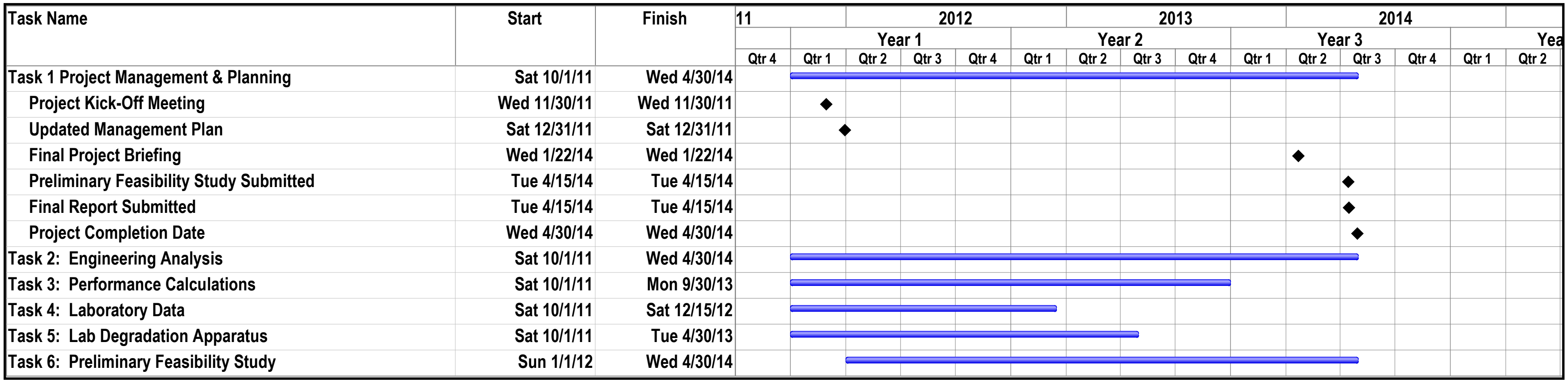


Figure 1.2 Overall Project Scope of Work

1.6 Project Schedule

The abbreviated project schedule (Budget Period 1) is shown in Figure 1.3, comprising 6 tasks spanning a total of 31 months.



Task Name	Start	Finish
Task 1 Project Management & Planning	Sat 10/1/11	Wed 4/30/14
Project Kick-Off Meeting	Wed 11/30/11	Wed 11/30/11
Updated Management Plan	Sat 12/31/11	Sat 12/31/11
Final Project Briefing	Wed 1/22/14	Wed 1/22/14
Preliminary Feasibility Study Submitted	Tue 4/15/14	Tue 4/15/14
Final Report Submitted	Tue 4/15/14	Tue 4/15/14
Project Completion Date	Wed 4/30/14	Wed 4/30/14
Task 2: Engineering Analysis	Sat 10/1/11	Wed 4/30/14
Task 3: Performance Calculations	Sat 10/1/11	Mon 9/30/13
Task 4: Laboratory Data	Sat 10/1/11	Sat 12/15/12
Task 5: Lab Degradation Apparatus	Sat 10/1/11	Tue 4/30/13
Task 6: Preliminary Feasibility Study	Sun 1/1/12	Wed 4/30/14

Figure 1.3 Project Schedule

1.7 Summary of Budget Period 1 Activities

1.7.1 Task 1 – Project Management and Planning

Objectives

The objectives of this task are to provide:

- Coordination and communication with US DOE-NETL and other project participants
- Timely and efficient execution of the project scope
- Monitoring and control of project scope, cost, schedule, and risk
- Maintenance and revision of the Project Management Plan as required

Work under this task also ensures that all technical project performance information is supplied to US DOE-NETL through the timely delivery of topical reports and a comprehensive final project report:

- *Preliminary Technical and Economic Feasibility Study (Task 6)*
- *Final Project Report*
- *Research Performance Progress Reports and Financial Reports (Quarterly)*
- *Other Periodic and Topical Reports.* Issued as required in accordance with the Project Management Plan and the "Federal Assistance Reporting Checklist"

Accomplishments

Work performed under Task 1 comprised coordinating activities related to the various tasks, providing the necessary resources, and completing the appropriate reports. Other specific activities included:

- A project *Kick-off Meeting* was held at the US DOE-NETL Pittsburgh campus on November 30, 2011.
- The *Project Management Plan* was updated based on changes made to the Statement of Project Objectives during contract negotiations, input from proposal reviewers, discussions with the US DOE-NETL Project Manager, and discussions held during the project Kick-off Meeting.
- A *technical presentation* was made at the annual NETL CO_2 Capture Technology Meeting held in Pittsburgh on July 9-12, 2012.
- A final project briefing was held at the US DOE-NETL Pittsburgh campus on January 22, 2014

1.7.2 Task 2 – Engineering Analysis

Objectives

The overall goal of this project is to identify, develop, and validate a concentrated piperazine-based solvent formulation that globally optimizes the technical, economic, and environmental performance of a CO_2 scrubbing system for coal-fired utility boilers. The initial stages of a solvent selection program (i.e., the work described, herein) are particularly challenging since initial candidate selections must be made without the benefit of good fundamental solvent property data, making it difficult to even roughly estimate the performance of a given candidate. Of course the work of this project builds on years of previous development work at B&W that had already narrowed the field to a family of solvent formulations comprising blends containing PZ in concentrations above about 14 wt%.

The specific objectives of Task 2 were to identify and evaluate promising solvent formulations, and to:

- Select *12 initial* candidates for more extensive evaluation under Tasks 3 and 4
- Select *4 final* candidates to carry forward

Methods

A 40.8 wt% PZ solvent formulation served as the prototype, or baseline, formulation throughout the Budget Period 1 work. It exhibits a variety of desirable characteristics that provided important quantitative measures of performance against which the predicted performance of new PZ-based candidates were judged. Further, the 40.8 wt% PZ solvent formulation had been well characterized by B&W through extensive testing at the laboratory, bench, and pilot scales supplemented by comprehensive rate-based computer simulation modeling. The 40.8 wt% PZ formulation also exhibits a variety of less-than-desirable performance characteristics that naturally served to establish initial performance goals for an improved PZ-based formulation.

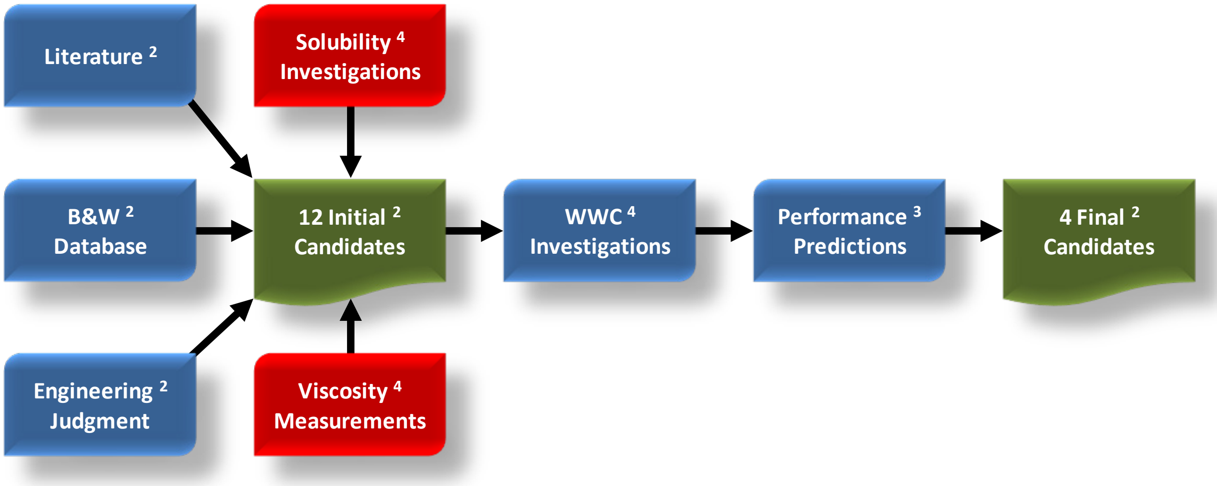


Figure 1.4 Overview of Budget Period 1 Solvent Selection Activities

The overall methodology used to identify, evaluate, and select promising solvent formulations is illustrated in Figure 1.4. The tasks under which each of the various supporting activities was performed are indicated by superscripts in the figure. The original project plans called for the "long list" of discovered solvents to be trimmed to 12 initial candidates using only *existing* B&W data, literature data, and engineering analysis. It soon became apparent, however, that existing information and theoretical considerations were not sufficient to make the needed judgments for innovative, never-been-tested, solvent formulations. Additional laboratory characterization tests, shown in red in Figure 1.4, were therefore conducted to provide the needed insights. The additional testing comprised solubility studies and the characterization of formulation viscosities.

Accomplishments

A "long list" of 55 potential PZ-based formulations, shown in Table 1.1, was developed based on literature review, previous B&W solvent work, and brainstorming activities. These formulations were then evaluated according their expected performance related to factors such as: heat of absorption, working capacity, kinetic rate, toxicity, solubility, degradation, volatility, corrosivity, viscosity, foaming tendency, surface tension, and raw material cost. It should be noted that quantitative information on these factors for these developmental formulations was, in general, not available at this early stage of the work. Many of the decisions made during this evaluation were of a very qualitative, "gut feel" nature. Information available in the literature or through earlier B&W work was supplemented by the added laboratory solubility and viscosity characterization studies.

Table 1.1 “Long List” of Candidate Solvent Formulations

Type	Formulation	Concentration *wt%*
Amine	PZ	40
	PZ	45
Amine Blend	PZ/DEEA	21/29
	PZ/2-PE/DMAE	12/7/30
Carbonate	K_2CO_3	20
	PZ/ Na_2CO_3	14/20
	PZ/ $(NH_4)_2CO_3$	14/20
	PZ/ K_2CO_3	13.8/22.14
	MAPA/ K_2CO_3	14/22
PZ / Organic	PZ/Sulfolane	40/5
	PZ/Sulfolane	40/10
	PZ/Sulfolane	40/15
	PZ/Sulfolane	40/20
	PZ/Sulfolane	40/30
	PZ/Methanol	40/2
	PZ/Ethanol	40/2
	PZ/Propanol	40/2
	PZ/Butanol	40/1
	PZ/Butanol	40/2
	PZ/Butanol	40/5
	PZ/Arg/Sulfolane	14.3/29.3/5
Amine Amino Acid Salt (AAAS)	MEA/Arg	7.4/20
	MEA/Pro	14.5/27.2
	MEA/Sar	15.2/22.6
	MEA/Tau	14/28.6
	PZ/(Arg/MAPA)	20/(20/10)
	PZ/(Arg/PZ)	20/(20/10)
	PZ/(Arg/Sar)	16/(25/3.6)
	PZ/(Sar/DMAPA)	20/(14/16)
	PZ/(SarMAPA)	20/(15/15)
	PZ/(Sar/MAPA)	20/(20/20)
	PZ/(Sar/PZ)	20/(15/15)
	PZ/(Dmg/DMAPA)	20/(30)
	PZ/(Dmg/MAPA)	20/(30)
	PZ/(Dmg/PZ)	20/(30)
	PZ/Dmg	20/23.9
	PZ/Arg	4/15
	PZ/Arg	9.9/19.6
	PZ/Arg	14/29
	PZ/His	15/27
	PZ/Lys	14.5/25
	PZ/Lys	16/26
	PZ/Lys	18.4/31.4
	PZ/Pro	19.2/25.7
	PZ/Pro	21/29
	PZ/Pro	22/29
	PZ/Pro	32/42
	PZ/Sar	20.3/21.1
	PZ/Sar	25/25
	PZ/Sar	26.5/27.7
	PZ/Tau	6.2/9
	PZ/Tau	12/17.8
	PZ/Tau	18.8/27
	PZ/Tau	21/30
	PZ/Tyr	13.7/29

This methodology resulted in the selection of 14 unique solvent formulations for further testing and evaluation under Tasks 3 and 4. The initial candidates are shown in Table 1.2.

Table 1.2 Selected Candidate Formulations

Category	Formulation	Composition (wt%)
Single Amine	PZ (baseline)	40.8
Amine Blend	PZ / DEEA	21 / 29
	PZ / 2-PE / DMAE	12 / 7 / 30
Amine/Amino Acid Salt	PZ / SarDMAPA	20 / 30
	PZ / SarMAPA	20 / 30
	PZ / SarMAPA	20 / 40
	PZ / SarPZ	20 / 30
	LysPZ	42
	ArgPZ	43
	ProPZ	50
	SarPZ	50
Inorganic Salt	MAPA / K_2CO_3	14 / 22
Organic Additive	PZ / Sulfolane	40 / 5
	PZ / Sulfolane	40 / 10

4 Final ^{2}
Candidates

Final candidate selection made use of the information generated during the initial selection process augmented by the results of laboratory characterization tests and performance predictions conducted under Tasks 4 and 3, respectively. Testing in the wetted-wall column provided CO_2 absorption rate and CO_2 solubility (VLE) data, and indirectly provided information on the enthalpy of CO_2 absorption. This information was then used in conjunction with B&W's existing in-house semi-empirical computer model to make preliminary predictions of solvent performance in a full-scale CO_2 scrubbing process. Key performance factors provided by the semi-empirical model included optimal lean and rich loadings, solvent CO_2 working capacity, absorber column liquid to gas mass flow ratio (L/G), required absorber packing height to achieve 90% CO_2 removal, heat of reaction for CO_2 absorption (ΔH_{abs}), and reboiler heat duty. Four final candidate formulations were thus chosen and are shown in Table 1.3. Had the project continued, these formulations would have been subjected to detailed characterization testing and performance evaluations in subsequent project phases.

Table 1.3 Final Candidate Formulations

Category	Formulation	Composition (wt%)
Amine Blend	PZ / DEEA	21 / 29
	PZ / 2-PE / DMAE	12 / 7 / 30
Amine/Amino Acid Salt	PZ / SarMAPA	20 / 30
Organic Additive	PZ / Sulfolane	40 / 5

1.7.3 Task 3 – Performance Calculations

Objectives

The objective of Task 3 was to provide CO_2 scrubbing process performance predictions for use in quantitatively evaluating the candidate formulations under Task 2. Process performance predictions are required to properly interpret the implications of the results of the wetted-wall column (WWC) tests, for example. WWC results do not directly provide information on regeneration energy requirements, for example, but it would be unreasonable to select candidate solvent formulations without considering this major performance factor. In the absence of actual process performance data, computer simulation modeling provides a means for estimating the needed information.

Methods

A rate-based semi-empirical process model was previously developed by B&W to support the early stages of solvent evaluation. A protocol for solvent screening using the semi-empirical model was subsequently established and validated against both more-rigorous simulation models and performance data from pilot-plant testing. The model can be used to estimate process performance on the basis of preliminary (and limited) laboratory data generated with the WWC. Some key parameters in the model include:

- 500 MW_e power plant
- CO_2 recovery rate is 90%
- Flue gas mass flow rate of 5,310,000 lbs/hr
- 12 vol% CO_2 (wet) in flue gas

- Flue gas pressure is 1.04 bars
- Structured packing is assumed
- Approach temperature for cross heat exchanger is 10 C
- Absorber diameter is kept the same *for all solvents*

While performance predictions could have been attempted using more rigorous Aspen Plus® simulations, the value of constructing such models in the early stages of solvent development work has been shown to be minimal in previous B&W studies.

Accomplishments

Performance Predictions **3**

The semi-empirical, rate-based model was used to estimate key performance parameters for the promising solvent formulation candidates. Only limited WWC experimental data is required to develop such a semi-empirical model for a specific solvent, which greatly enhanced the efficiency of the solvent evaluation and selection tasks. As described in the previous section, seven of the fourteen candidates carried through WWC testing were deemed of sufficient promise to warrant semi-empirical model evaluation. Both 40.8 wt% PZ, the baseline PZ-based formulation, and 30 wt% MEA, a widely-used acid gas removal solvent, were also included in the study for comparison purposes. Semi-empirical model studies were thus conducted on the following nine solvent formulations:

- 30 wt% MEA
- 40.8 wt% PZ
- 29 wt% DEEA / 21 wt% PZ
- 30 wt% DMAE / 7 wt% 2-PE / 12 wt% PZ
- 30 wt% SarMAPA / 20 wt% PZ
- 30 wt% SarPZ / 20 wt% PZ
- 5 wt% Sulf / 40.8 wt% PZ
- 43 wt% ArgPZ
- 50 wt% SarPZ

The B&W semi-empirical model was used to estimate optimal lean and rich loadings, solvent CO_2 working capacity (based on the optimal rich and lean loadings), absorber column liquid to gas mass flow ratio (L/G), required absorber packing height to achieve 90% CO_2 removal, heat of reaction for CO_2 absorption (ΔH_{abs}), and reboiler heat duty for each of the candidate formulations. The selections were primarily made on the basis of reboiler heat duty and cyclical, or working, capacity, since these two performance factors tend to encompass the net influences of the remaining factors. The four selected formulations include:

- 29 wt% DEEA/21 wt% PZ
- 30 wt% DMAE/7 wt% 2-PE/12 wt% PZ
- 5 wt% Sulf/40.8 wt% PZ
- 30 wt% SarMAPA/20 wt% PZ

The selection of the first three candidates on list was straightforward due to their low estimated reboiler heat duty requirements. Two of the formulations, 30 DMAE/7 2-PE/12 PZ and 5 Sulf/40.8 PZ, outperform 30 MEA by almost 30%. Further, the working capacity of the 5 Sulf/40.8 PZ formulation is over 100% higher than that of 30 MEA. Reboiler heat duty requirements for SarMAPA/PZ and SarPZ/PZ were quite similar to one another, however. The SarMAPA/PZ formulation was ultimately chosen as the fourth candidate due to its higher working capacity and slightly faster absorption rate.

Task 4 – Laboratory Data

Objectives

The objective of Task 4 was to enable meaningful solvent evaluations by providing preliminary but reliable property data for the candidate formulations. The original project plan called for the laboratory work to focus exclusively on WWC testing. However, as described earlier, it became necessary to also characterize the solubility and viscosity characteristics of the candidate formulations. This information, crucial to good decision making, simply could not be generated from first principles for the unique solvent formulations of interest in this study.

Methods

Solubility. Scoping experiments to determine the solubility characteristics of candidate formulations were conducted. Solutions were gravimetrically prepared using stock chemicals and high-purity water. The neat solutions were visually assessed for solubility during preparation, both immediately following mixing and after some time had elapsed. Then, CO_2 was gravimetrically reacted with the solvent to achieve a target CO_2 loading condition. Solubility observations were again made over time.

A significant complication was the tendency for $H^+PZCOO^-\cdot H_2O$ solutions to remain in a state of supersaturation for extended periods (months). The crystallization behavior of these relatively large-molecule crystals is apparently kinetically controlled, and the process by which the molecules become sufficiently well organized to form crystals can be quite slow. This behavior had been noted in our previous testing in the laboratory and also during pilot plant testing. It resulted in significant laboratory trial-and-error work to find ways to ensure that supersaturated solutions crystallized reliably, and in manageably short times. In the instances where the components appeared to be completely dissolved (clear solution), it became routine to add a seed crystal of the expected precipitate to ensure that the solution was not in a state of supersaturation. As a seed crystal was added to a supersaturated solution, crystal growth generally proceeded rapidly as illustrated in Figure 1.5.

Solutions that contained solids were heated and an approximate saturation temperature was thus obtained by observing the temperature at which all solids were dissolved. Approximate solubility operating "windows" were thus generated for the candidate formulations. These were then judged against the known operating window for the baseline formulation, 40.8 wt% PZ.

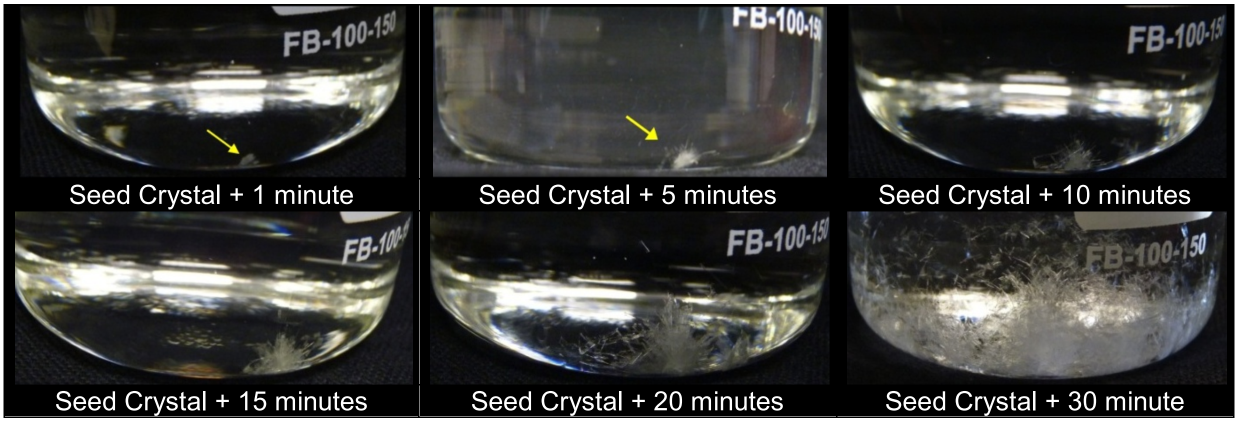

Seed Crystal + 1 minute
Seed Crystal + 5 minutes
Seed Crystal + 10 minutes
Seed Crystal + 15 minutes
Seed Crystal + 20 minutes
Seed Crystal + 30 minute

Figure 1.5 Crystal Growth in Rich PZ After Seeding

Viscosity. A highly viscous solvent may result in

- Low mass transfer rates in the absorber and regenerator,
- Low heat transfer rates in the cross heat exchanger and other heat transfer equipment, and
- High pumping power requirements.

These impacts of solvent viscosity have been clearly seen in previous bench- and pilot-scale testing of CO_2 scrubbing systems at B&W. Absorber performance has been seen to be surprisingly sensitive to even small changes in temperature due to its impact on solution viscosity. Through such testing it has been determined that solvent viscosity under absorber conditions (roughly 40-50 C) should be below about 10 cP – certainly below 20 cP.

The viscosity of candidate formulations depends on component type and concentration, CO_2 loading, and temperature. As with solubility behavior, it is difficult to accurately predict solution viscosity a priori. Viscosity measurements using a simple laboratory method were therefore made to ensure that the candidate formulations exhibited acceptable flow characteristics.

Wetted-Wall Column. B&W's wetted-wall column was used to collect CO_2 absorption rate and solubility data on candidate solvent formulations using previously established and validated experimental protocols. Such measurements were crucial to the proper selection of candidate solvent formulations. CO_2 absorption rate, or flux, and equilibrium CO_2 solubility data were obtained at different temperatures under various CO_2 loading conditions using the WWC. These data were then used to make preliminary performance predictions, as described under Task 3, which in turn were used to support the candidate selection methodology (Task 2).

Accomplishments

At least 141 solutions were prepared and evaluated in the laboratory.

Solubility ^{4} Investigations

Several candidate formulations of concentrated PZ solvents containing carbonates, other amines, and salts of amino acids, were investigated to establish a *very preliminary* understanding of their solubility behavior. Also evaluated were organic additives specifically designed to improve the solubility of PZ and its carbamates. Carbonate salts and the salts of amino acids, of interest primarily for reasons other than solubility improvement, tended to exhibit limited solubility under relevant CO_2 scrubbing conditions, adding a layer of complication onto the already complicated solubility behavior of PZ itself. Eight candidate formulations were eliminated from consideration based on their solubility characteristics, alone. Several other candidates exhibited what was considered to be only marginally acceptable solubility characteristics.

Viscosity ^{4} Measurements

A Cannon-Fenske style glass capillary viscometer was used to make preliminary measurements of the kinematic viscosity of several candidate solvent formulations at 20 and 40 C and various CO_2 loadings. Approximately 50 tests were conducted. Using B&W's "rule of thumb", six candidates with dynamic viscosities greater than about 10 cP at absorber conditions (about 40 C) were eliminated from further consideration. Several other candidates exhibited marginally acceptable viscosity characteristics.

WWC^{4} Investigations

The 14 solvent formulations selected during the initial evaluation were characterized using the WWC. Several of the candidate formulations exhibited CO_2 absorption rates comparable to that of 40.8 wt% PZ, the baseline solvent for this study. Three solvents that exhibited impressive CO_2 absorption rates were PZ/2-PE/DMAE (12/7/30), PZ/Sulfolane (40/5) and PZ/Sulfolane (40/10). As anticipated, none of the candidate formulations exhibited absorption rates measurably higher than that of 40.8 wt% PZ.

CO_2 cyclical or working capacity was estimated using VLE data obtained from the WWC at different CO_2 loadings. Several of the candidate formulations exhibited higher theoretical maximum capacities than that of 40.8 wt% PZ. These included PZ/2-PE/DMAE (12/7/30), PZ/DEEA (21/29), PZ/Sulfolane (40/5), and PZ/Sulfolane (40/10).

During WWC testing, six of the 14 initial candidates were found to exhibit characteristics which made them noncompetitive and were eliminated from further consideration. In general, once a formulation was determined to be noncompetitive WWC testing was stopped. Overall, WWC testing resulted in eight candidate formulations being carried forward into the performance prediction (modeling) evaluation conducted under Task 3.

Task 5 – Laboratory Degradation Apparatus

Objectives

The objective of this task was to design and install a Continuous Solvent Degradation System (CSDS) to enable subsequent comprehensive solvent degradation investigations to be conducted. The final selection of an optimized solvent formulation will absolutely require high quality, representative, solvent degradation data.

Methods

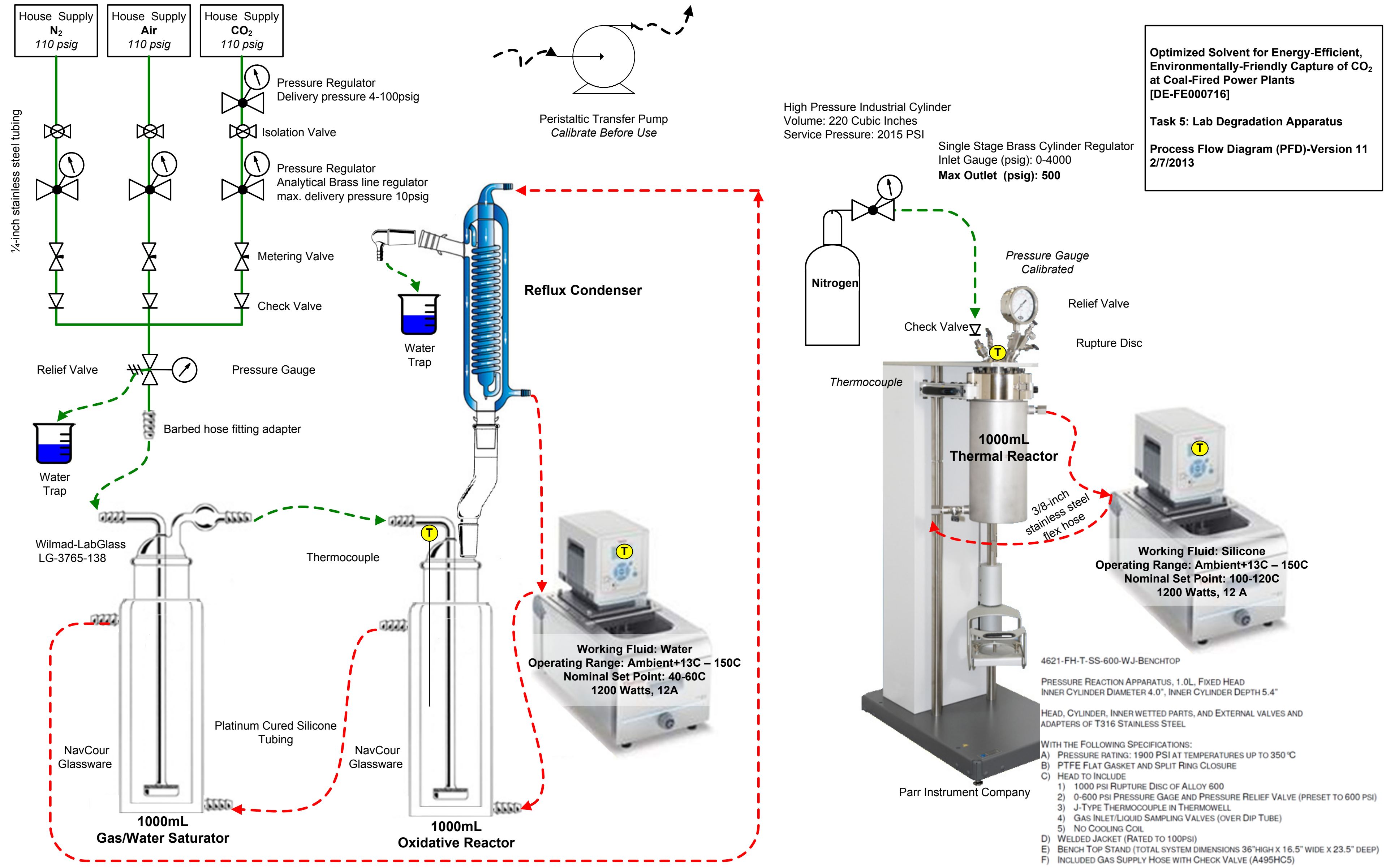
Amine solvents such as MEA or PZ chemically degrade in a variety of ways including:

- *Thermal Degradation* due to exposure to the high temperatures of the regeneration process,
- *Oxidative Degradation* due the presence of oxygen in the flue gas,
- *Carbamate Polymerization* due to the presence of CO_2, and
- *Heat-Stable Salt Formation* resulting from reactions with flue gas constituents such as SO_X, NO_X, HCl, etc.

Degradation reactions can be accelerated by the presence of degradation or corrosion products and heat-stable salts, and through the catalytic effects of various metals. Metals can be present due to the corrosion of process equipment or the presence of fly ash or limestone from the upstream power plant processes.

The CSDS, shown schematically in Figure 1.6, is intended to simulate key features of industrial CO_2 capture processes in a representative way including cyclical absorption and regeneration process conditions, and the impacts of various contaminant species. The CSDS has been designed for continuous, unattended operation for tests lasting 100-1000 hours or more, and has been installed in an existing vented hood in B&W's CO_2 Control Laboratory. By design, it is *not* intended to replicate the entire CO_2 scrubbing process at small scale. Rather, it is designed to recreate the critical degradation-related conditions representative of an industrial CO_2 scrubbing process in a manner that can be safely operated unattended.

The oxidative reactor simulates low-temperature, atmospheric-pressure absorber conditions and the thermal reactor simulates high-temperature regenerator conditions in the range of 100-150 C (212-302 F). Solvent samples are switched between these systems for alternating exposure to oxygen and heat. Decoupling the two vessels is a practical simplification that provides several safety benefits by segregating the oxygen-containing and high-temperature vessels, and by reducing the complexity of high-pressure safeguards.



Optimized Solvent for Energy-Efficient, Environmentally-Friendly Capture of CO_2 at Coal-Fired Power Plants
[DE-FE000716]

Task 5: Lab Degradation Apparatus

Process Flow Diagram (PFD)-Version 11
2/7/2013

4621-FH-T-SS-600-WJ-Benchtop

Pressure Reaction Apparatus, 1.0L, Fixed Head
Inner Cylinder Diameter 4.0", Inner Cylinder Depth 5.4"

Head, Cylinder, Inner wetted parts, and External valves and adapters of T316 Stainless Steel

With the Following Specifications:
A) Pressure rating: 1900 PSI at temperatures up to 350°C
B) PTFE Flat Gasket and Split Ring Closure
C) Head to Include
    1) 1000 psi Rupture Disc of Alloy 600
    2) 0-600 psi Pressure Gage and Pressure Relief Valve (preset to 600 psi)
    3) J-Type Thermocouple in Thermowell
    4) Gas Inlet/Liquid Sampling Valves (over Dip Tube)
    5) No Cooling Coil
D) Welded Jacket (Rated to 100psi)
E) Bench Top Stand (total system dimensions 36"high x 16.5" wide x 23.5" deep)
F) Included Gas Supply Hose with Check Valve (A495HC5)

Figure 1.6 CSDS Detailed Design

Accomplishments

The CSDS has been installed in an existing 8-foot fume hood in the B&W CO_2 Control Laboratory (see Figure 1.7), and individual component shakedown has been completed. Approximately half of the hood space is dedicated to the CSDS apparatus, itself, while the remaining bench-top provides space for solvent preparation and wet chemistry analysis activities. All work under Task 5, and indeed all work under this project, has been conducted in accordance with the B&W Research Center Standard Practice Quality Assurance (QA) Manual which is compliant to ISO-9001:2008. All equipment has been installed; and the system is ready for use in subsequent project budget periods.

Figure 1.7 Continuous Solvent Degradation System (CSDS)

1.8 Conclusions

Project accomplishments during Budget Period 1 may be summarized as follows:

- The planned scope of work of Budget Period 1 has been successfully completed within the original project budget.

- Over 55 PZ-based solvent formulation candidates were identified and evaluated including PZ solutions containing other amines, amino acid salts, inorganic carbonate salts, and organic additives.
- Laboratory characterization work involved the preparation of over 140 solvent solutions. In addition to the planned WWC testing, the laboratory work comprised additional, unplanned testing to characterize candidate solubility and viscosity characteristics. This additional work was necessitated by the difficulties associated with predicting such properties for innovative solvent formulations where little previous work had been done.
- An initial set of 14 promising candidate formulations were comprehensively evaluated using B&W's WWC to provide quantitative vapor-liquid equilibrium (VLE), mass transfer, and heat of reaction data. The 14 formulations tested included 40.8 wt% PZ, which served as the baseline formulation throughout the Budget Period 1 work.
- The results of the WWC testing were used in conjunction with B&W's in-house semi-empirical process simulation model to predict required absorber packing height and L/G, reboiler heat duty, and solvent CO_2 working capacity for 7 remaining candidates. Model results were also developed for 30% MEA and 40.8% PZ for comparison purposes.
- Engineering evaluation augmented by laboratory data and performance predictions resulted in the selection of 4 final candidate formulations. The 4 recommended candidates are:
  - ✓ Piperazine (21 wt%) / Diethylethanolamine (29 wt%)
  - ✓ Piperazine (12 wt%) / 2-Piperidineethanol (7 wt%) / Dimethylethanolamine (30 wt%)
  - ✓ Piperazine (20 wt%) / { Sarcosine (15 wt%) / 3-(Methylamino)propylamine (15 wt%) }
  - ✓ Piperazine (40 wt%) / Sulfolane (5 wt%)
- A Continuous Solvent Degradation System (CSDS) was designed, fabricated, and installed in B&W's CO_2 Control Laboratory to enable comprehensive solvent degradation investigations to be conducted. The CSDS has been designed to representatively simulate solvent exposure conditions in an industrial CO_2 scrubbing process, and to provide for continuous, unattended operation for tests lasting 100-1000 hrs or more.
- A Preliminary Technical and Economic Feasibility Study was completed to further develop the proposed solvent concept and to establish a quantitative basis for subsequent process development and bench-scale testing. The study provides a quantitative measure of the potential performance improvements offered by the advanced process in terms of factors such as levelized cost of electricity (LCOE), cost of CO_2 capture, and parasitic power consumption.

2.0 PRELIMINARY TECHNICAL AND ECONOMIC FEASIBILITY STUDY (TASK 6)

2.1 Objective

The objective of Task 6, Preliminary Technical and Economic Feasibility Study, was to further develop the proposed solvent concept and to establish a quantitative basis for subsequent process development and bench-scale testing. The overall approach was to consider the application of an advanced PZ-based capture process to a 550 MW_e (net) coal-fired power plant. The study provides a quantitative measure of the potential performance improvements offered by the advanced process in terms of factors such as levelized cost of electricity (LCOE), cost of CO_2 capture, and parasitic power consumption. It also quantifies the sensitivity of power plant performance to various process design features, identifies gaps in design information needed for successful scale-up in later phases of process development, highlights additional laboratory data that may be required, and establishes technology performance targets.

2.2 Methods

The Integrated Environmental Control Model (IECM)[1,2], developed by Carnegie Mellon University's Department of Engineering & Public Policy with over two decades of continuous support from US DOE-NETL, was used to generate meaningful economic data for the performance of advanced solvent systems. IECM is a computer modeling program that facilitates systematic cost and performance analyses of emission control equipment at coal-fired power plants. The technical and economic assessment methodology incorporated in the IECM is based on the Electric Power Research Institute's Technical Assessment Guide (EPRI TAG™)[3]. The IECM allows the user to configure the power plant by selecting from a variety of pollutant control technologies:

> *Power Plants.* PC boilers (subcritical, supercritical, and ultra-supercritical), integrated coal gasification & combined cycle (IGCC), natural gas combined cycle (NGCC), oxyfuel combustion
>
> *NO_X Control.* Wall, tangential, and cyclone firing, low NO_X burner (LNB) with over-fire air (OFA), selective catalytic reduction (SCR), selective non-catalytic reduction (SNCR), natural gas reburn

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[1] http://www.cmu.edu/epp/iecm/index.html

[2] Berkenpas, M.B., et. al., IECM Technical Documentation Updates, Vol. I to V, Final Report to USDOE/NETL from Carnegie Mellon University, (November 2009, revised March 2012).

[3] EPRI. *TAG™ Technical Assessment Guide: Electricity Supply - 1993,* Volume 1, Rev. 7, Report No. TR-102276, Electric Power Research Institute, Palo Alto, CA, June 1993.

SO_2 Control. Acid gas removal w/sulfur recovery, wet limestone w/forced oxidation (LSFO), wet limestone with dibasic acid, lime spray dryer, Mg-Lime Process

Particulate Matter Control. Electrostatic precipitator (ESP), reverse gas fabric filter, reverse gas sonic fabric filter, shake and deflate fabric filter, pulse-jet fabric filter

Mercury Control. Activated carbon injection (with and without spray cooling), intrinsic capture of mercury by other pollution control technologies

CO_2 Capture & Storage. Amine scrubber, ammonia scrubber, membrane separation, pipeline transport, enhanced oil recovery storage (EOR), deep saline reservoir storage, ocean storage, enhanced coalbed methane storage, water-gas shift reactor, Selexol scrubber, chemical looping, O_2-CO_2 recycle (Oxyfuel)

The IECM also allows uncertainties in performance and cost to be characterized for key design criteria. The uncertainties can be iterated across the entire emission control system.

The IECM provided an ideal platform for estimating the performance impacts of an advanced PZ-based solvent formulation at this early stage of the project. A more rigorous, bottom-up approach to performance and cost estimation using the AspenPlus® platform, for example, would yield no more accurate results in light of the fact that the candidate formulations have not yet been properly characterized or subjected to performance testing. A more detailed approach would be appropriate for later stages of the solvent development effort.

Assumptions for system boundaries, process design, and economic analysis used for the IECM evaluations were based on the guidelines provided in Attachment 3 of the original US DOE-NETL Funding Opportunity Announcement[1]. The IECM was used to estimate such factors as the levelized cost of electricity (LCOE), cost of CO_2 capture, and parasitic power consumption for various cases involving the application of the PZ-based process concept to a 550 MW_e (net) coal-fired power plant. For comparison purposes similar cases were developed using existing IECM input parameters based on the commercial Fluor Econamine FG Plus^{SM} CO_2 scrubbing process.

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[1] "Bench-Scale and Slipstream Development and Testing of Post-Combustion Carbon Dioxide Capture and Separation Technology for Application to Existing Coal-Fired Power Plants", US DOE-NETL, Funding Opportunity Number DE-FOA-0000403, Issued 1/31/2011.

2.3 Modeling Assumptions

Process Considerations. In the process of interest, traditionally referred to as an absorption-stripping process, CO_2 is removed from the flue gas using a wet scrubber, or absorber, very much akin to the wet scrubbers used for removing SO_2 from flue gases. There are some important differences between CO_2 and SO_2 scrubbers, however. CO_2 is present in much larger quantities than SO_2, meaning that, in general, throwaway processes are not attractive and the solvent must be regenerable, or reusable. CO_2 is also more difficult to remove from flue gases than SO_2, primarily due to its lower reactivity and very slow rate of hydration in water.

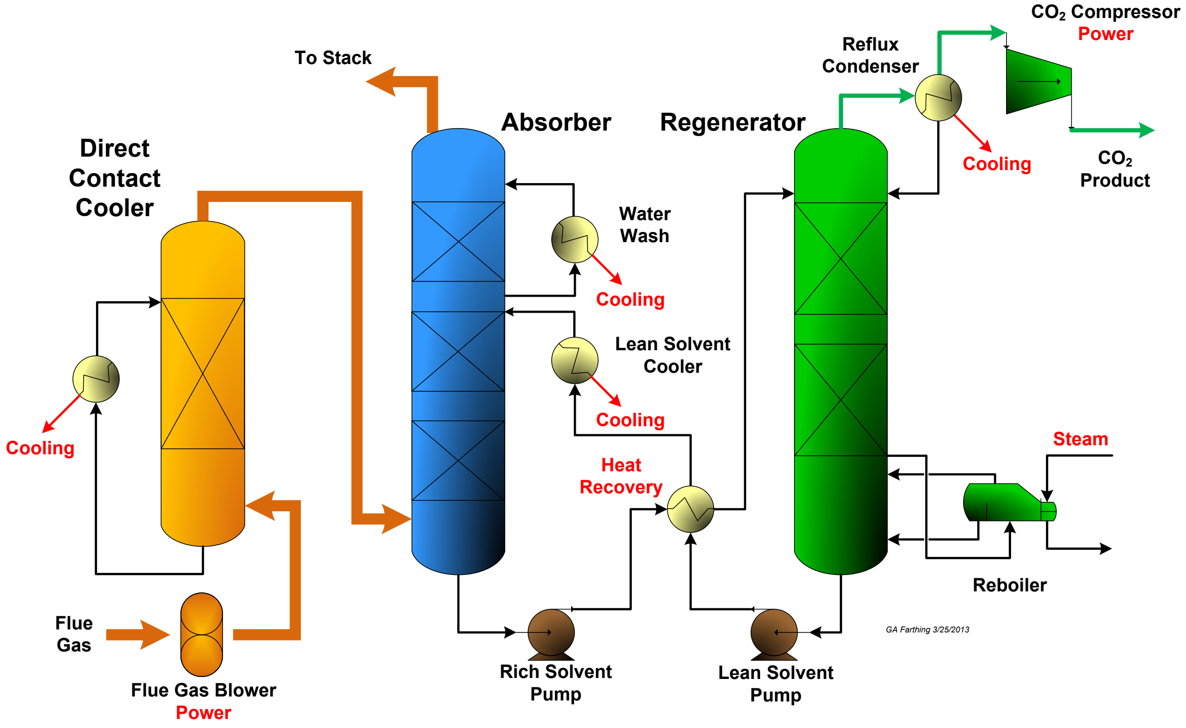


Figure 2.1 Regenerable Solvent Process

A schematic of a regenerable solvent CO_2 scrubbing process is shown in Figure 2.1. The flue gas stream from which CO_2 is to be removed is contacted with lean solvent (solvent which has not yet absorbed much CO_2) in an absorber vessel, or scrubber. CO_2 is absorbed by the solvent, and the clean flue gas is exhausted through the stack. The rich solvent (solvent which has absorbed a significant amount of CO_2) is then pumped to a regenerator wherein a temperature-swing process is used to remove (more-or-less distill, or strip) the absorbed CO_2 from the solvent for subsequent storage. Energy, often in the form of low-pressure steam supplied to a reboiler, is required to free the CO_2 from the rich solvent. The regenerated solvent is then pumped back to the absorber for reuse.

CO_2 scrubbing systems using simple amines have been successfully applied in the petrochemical industry for decades. A major disadvantage of these systems, however, when applied to coal-fired power plants, is their high cost. It is estimated that a conventional amine-based CO_2 scrubbing process would reduce the net electrical output of the power plant by nearly one-third, and increase the cost of electricity by 60 to100%.

As a concrete example, consider the conventional amine-based CO_2 scrubbing process based on the use of a monoethanolamine (NH_2 CH_2 CH_2 OH, or MEA) solvent. MEA is a primary amine that reacts with CO_2 by way of a reversible, exothermic reaction in the absorber to form (primarily) carbamate. The rich amine solution is then sent to the regenerator wherein CO_2 is released by driving the chemical equilibrium from carbamate back to amine. This is accomplished by heating the solution to 110-120 C using low-pressure steam supplied to the reboiler. Heating the solution not only causes the equilibrium solubility of CO_2 to decrease, but also evaporates (boils) some of the water. The water vapor reduces the partial pressure of CO_2 in the gas phase, thereby increasing the driving force for CO_2 desorption and “stripping” the CO_2 from the MEA solvent. The regenerator requires energy input on the order of 3.7-4.0 GJ/tonne CO_2 (1,590-1,720 Btu/lb CO_2). This is a great deal of energy, amounting to about 40% of the heating value of the original carbon in the coal! At a power plant it is generally anticipated that this large amount of energy would be supplied to the reboiler in the form steam extracted ahead of the low-pressure turbine, dramatically reducing the amount of electricity produced by the power plant.

For most regenerable solvent processes the reboiler heat duty comprises three factors:

- Sensible heat – the heat required to raise the temperature of the solvent from the temperature of the rich solvent leaving the absorber to the operating temperature of the regenerator
- Heat of reaction – the energy that must be supplied to reverse the exothermic CO_2 absorption reaction
- Stripping steam – the latent heat associated with the vaporization of water from the solvent in the regenerator column

The sensible heat component depends, in part, on the heat capacity of the solvent and on the solvent circulation rate, which depends on the CO_2 carrying capacity of the solvent. The stripping steam component depends on the thermodynamic characteristics of the solvent-CO_2

system, and on the pressure at which the regenerator operates. The heat of reaction component obviously depends on the mechanism and thermodynamic details of the chemical reaction(s) of CO_2 with the solvent.

Solvent Considerations. The physical, chemical, and thermodynamic properties of the solvent are of critical importance in determining the performance of a CO_2 scrubbing process. They have a wide variety of impacts on overall system performance measures such as capital cost, operating cost, operability and reliability, and safety and environmental considerations. A few examples of these considerations are illustrated in Figure 2.2.

The CO_2 absorption process may be characterized as comprising mass transfer accompanied by chemical reaction. The chemical reaction greatly enhances the rate of mass transfer by removing (through chemical reaction) absorbed CO_2 in the liquid phase from the region of the gas-liquid interface, thereby providing a strong concentration driving force for CO_2 absorption. For the solvents of interest, here, the ***kinetics*** of the chemical reaction between CO_2 and the solvent help to determine the rate of CO_2 absorption which, in turn, directly affects the height of the absorber required to achieve the desired CO_2 removal efficiency.

The difference in CO_2 concentration between the rich and lean solvent streams determines the amount of solvent that must be circulated to yield the desired amount of CO_2 removal. The CO_2 working ***capacity*** is an important performance characteristic of a solvent because it helps to determine the size of the absorber and regenerator vessels, as well as the size of related pumps, heat exchangers, etc. It also greatly impacts the amount of energy required for the process, primarily through the sensible heat component of reboiler duty, but also through its impact on pump power requirements. The capacity of a solvent is determined by the thermodynamic characteristics of the solvent at the relevant process operating conditions.

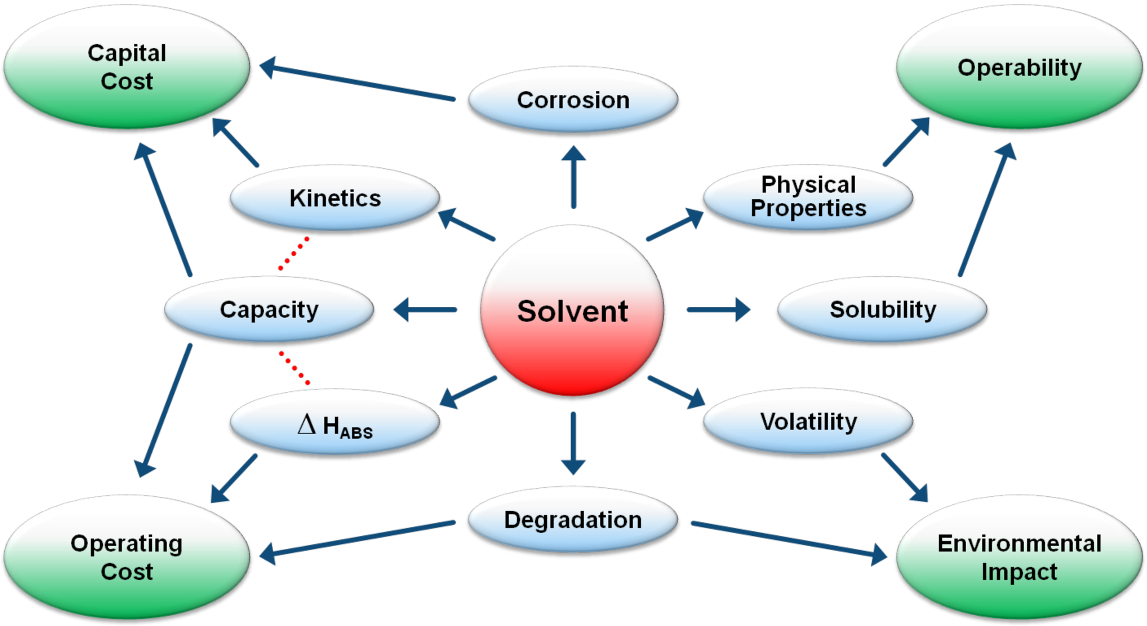


Figure 2.2 Solvent Selection Considerations

The chemical reaction between CO_2 and the solvent in the absorber is exothermic with a heat of reaction equal to ΔH_{abs}. The same amount of energy must be supplied to reverse this reaction in the regenerator, directly contributing to the energy required for regeneration. All things being equal, it would seem to be desirable to choose a solvent with a low heat of reaction if the goal is to reduce the regeneration energy required. All things are not equal, however, and such solvents rarely perform well on flue gas. Solvents with low heats of reaction tend to have low absorption rates and vapor-liquid equilibrium (VLE) characteristics less suitable to a temperature-swing regeneration process. There are good fundamental thermodynamic reasons why these solvent characteristics are not truly independent variables (as indicated by the dotted lines in Figure 2.2). Selection of a solvent therefore almost always involves a compromise which seeks to optimally balance competing effects.

The ***volatility*** of the solvent at the conditions at the top of the absorber greatly impacts overall process performance. Volatile solvent allowed to escape the absorber through the stack becomes a volatile organic compound (VOC) emission, potentially creating an important and undesirable environmental impact. Attempting to contain these emissions through the use of a water wash section at the top of the absorber increases cost and can also impact the process water balance. This can result in a contaminated wastewater discharge stream, another possible environmental impact. Finally, any solvent lost from the process through evaporation must be replaced, contributing to solvent make-up cost.

The operating range in terms of allowable CO_2 loading, for example, can be significantly limited by the ***solubility*** of the solvent and/or its reaction products. Ammonia, sodium and potassium carbonates, piperazine, and amino acid systems are all significantly impacted by issues of solubility. In addition to their impact on system CO_2 removal performance, solubility issues can greatly impact process operability and reliability due to the potential for the formation of troublesome deposits during normal process operation, system transients, and solvent handling operations.

Amine solvents are typically subject to chemical ***degradation*** and degrade in a variety of ways: thermal degradation due to exposure to the high temperatures of the regeneration process, oxidative degradation due the presence of oxygen in the flue gas, carbamate polymerization, etc. The solvent is also degraded through reaction with flue gas contaminants such as SO_X, NO_X, HCl, and others which form heat-stable salts. Unlike CO_2, these gases are not released during the solvent regeneration process and slowly render the solvent unreactive. The inlet concentrations of SO_X, NO_2, etc., must therefore be kept low, ideally as low as ~1 ppm. For the coal-fired power plant application the CO_2 scrubbing system is therefore placed downstream of conventional pollution control equipment, as illustrated in Figure 2.3, to minimize the detrimental impacts of flue gas impurities on CO_2 capture process performance.

Degradation reactions can be accelerated by the presence of degradation or corrosion products and heat-stable salts, and through the catalytic effects of various metals (possibly originating with the coal fly ash). Degradation results in the need for additional solvent makeup, and for solvent reclaiming to remove degradation products and heat-stable salts from the circulating solvent. Many of the possible degradation products removed by the reclaiming process are hazardous and result in a hazardous solid waste stream. Volatile degradation products can also contribute to VOC emissions at the stack. The formation and emission of nitrosamines are of particular concern

Solvent solutions used for CO_2 scrubbing, and their degradation products, are often corrosive. Their corrosivity depends on CO_2 loading, concentration, chemical speciation, metallurgy, and local conditions. ***Corrosion*** can be greatly impacted by the presence of heat-stable salts and the products of corrosion and solvent degradation. Corrosion is often controlled through the use of corrosion inhibitors, which can, in turn, influence solvent degradation rates. Corrosion concerns directly impact capital cost through the selection of corrosion-resistant materials of construction, and operating cost through the cost of inhibitors, increased solvent degradation rates, and higher system maintenance costs.

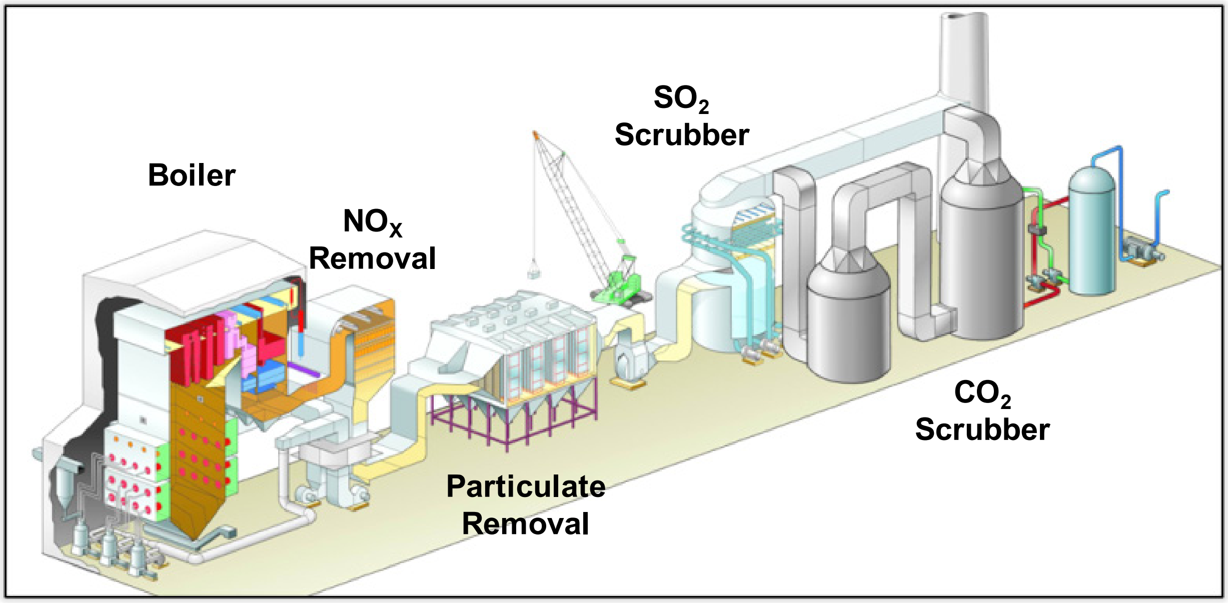


Figure 2.3 CO_2 Capture at Coal-Fired Power Plant

The chemical and thermodynamic characteristics of a solvent certainly help to determine its performance with respect to issues such as CO_2 removal, energy requirements, degradation, and corrosion, but they also directly impact a variety of factors such as operability, reliability, and EH&S. A solvent that has hazardous characteristics (toxicity, flammability, etc.) can clearly present environmental and safety risks. Addressing these risks may, in turn, result in difficult solvent handling operations, complicated automated control systems, and special requirements for the disposal of waste materials, all of which increase cost. Solvent ***physical properties*** also strongly influence the design and performance of a CO_2 scrubbing system. Solvent viscosity impacts the mass transfer performance of the absorber, and surface tension can impact the wettability of packing surfaces and the foaming tendencies of a solvent. Viscosity, density, and heat capacity all impact the performance of process heat exchangers.

Capture System Performance. A rate-based semi-empirical model was previously developed by B&W to support the early stages of solvent evaluation. It is primarily used to predict required absorber packing height, reboiler heat duty, and solvent CO_2 cyclic capacity on the basis of preliminary laboratory data generated with the WWC. Some key features of the model include:

- 500 MW_e power plant
- CO_2 recovery rate is 90%
- Flue gas mass flow rate of 5,310,000 lbs/hr
- 12 vol% CO_2 (wet) in flue gas

- Flue gas pressure is 1.04 bars
- Structured packing is assumed
- Approach temperature for cross heat exchanger is 10 C
- Absorber diameter is kept the same *for all solvents*

The semi-empirical, rate-based model was used to estimate key performance parameters for the promising solvent formulation candidates. Only limited WWC experimental data is required to develop such a semi-empirical model for a specific solvent, which greatly enhanced the efficiency of the solvent evaluation and selection tasks. As described in the previous section, seven of the fourteen candidates carried through WWC testing were deemed of sufficient promise to warrant semi-empirical model evaluation. Both 40.8 wt% PZ (8m PZ), the baseline PZ-based formulation, and 30 wt% MEA, a widely-used acid gas removal solvent, were also included in the study for comparison purposes. Semi-empirical model studies were thus conducted on the following nine solvent formulations:

- 30 wt% MEA
- 40.8 wt% PZ
- 29 wt% DEEA / 21 wt% PZ
- 30 wt% DMAE / 7 wt% 2-PE / 12 wt% PZ
- 30 wt% SarMAPA / 20 wt% PZ
- 30 wt% SarPZ / 20 wt% PZ
- 5 wt% Sulf / 40.8 wt% PZ
- 43 wt% ArgPZ
- 50 wt% SarPZ

The B&W semi-empirical model was used to estimate optimal lean and rich loadings, solvent CO_2 working capacity (based on the optimal rich and lean loadings), absorber column liquid to gas mass flow ratio (L/G), required absorber packing height to achieve 90% CO_2 removal, heat of reaction for CO_2 absorption (ΔH_{abs}), and reboiler heat duty for each of the candidate formulations. This information, summarized in Table 2.1, was used to select the final candidate formulations under Task 2. The selections were primarily made on the basis of reboiler heat duty and cyclical, or working, capacity, since these two performance factors tend to encompass the net influences of the remaining factors. The four selected formulations, highlighted in green in Table 2.1, include:

- 29 wt% DEEA/21 wt% PZ
- 30 wt% DMAE/7 wt% 2-PE/12 wt% PZ
- 5 wt% Sulf/40.8 wt% PZ
- 30 wt% SarMAPA/20 wt% PZ

The selection of the first three candidates on list was straightforward due to their low estimated reboiler heat duty requirements. Two of the formulations, 30 DMAE/7 2-PE/12 PZ and 5 Sulf/40.8 PZ, outperform MEA by almost 30%. Further, the working capacity of the 5 Sulf/40.8 PZ formulation is over 100% higher than that of 30 MEA. Reboiler heat duty requirements for SarMAPA/PZ and SarPZ/PZ were quite similar to one another, however. The SarMAPA/PZ formulation was ultimately chosen as the fourth candidate due to its higher working capacity and slightly faster absorption rate.

Table 2.1 Summary of Performance Prediction Results and Selection

(Baseline solvents: Yellow; Selected solvents: Green; Rejected solvents: Red)

Formulation	α_{Lean}	α_{Rich}	Cyclical Capacity (mol CO_2/ kg solvent)	Absorber L/G (mass/mass)	Packing Height for 90% CO_2 Removal (ft)	Average Heat of Absorption, ΔH_{abs} (kJ/mol)	Reboiler Heat Duty (Btu/lb CO_2)
30 MEA	0.25	0.50	1.2	3.0	40	82.0	1,794
40.8 PZ	0.24	0.43	1.8	2.1	16	63.1	1,393
29 DEEA 21 PZ	0.18	0.47	2.2	1.7	33	71.2	1,411
30 DMAE 7 2PE 12 PZ	0.10	0.44	2.3	1.6	41	60.5	1,300
30 SarMAPA 20 PZ	0.28	0.49	1.7	2.2	40	73.1	1,504
30 SarPZ 20 PZ	0.23	0.40	1.4	2.7	49	67.7	1,493
5 Sulf 40 PZ	0.20	0.46	2.6	1.4	16	63.1	1,335
43 ArgPZ	0.24	0.46	1.1	3.4	26	65.8	1,541
50 SarPZ	0.21	0.39	1.0	3.6	17	68.8	1,593

2.4 IECM Results

The IECM was used to estimate such factors as the levelized cost of electricity (LCOE), cost of CO_2 capture, and parasitic power consumption for various cases involving the application of the PZ-based process concept to a 550 MW_e (net) coal-fired power plant. It should be noted that the modeling results presented, herein, are based on the estimated properties and performance of a *hypothetical* advanced PZ-based solvent, and not on the specific properties of one of the four candidate formulations. This is due to the fact that the candidate formulations have not yet been sufficiently characterized to permit a detailed analysis of a specific solvent formulation.

For comparison purposes capture plant cases were developed based on *existing* IECM input parameters for the commercial Fluor Econamine FG Plus^{SM} CO_2 scrubbing process. These cases are referred to as the “Conventional Amine” process. *All* capture plant cases are compared to the Reference Plant case (Case-R) for the purposes of calculating such things as “Avoided Cost” and percentage increase in the LCOE.

The case descriptors “new” and “retrofit” are used in a specific way in this study. *New plant* cases simply refer to simulations where the heat input (coal flow) to the power plant was *adjusted* to yield a net plant electrical output of 550 MW_e. In other words the size of the base plant was adjusted to accommodate the parasitic power requirements of the CO_2 scrubbing process and yield the desired plant output (550 MW_e).

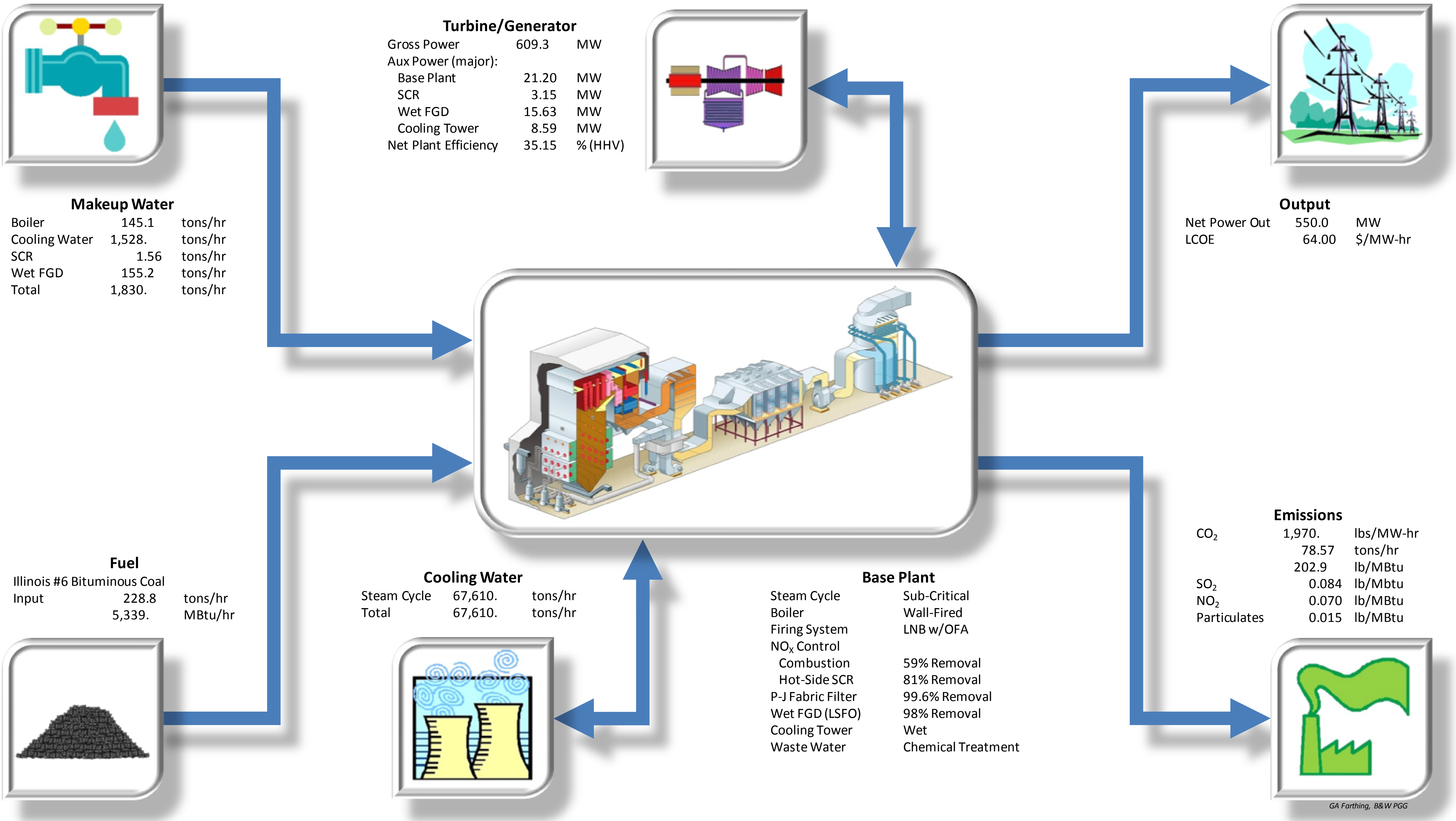
Retrofit plant cases refer to simulations where the heat input (coal flow) to the power plant was *held constant* at the value equal to that of the Reference Plant. In other words the size of the base plant was held constant at that of the Reference Plant, and the plant output was allowed to drop according to the parasitic power requirements of the CO_2 scrubbing process – the idea being that this case reflects what would happen if the capture process were applied to an existing 550 MW_e (net) plant.

All cases are based on a 20-year plant life, an 85% capacity factor, and constant 2007 dollars. All capture plant cases include the cost of CO_2 compression to 2000 psia, but do not include CO_2 product transportation and storage costs. The results of the IECM modeling effort are described in the following sections for each of the power plant configurations investigated.

2.4.1 Case R: Reference Plant

The input plant design parameters and resulting performance of the Reference Plant (Case-R) are illustrated in Figure 2.4. It has been configured to match as closely as possible the US DOE-NETL evaluation guidelines, and is based on a state-of-the-art 550 MW_e (net), subcritical power plant firing an Illinois #6 bituminous coal. *All* capture plant cases are compared to the Reference Plant case for the purposes of calculating such things as “Avoided Cost” and percentage increase in the LCOE.

Case R: Reference Plant



Turbine/Generator

Gross Power	609.3	MW
Aux Power (major):		
Base Plant	21.20	MW
SCR	3.15	MW
Wet FGD	15.63	MW
Cooling Tower	8.59	MW
Net Plant Efficiency	35.15	% (HHV)

Makeup Water

Boiler	145.1	tons/hr
Cooling Water	1,528.	tons/hr
SCR	1.56	tons/hr
Wet FGD	155.2	tons/hr
Total	1,830.	tons/hr

Output

Net Power Out	550.0	MW
LCOE	64.00	$/MW-hr

Fuel

Illinois #6 Bituminous Coal

Input	228.8	tons/hr
	5,339.	MBtu/hr

Cooling Water

Steam Cycle	67,610.	tons/hr
Total	67,610.	tons/hr

Base Plant

Steam Cycle	Sub-Critical
Boiler	Wall-Fired
Firing System	LNB w/OFA
NO_x Control	
Combustion	59% Removal
Hot-Side SCR	81% Removal
P-J Fabric Filter	99.6% Removal
Wet FGD (LSFO)	98% Removal
Cooling Tower	Wet
Waste Water	Chemical Treatment

Emissions

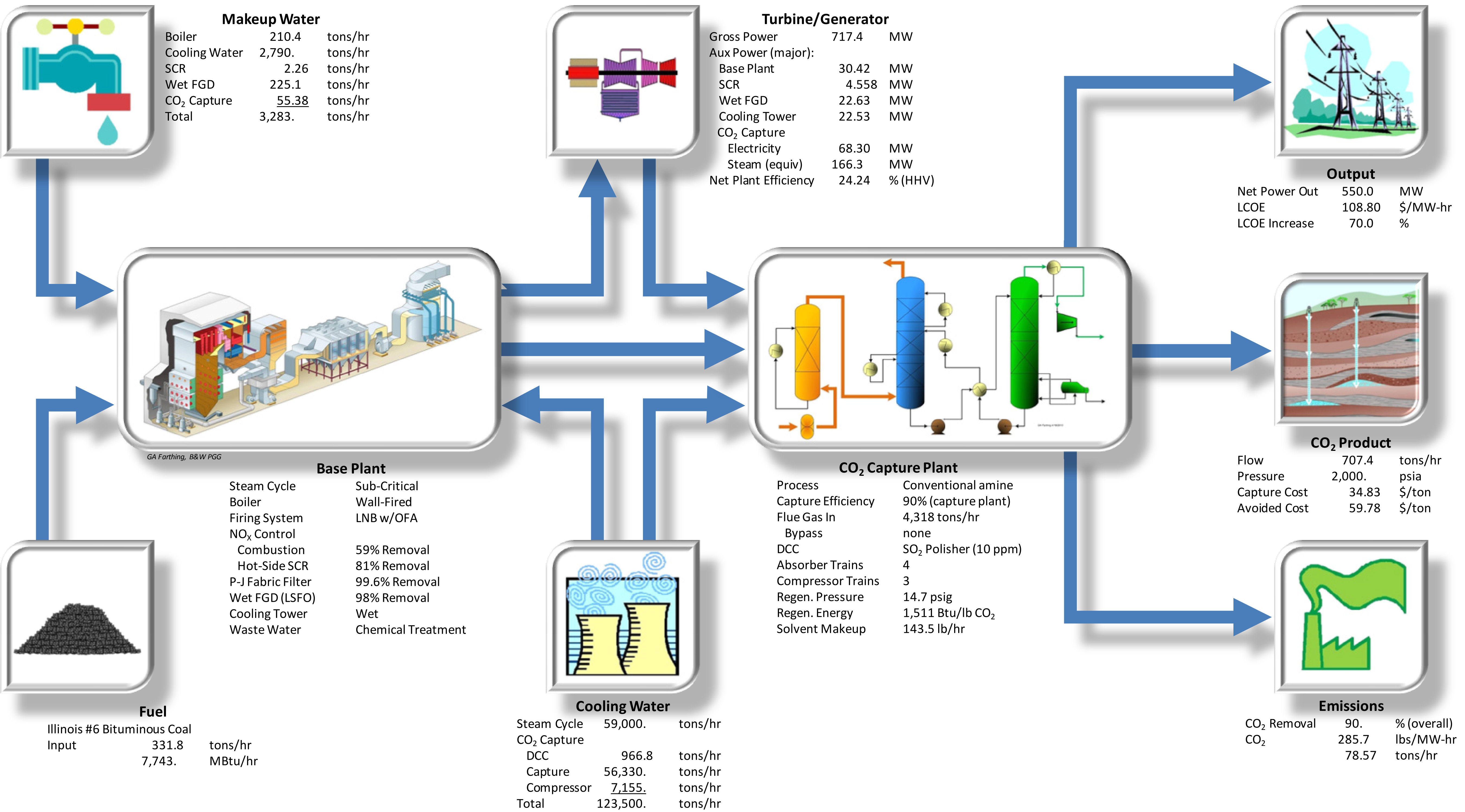
CO_2	1,970.	lbs/MW-hr
	78.57	tons/hr
	202.9	lb/MBtu
SO_2	0.084	lb/Mbtu
NO_2	0.070	lb/Mbtu
Particulates	0.015	lb/MBtu

Figure 2.4 Case R: Reference Plant

2.4.2 Conventional Amine Capture Plants

New and retrofit conventional amine capture plant model simulations, Cases AM-N (new) and AM-R (retrofit), are shown in Figure 2.5 and Figure 2.6, respectively. These cases are based on the use of the existing IECM configuration template for the Flour Econamine FG Plus^{SM} CO_2 scrubbing process, and are intended to provide a quantitative baseline for *capture plant* performance against which the performance of the advanced PZ-based process can be compared. The base plant configuration (input parameters) is identical to that of the Reference Plant in both cases, but its size in the two cases reflects the new and retrofit scenarios.

Case AM-N: Conventional Amine Capture Plant (New)



Makeup Water

Boiler	210.4	tons/hr
Cooling Water	2,790.	tons/hr
SCR	2.26	tons/hr
Wet FGD	225.1	tons/hr
CO_2 Capture	55.38	tons/hr
Total	3,283.	tons/hr

Turbine/Generator

Gross Power	717.4	MW
Aux Power (major):		
Base Plant	30.42	MW
SCR	4.558	MW
Wet FGD	22.63	MW
Cooling Tower	22.53	MW
CO_2 Capture		
Electricity	68.30	MW
Steam (equiv)	166.3	MW
Net Plant Efficiency	24.24	% (HHV)

Output

Net Power Out	550.0	MW
LCOE	108.80	$/MW-hr
LCOE Increase	70.0	%

Base Plant

Steam Cycle	Sub-Critical
Boiler	Wall-Fired
Firing System	LNB w/OFA
NO_x Control	
Combustion	59% Removal
Hot-Side SCR	81% Removal
P-J Fabric Filter	99.6% Removal
Wet FGD (LSFO)	98% Removal
Cooling Tower	Wet
Waste Water	Chemical Treatment

CO_2 Capture Plant

Process	Conventional amine
Capture Efficiency	90% (capture plant)
Flue Gas In	4,318 tons/hr
Bypass	none
DCC	SO_2 Polisher (10 ppm)
Absorber Trains	4
Compressor Trains	3
Regen. Pressure	14.7 psig
Regen. Energy	1,511 Btu/lb CO_2
Solvent Makeup	143.5 lb/hr

CO_2 Product

Flow	707.4	tons/hr
Pressure	2,000.	psia
Capture Cost	34.83	$/ton
Avoided Cost	59.78	$/ton

Fuel

Illinois #6 Bituminous Coal

Input	331.8	tons/hr
	7,743.	MBtu/hr

Cooling Water

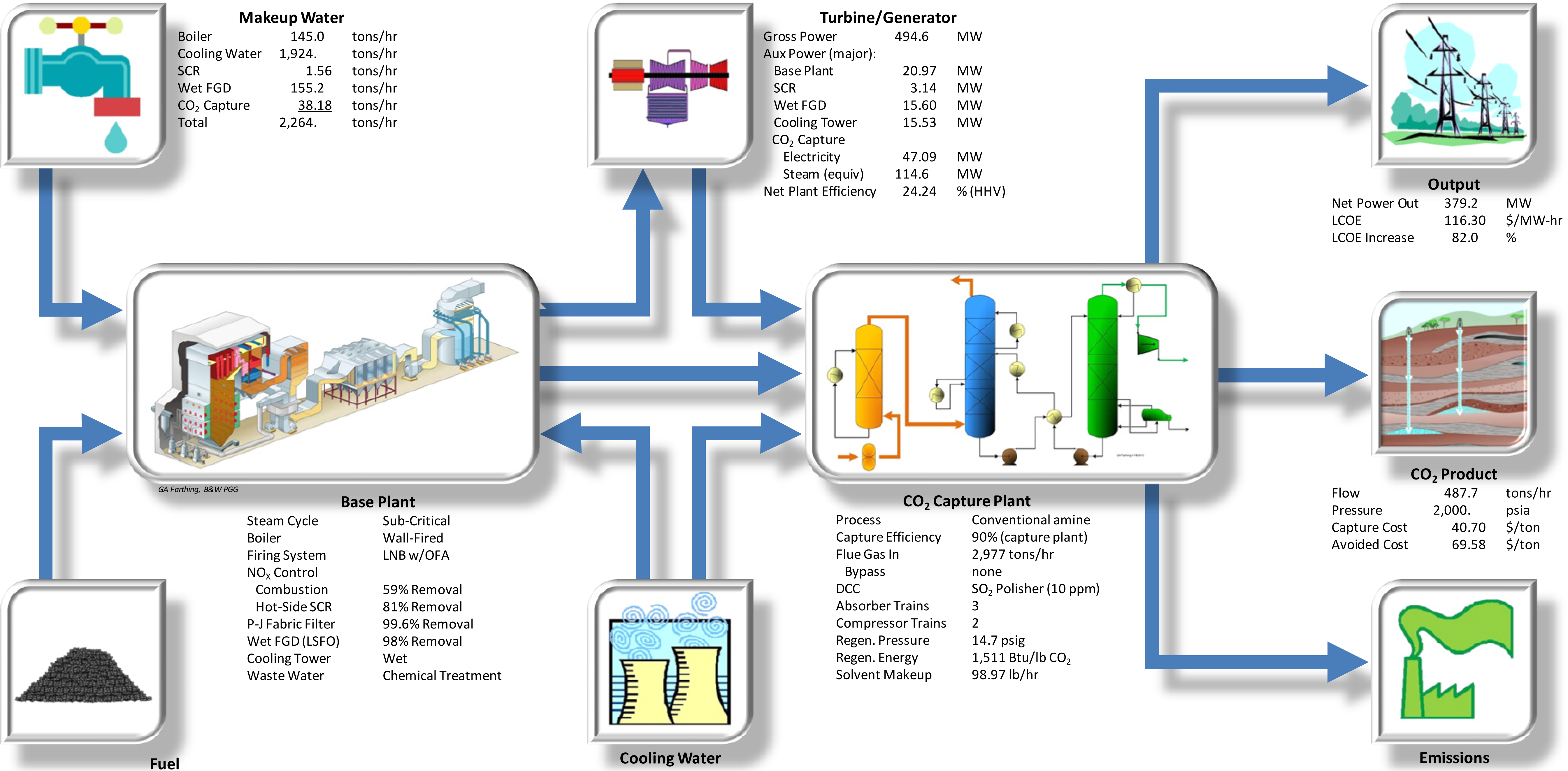
Steam Cycle	59,000.	tons/hr
CO_2 Capture		
DCC	966.8	tons/hr
Capture	56,330.	tons/hr
Compressor	7,155.	tons/hr
Total	123,500.	tons/hr

Emissions

CO_2 Removal	90.	% (overall)
CO_2	285.7	lbs/MW-hr
	78.57	tons/hr

Figure 2.5 Case AM-N: Conventional Amine Capture Plant (New)

Case AM-R: Conventional Amine Capture Plant (Retrofit)



Makeup Water

Boiler	145.0	tons/hr
Cooling Water	1,924.	tons/hr
SCR	1.56	tons/hr
Wet FGD	155.2	tons/hr
CO_2 Capture	38.18	tons/hr
Total	2,264.	tons/hr

Turbine/Generator

Gross Power	494.6	MW
Aux Power (major):		
Base Plant	20.97	MW
SCR	3.14	MW
Wet FGD	15.60	MW
Cooling Tower	15.53	MW
CO_2 Capture		
Electricity	47.09	MW
Steam (equiv)	114.6	MW
Net Plant Efficiency	24.24	% (HHV)

Output

Net Power Out	379.2	MW
LCOE	116.30	$/MW-hr
LCOE Increase	82.0	%

Base Plant

Steam Cycle	Sub-Critical
Boiler	Wall-Fired
Firing System	LNB w/OFA
NO_x Control	
Combustion	59% Removal
Hot-Side SCR	81% Removal
P-J Fabric Filter	99.6% Removal
Wet FGD (LSFO)	98% Removal
Cooling Tower	Wet
Waste Water	Chemical Treatment

CO_2 Capture Plant

Process	Conventional amine
Capture Efficiency	90% (capture plant)
Flue Gas In	2,977 tons/hr
Bypass	none
DCC	SO_2 Polisher (10 ppm)
Absorber Trains	3
Compressor Trains	2
Regen. Pressure	14.7 psig
Regen. Energy	1,511 Btu/lb CO_2
Solvent Makeup	98.97 lb/hr

CO_2 Product

Flow	487.7	tons/hr
Pressure	2,000.	psia
Capture Cost	40.70	$/ton
Avoided Cost	69.58	$/ton

Fuel

Illinois #6 Bituminous Coal

Input	228.7	tons/hr
	5,339.	MBtu/hr

Cooling Water

Steam Cycle	40,680.	tons/hr
CO_2 Capture		
DCC	666.6	tons/hr
Capture	38,840.	tons/hr
Compressor	4,933.	tons/hr
Total	85,120.	tons/hr

Emissions

CO_2 Removal	90.	% (overall)
CO_2	285.7	lbs/MW-hr
	54.17	tons/hr

Figure 2.6 Case AM-R: Conventional Amine Capture Plant (Retrofit)

2.4.3 Advanced PZ-Based Capture Plants

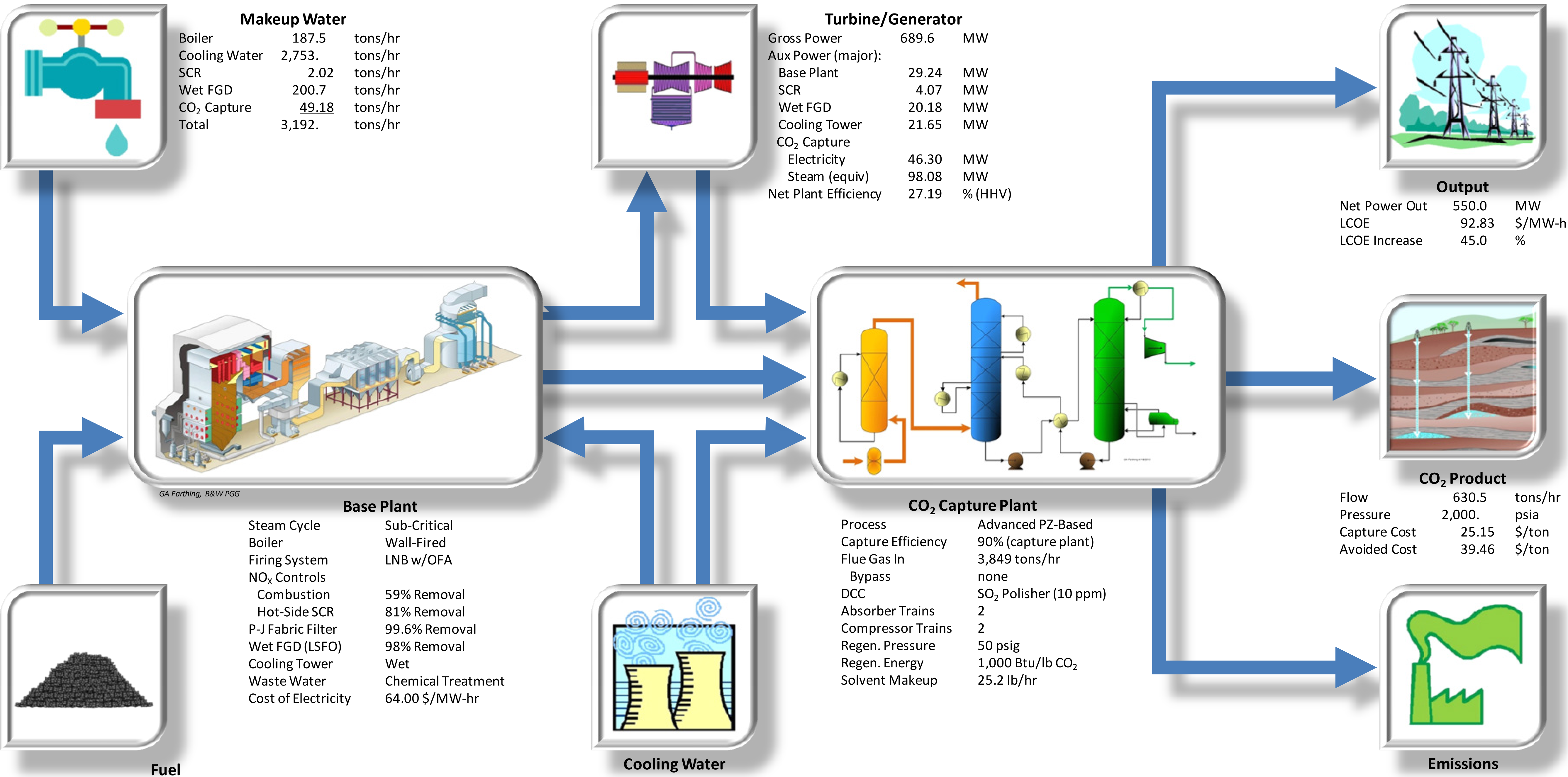
New and retrofit advanced PZ-based capture plant model simulations, Cases PZ-N (new) and PZ-R (retrofit), are shown in Figure 2.7 and Figure 2.8, respectively. These cases are intended to estimate the performance of an advanced capture process based on the use of an advanced PZ-based solvent formulation. Each is directly comparable with the corresponding Conventional Amine case, Cases AM-N (new) and AM-R (retrofit), respectively. All four cases conform to the US DOE-NETL evaluation guidelines, and therefore use the same base plant configuration.

The improved performance of the PZ-based plants relative to the conventional amine plants is primarily due to the following factors:

- *Absorber Size.* The absorber packing height required to achieve the target CO_2 removal efficiency is reduced due to the high absorption rates achievable with the PZ-based formulation. Required absorber packing height for all of the advanced PZ-based cases, relative to that of the conventional amine cases, is based on the estimates provided by B&W's semi-empirical model presented in Section 2.3.
- *Reboiler Heat Duty.* The required regeneration energy is lower due to the higher CO_2 working capacity and favorable thermodynamic behavior of the PZ-based formulation. Again, the reboiler heat duty for all of the advanced PZ-based cases, relative to that of the conventional amine cases, is based on the estimates provided by B&W's semi-empirical model presented in Section 2.3.
- *Compression Energy.* Parasitic power consumption associated with CO_2 compression is reduced due to the ability to regenerate the solvent at elevated pressure, which, in turn, is enabled by the good resistance to thermal degradation exhibited by the PZ-based formulation. CO_2 compression system capital cost and parasitic power consumption are based on operation of the CO_2 regenerator at a pressure of 50 psig.
- *Solvent Makeup.* Solvent makeup cost is estimated to be reduced due to the lower volatility and good resistance to degradation characteristic of the PZ-based formulation. These savings are somewhat offset by the higher raw material cost of PZ relative to that of MEA.
- *Reclaimer Waste.* Disposal costs associated with the disposal of reclaimer waste products are reduced due, again, to the solvent's resistance to degradation and, indirectly, to its lower corrosivity.

While aggressive, B&W believes that these assumptions realistically represent the potential performance of a coal-fired power plant equipped with an advanced PZ-based CO_2 scrubbig process.

Case PZ-N: Advanced PZ-Based Capture Plant (New)



Makeup Water

Boiler	187.5	tons/hr
Cooling Water	2,753.	tons/hr
SCR	2.02	tons/hr
Wet FGD	200.7	tons/hr
CO_2 Capture	49.18	tons/hr
Total	3,192.	tons/hr

Turbine/Generator

Gross Power	689.6	MW
Aux Power (major):		
Base Plant	29.24	MW
SCR	4.07	MW
Wet FGD	20.18	MW
Cooling Tower	21.65	MW
CO_2 Capture		
Electricity	46.30	MW
Steam (equiv)	98.08	MW
Net Plant Efficiency	27.19	% (HHV)

Output

Net Power Out	550.0	MW
LCOE	92.83	$/MW-hr
LCOE Increase	45.0	%

Base Plant

Steam Cycle	Sub-Critical
Boiler	Wall-Fired
Firing System	LNB w/OFA
NO_x Controls	
Combustion	59% Removal
Hot-Side SCR	81% Removal
P-J Fabric Filter	99.6% Removal
Wet FGD (LSFO)	98% Removal
Cooling Tower	Wet
Waste Water	Chemical Treatment
Cost of Electricity	64.00 $/MW-hr

CO_2 Capture Plant

Process	Advanced PZ-Based
Capture Efficiency	90% (capture plant)
Flue Gas In	3,849 tons/hr
Bypass	none
DCC	SO_2 Polisher (10 ppm)
Absorber Trains	2
Compressor Trains	2
Regen. Pressure	50 psig
Regen. Energy	1,000 Btu/lb CO_2
Solvent Makeup	25.2 lb/hr

CO_2 Product

Flow	630.5	tons/hr
Pressure	2,000.	psia
Capture Cost	25.15	$/ton
Avoided Cost	39.46	$/ton

Fuel

Illinois #6 Bituminous Coal		
Input	295.7	tons/hr
	6,902.	MBtu/hr

Cooling Water

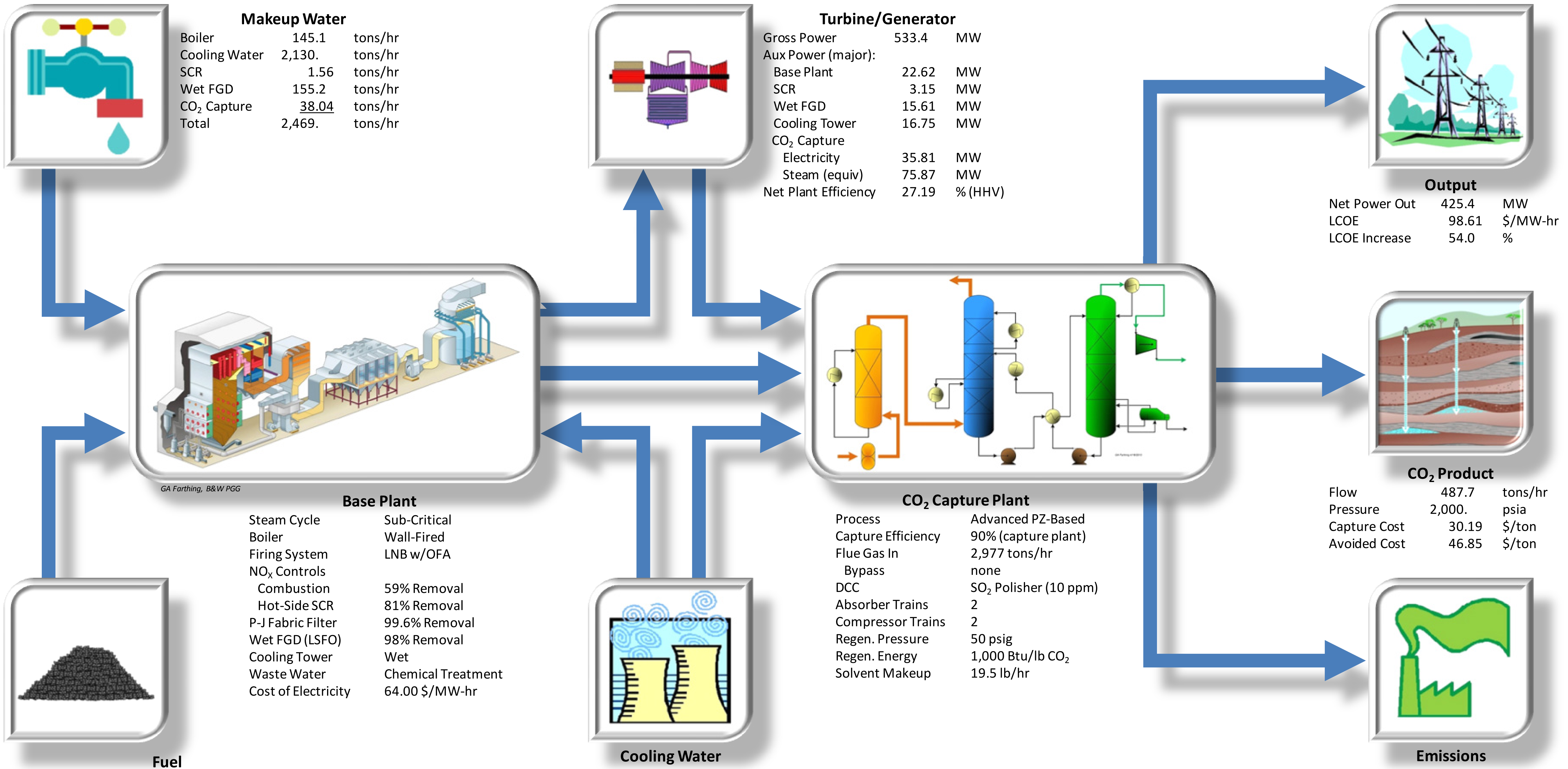
Steam Cycle	64,370.	tons/hr
CO_2 Capture		
DCC	861.8	tons/hr
Capture	50,220.	tons/hr
Compressor	6,377.	tons/hr
Total	121,800.	tons/hr

Emissions

CO_2 Removal	90.	% (overall)
CO_2	254.7	lbs/MW-hr
	70.04	tons/hr

Figure 2.7 Case PZ-N: Advanced PZ-Based Capture Plant (New)

Case PZ-R: Advanced PZ-Based Capture Plant (Retrofit)



Makeup Water

Boiler	145.1	tons/hr
Cooling Water	2,130.	tons/hr
SCR	1.56	tons/hr
Wet FGD	155.2	tons/hr
CO_2 Capture	38.04	tons/hr
Total	2,469.	tons/hr

Turbine/Generator

Gross Power	533.4	MW
Aux Power (major):		
Base Plant	22.62	MW
SCR	3.15	MW
Wet FGD	15.61	MW
Cooling Tower	16.75	MW
CO_2 Capture		
Electricity	35.81	MW
Steam (equiv)	75.87	MW
Net Plant Efficiency	27.19	% (HHV)

Output

Net Power Out	425.4	MW
LCOE	98.61	$/MW-hr
LCOE Increase	54.0	%

Base Plant

Steam Cycle	Sub-Critical
Boiler	Wall-Fired
Firing System	LNB w/OFA
NO_x Controls	
Combustion	59% Removal
Hot-Side SCR	81% Removal
P-J Fabric Filter	99.6% Removal
Wet FGD (LSFO)	98% Removal
Cooling Tower	Wet
Waste Water	Chemical Treatment
Cost of Electricity	64.00 $/MW-hr

CO_2 Capture Plant

Process	Advanced PZ-Based
Capture Efficiency	90% (capture plant)
Flue Gas In	2,977 tons/hr
Bypass	none
DCC	SO_2 Polisher (10 ppm)
Absorber Trains	2
Compressor Trains	2
Regen. Pressure	50 psig
Regen. Energy	1,000 Btu/lb CO_2
Solvent Makeup	19.5 lb/hr

CO_2 Product

Flow	487.7	tons/hr
Pressure	2,000.	psia
Capture Cost	30.19	$/ton
Avoided Cost	46.85	$/ton

Fuel

Illinois #6 Bituminous Coal

Input	228.8	tons/hr
	5,339.	MBtu/hr

Cooling Water

Steam Cycle	49,790.	tons/hr
CO_2 Capture		
DCC	666.6	tons/hr
Capture	38,840.	tons/hr
Compressor	4,933.	tons/hr
Total	94,230.	tons/hr

Emissions

CO_2 Removal	90.	% (overall)
CO_2	254.7	lbs/MW-hr
	54.18	tons/hr

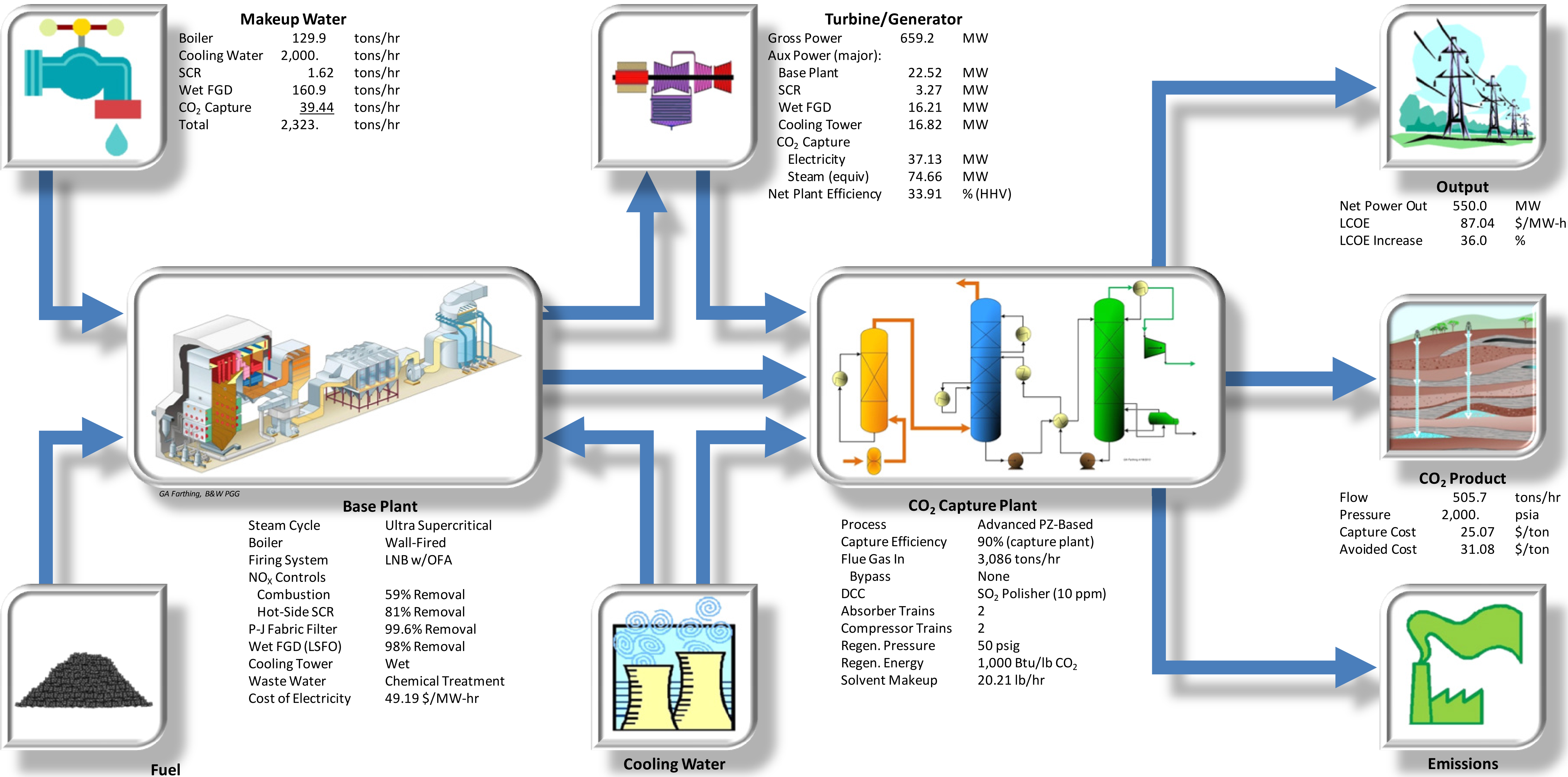
Figure 2.8 Case PZ-R: Advanced PZ-Based Capture Plant (Retrofit)

2.4.4 Advanced, Ultra-Supercritical, PZ-Based Capture Plants

Alternative advanced PZ-based capture plant model simulations, Cases PZ-NU (new USC) and PZ-NUC (new USC, Compliant), are shown in Figure 2.9 and Figure 2.10, respectively. These two cases use the same *capture plant* inputs as the other PZ-based cases. *However, they depart from the US DOE-NETL evaluation guidelines by specifying a high efficiency, ultra-supercritical steam cycle plant as the base plant.* These cases are included to quantify the performance impacts of applying the advanced PZ-based process to an ultra-supercritical base plant and of using a partial-capture (slipstream) scenario to meet US EPA’s proposed carbon pollution standard for new coal-fired power plants.

- Case PZ-NU (new USC) illustrates the performance impacts of applying the advanced PZ-based capture process to a new, ultra-supercritical base plant, instead of the subcritical base plant of the Reference Plant case.
- Case PZ-NUC (new USC, Compliant) carries this analysis further by assuming that a CO_2 emission rate of only 1,100 lbs CO_2/MW-hr (net) must be achieved, rather than the 90% CO_2 capture assumed for all other cases. This emission rate actually exceeds the requirements of the proposed carbon pollution standard for new coal-fired power plants (1,100 lbs CO_2/MW-hr (gross)) issued by the U.S. Environmental Protection Agency on Sept. 20, 2013.

Case PZ-NU: Advanced PZ-Based Capture Plant (New USC)



Makeup Water

Boiler	129.9	tons/hr
Cooling Water	2,000.	tons/hr
SCR	1.62	tons/hr
Wet FGD	160.9	tons/hr
CO_2 Capture	39.44	tons/hr
Total	2,323.	tons/hr

Turbine/Generator

Gross Power	659.2	MW
Aux Power (major):		
Base Plant	22.52	MW
SCR	3.27	MW
Wet FGD	16.21	MW
Cooling Tower	16.82	MW
CO_2 Capture		
Electricity	37.13	MW
Steam (equiv)	74.66	MW
Net Plant Efficiency	33.91	% (HHV)

Output

Net Power Out	550.0	MW
LCOE	87.04	$/MW-hr
LCOE Increase	36.0	%

GA Farthing, B&W PGG

Base Plant

Steam Cycle	Ultra Supercritical
Boiler	Wall-Fired
Firing System	LNB w/OFA
NO_x Controls	
Combustion	59% Removal
Hot-Side SCR	81% Removal
P-J Fabric Filter	99.6% Removal
Wet FGD (LSFO)	98% Removal
Cooling Tower	Wet
Waste Water	Chemical Treatment
Cost of Electricity	49.19 $/MW-hr

CO_2 Capture Plant

Process	Advanced PZ-Based
Capture Efficiency	90% (capture plant)
Flue Gas In	3,086 tons/hr
Bypass	None
DCC	SO_2 Polisher (10 ppm)
Absorber Trains	2
Compressor Trains	2
Regen. Pressure	50 psig
Regen. Energy	1,000 Btu/lb CO_2
Solvent Makeup	20.21 lb/hr

CO_2 Product

Flow	505.7	tons/hr
Pressure	2,000.	psia
Capture Cost	25.07	$/ton
Avoided Cost	31.08	$/ton

Fuel

Illinois #6 Bituminous Coal

Input	237.2	tons/hr
	5,535.	MBtu/hr

Cooling Water

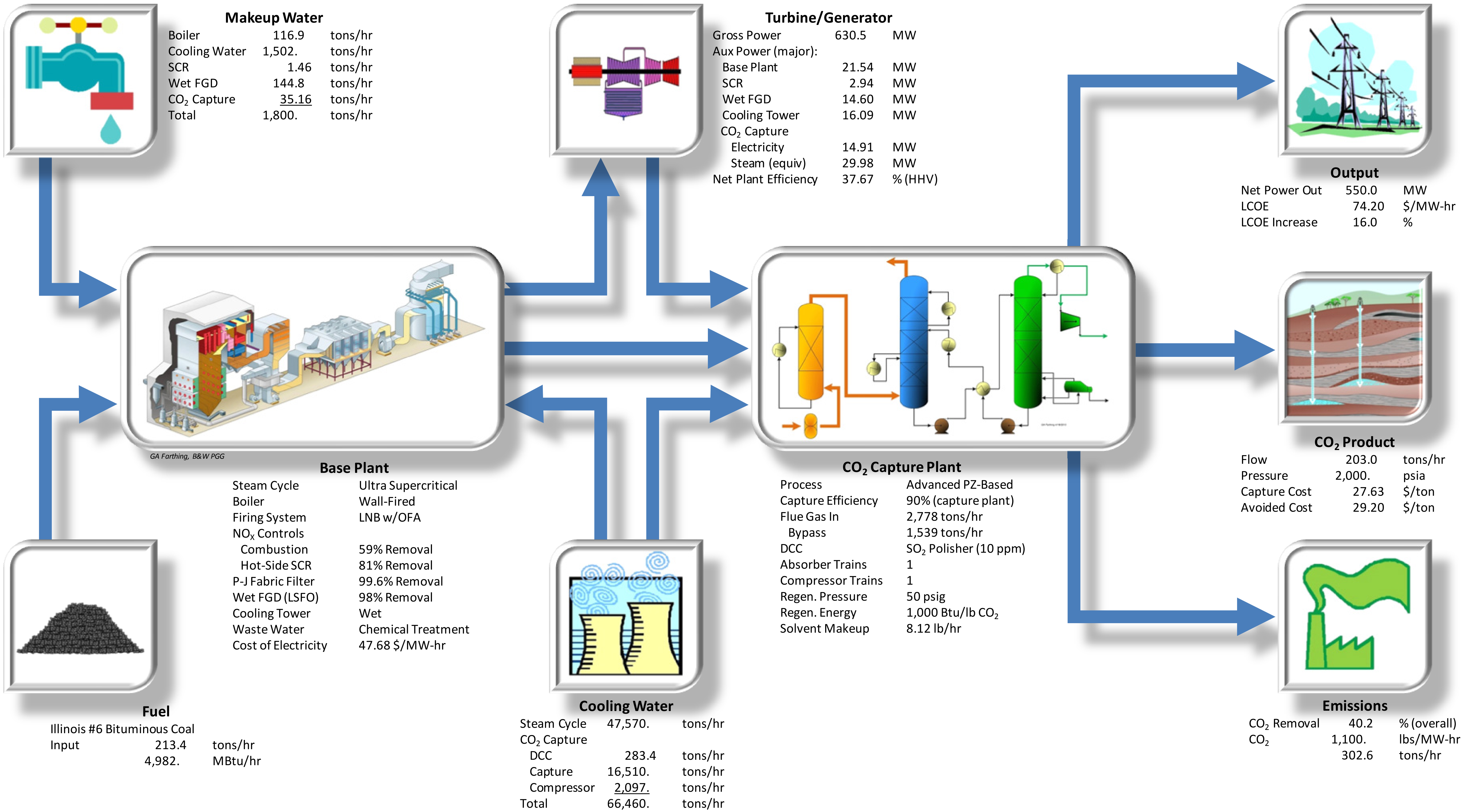
Steam Cycle	42,430.	tons/hr
CO_2 Capture		
DCC	691.1	tons/hr
Capture	40,270.	tons/hr
Compressor	5,114.	tons/hr
Total	88,500.	tons/hr

Emissions

CO_2 Removal	90.0	% (overall)
CO_2	204.2	lbs/MW-hr
	56.17	tons/hr

Figure 2.9 Case PZ-NU: Advanced PZ-Based Capture Plant (New USC)

Case PZ-NUC: Advanced PZ-Based Capture Plant (New USC, Compliant)



Makeup Water

Boiler	116.9	tons/hr
Cooling Water	1,502.	tons/hr
SCR	1.46	tons/hr
Wet FGD	144.8	tons/hr
CO_2 Capture	35.16	tons/hr
Total	1,800.	tons/hr

Turbine/Generator

Gross Power	630.5	MW
Aux Power (major):		
Base Plant	21.54	MW
SCR	2.94	MW
Wet FGD	14.60	MW
Cooling Tower	16.09	MW
CO_2 Capture		
Electricity	14.91	MW
Steam (equiv)	29.98	MW
Net Plant Efficiency	37.67	% (HHV)

Output

Net Power Out	550.0	MW
LCOE	74.20	$/MW-hr
LCOE Increase	16.0	%

Base Plant

Steam Cycle	Ultra Supercritical
Boiler	Wall-Fired
Firing System	LNB w/OFA
NO_x Controls	
Combustion	59% Removal
Hot-Side SCR	81% Removal
P-J Fabric Filter	99.6% Removal
Wet FGD (LSFO)	98% Removal
Cooling Tower	Wet
Waste Water	Chemical Treatment
Cost of Electricity	47.68 $/MW-hr

CO_2 Capture Plant

Process	Advanced PZ-Based
Capture Efficiency	90% (capture plant)
Flue Gas In	2,778 tons/hr
Bypass	1,539 tons/hr
DCC	SO_2 Polisher (10 ppm)
Absorber Trains	1
Compressor Trains	1
Regen. Pressure	50 psig
Regen. Energy	1,000 Btu/lb CO_2
Solvent Makeup	8.12 lb/hr

CO_2 Product

Flow	203.0	tons/hr
Pressure	2,000.	psia
Capture Cost	27.63	$/ton
Avoided Cost	29.20	$/ton

Fuel

Illinois #6 Bituminous Coal		
Input	213.4	tons/hr
	4,982.	MBtu/hr

Cooling Water

Steam Cycle	47,570.	tons/hr
CO_2 Capture		
DCC	283.4	tons/hr
Capture	16,510.	tons/hr
Compressor	2,097.	tons/hr
Total	66,460.	tons/hr

Emissions

CO_2 Removal	40.2	% (overall)
CO_2	1,100.	lbs/MW-hr
	302.6	tons/hr

Figure 2.10 Case PZ-NUC: Advanced PZ-Based Capture Plant (New USC, Compliant)

2.5 Conclusions – Task 6

A Preliminary Technical and Economic Feasibility Study was completed to further develop the proposed solvent concept and to establish a quantitative basis for subsequent process development and bench-scale testing. The study provides a quantitative measure of the potential performance improvements offered by the advanced process in terms of factors such as levelized cost of electricity (LCOE), cost of CO_2 capture, and parasitic power consumption.

The results of seven case studies using the IECM are summarized in Table 2.2. It can be seen that application of the advanced PZ-based process is projected to significantly reduce the cost and parasitic power impacts of CO_2 capture relative to application of the conventional amine process. Looking at just the "new" capture plant cases *relative to the performance of the Reference Plant*:

- The conventional amine process reduces net plant efficiency by 31% and increases the LCOE by 70%
- The advanced PZ-based process reduces net plant efficiency by 23% and increases the LCOE by 45%.
- The advanced PZ-based process used in conjunction with an ultra-supercritical base plant reduces net plant efficiency by only 4% and increases the LCOE by 36%.
- The advanced PZ-based process used in conjunction with an ultra-supercritical base plant and designed to meet a 1,100 lbs CO_2/MW-hr (net) emission rate actually *increases* net plant efficiency by 7% and increases the LCOE by only 16%.

Table 2.2 Capture Plant Case Studies

Performance Measures	Reference Plant	Conventional Amine Capture Plant		Advanced PZ-Based Captue Plant			
	Case-R Baseline	*Case AM-N New*	*Case AM-R Retrofit*	*Case PZ-N New*	*Case PZ-R Retrofit*	*Case PZ-NU New USC*	*Case PZ-NUC New USC Compliant*
Net Electrical Output, MW	550	550	379.2	550	425.4	550	550
CO_2 Capture Efficiency, %	-	90	90	90	90	90	40.2
Fuel Input (HHV), Mbtu/hr	5,339	7,743	5,339	6,902	5,339	5,535	4,982
Gross Electrical Output, MW	609.3	717.4	494.6	689.6	533.4	659.2	630.5
Net Plant Efficiency (HHV), %	35.15	24.24	24.24	27.19	27.19	33.91	37.67
CO_2 Emitted, lb/MW-hr	1,970	285.7	285.7	254.7	254.7	204.2	1,100
Cost of CO_2 Captured, $/ton	-	34.83	40.70	25.15	30.19	25.07	27.63
Cost of CO_2 Avoided, $/ton	-	59.78	69.58	39.46	46.85	31.08	29.20
LCOE, $/MW-hr	64.00	108.80	116.30	92.83	98.61	87.04	74.20
LCOE Increase, $/MW-hr	-	44.80	52.30	28.83	34.61	23.04	10.20
LCOE Increase, %	-	70	82	45	54	36	16

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