B&W PGG's RSAT<sup>™</sup> Process and Field Demonstration of the OptiCap<sup>™</sup> Solvent at the US-DOE's National Carbon Capture Center Final Report



# power generation group

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## **ABSTRACT / EXECUTIVE SUMMARY**

Babcock & Wilcox Power Generation Group, Inc. (B&W PGG) engineers successfully executed a three-month test campaign using the OptiCap<sup>TM</sup> solvent during the fall of 2011 at the National Carbon Capture Center (NCCC) Pilot Solvent Test Unit (PSTU) in Wilsonville, Alabama. The test campaign was designed to address four major goals: (1) gather data for process simulation model validation, (2) characterize effluent streams (including stack emissions as well as liquid and solid wastes), (3) gather data on solvent degradation and reclamation, and (4) perform corrosion studies in order to help determine appropriate materials of construction for a commercial plant. In addition, B&W PGG sought to verify the solubility limits of the OptiCap solvent.

During the NCCC campaign, one hundred fourteen (114) test conditions including replicates were run for model validation purposes. Using the collected data, the model has proven to have the capability to adequately predict column sizes, regeneration energy values, and many other performance indicators. Some minor adjustments are needed to better predict the absorber bulge maximum temperature, absorber sump temperature, and a few other parameters; however, the model appears to be adequate at predicting performance over the wide range of test conditions conducted at NCCC.

Actual measured regeneration energy values for the various test conditions ranged from 1,098 to 1,570 Btu/lb  $CO_2$ . By designing the cross heat exchanger specifically for the OptiCap solvent, B&W PGG process simulation models predict regeneration energy values below 1,050 Btu/lb  $CO_2$ .

In addition, a thorough corrosion program was employed at NCCC using a combination of stainless and carbon steel weight loss (WL) coupons and electrical resistance (ER) probes in order to measure the corrosivity of the OptiCap solvent. Also, solvent samples were extracted from the process on a weekly basis and later subjected to electrochemical testing at BWRC. Results gathered from the WL coupons gave an average corrosion rate between zero and seventeen mils per year (mpy). Electrochemical tests were conducted on the weekly samples and compared to a 30 wt% monoethanolamine (MEA) baseline.

Liquid samples were also extracted from the PSTU on a weekly basis in order to understand the solvent degradation rate and the change in chemical composition. Due to the complex chemistry, characterization of the chemical species and the overall degradation rate has been a difficult task to complete. Lab analysis indicates that the OptiCap solvent degradation rate at elevated pressures will be significantly less than for 30wt% MEA, which is operated at much lower regeneration pressures. However, an exact degradation comparison cannot be completed until the majority of the degradation species are identified.

In an effort to analyze the gaseous stream leaving the wash tower, a combination of techniques was employed. Continuous data measurements were collected for the some of the test cases using the existing Fourier transform infrared (FTIR) spectrometer; however, this equipment was not operational for entire test program. In addition, B&W PGG engineers worked with Southern Research Institute (SRI) to collect four, one-hour batch samples to further characterize the gas stream leaving the wash tower. Results from both techniques have indicated that the volatile amine emissions were higher than modeling and laboratory predictions. Statistical analysis suggests that increased emission levels may be due to aerosols, but this hypothesis must be further investigated to better understand the relationship between these parameters, as well as to confirm practical solutions. This is a phenomenon which has also been recently observed and documented at other test facilities using other solvents including MEA<sup>1</sup>.

Gas and liquid samples were also taken at the PSTU for nitrosamine analysis. In the four gas samples analyzed by SRI, nitrosamines were observed in only one sample, and the concentration was below 0.1 ppb. Liquid analysis showed the concentration of mononitroso-OptiCap (MNOC) was dependent upon the inlet  $NO_2$  concentration and was controlled by the regenerator sump temperature.

During operation at the NCCC, B&W PGG engineers experienced several planned and unplanned shutdowns of the PSTU as well as typical boiler load cycling. By using the emergency handling procedures developed by B&W PGG, no solvent solubility issues were experienced in the circulating system, This was believed to be a risk area prior to the testing, due to unique characteristics of the OptiCap solvent . An important result from the test campaign was that solubility is not a concern if the solvent is kept warm and circulating.

Further research is required to understand the correlation of amine volatility with the presence of aerosols, as well as to verify the degradation rate. However, many important properties including corrosivity, regeneration energy, and degradation rate are sufficiently more favorable than MEA, and solvent solubility is manageable given appropriate engineering design and risk procedures. Based on the NCCC results, the OptiCap solvent is a commercially viable solvent ready for large-scale, long-term demonstration.

## **1.0 INTRODUCTION**

The United States Department of Energy (DOE) together with Southern Company Services (SCS) constructed the National Carbon Capture Center (NCCC) in Wilsonville, Alabama. The NCCC is a carbon dioxide (CO<sub>2</sub>) post-combustion capture (PCC) test facility partially comprised of the Pilot Solvent Test Unit (PSTU), which contains typical equipment that may be required for post combustion  $CO_2$  capture processes. The equipment was sized for operation using 30% MEA while also having the flexibility to operate the unit with a variety of different solvents.

This facility provided Babcock and Wilcox Power Generation Group, Inc. (B&W PGG) the opportunity to further investigate its OptiCap solvent and aspects of the RSAT<sup>TM</sup> (Regenerable Solvent Absorption Technology) technology in commercially representative flue gas conditions while experiencing typical plant upsets and boiler load changes that are observed in today's power producing facilities, before the technology is deployed at a larger commercial demonstration scale. In addition, this opportunity provided the first time that the OptiCap solvent had been operated for an extended period of time on coal-fired flue gas.

B&W PGG completed a three-month test campaign using its proprietary OptiCap solvent at the PSTU from September 15, 2011 through December 7, 2011. The test run spanned approximately 2,000 hours. A thorough test plan developed through the aid of Six Sigma tools was successfully executed during this time frame. The test plan focused on validation of a B&W PGG simulation model, optimization of regeneration energy, solvent management, and corrosivity.

While the PSTU was not designed or optimized specifically for the OptiCap solvent (examples of which include three packed beds in the absorber and two packed beds in the regenerator, oversized valves designed for operation at low regenerator pressure and high liquid flow rates, and an undersized reflux pump), the unit did provide much useful performance data and operational experience for the continued development of the RSAT technology. The 3-month campaign duration did not allow for sufficient time to fully characterize a few key time-dependent parameters, such as solvent degradation, which must ideally be measured for an extended period of time on actual flue gas. Longer campaigns would better allow for process optimization and greater understanding of key variables which could significantly impact parameters such as solvent make-up rate, materials of construction, nitrosamine formation, and emissions, which will in turn significantly impact the levelized cost of electricity (LCOE) for all PCC technologies. Other improvements which could be made to the PSTU include automatic pre-scrubber control and increased flexibility in terms of solvent preparation equipment.

# 2.0 BACKGROUND

For more than 140 years, B&W PGG has been a leading provider of fossil-fired steam generating equipment for utility and industrial applications. Responding to coal-fired power plant air emissions regulations in the early 1970s, B&W PGG began designing and supplying air quality control systems (AQCS) for sulfur dioxide (SO<sub>2</sub>) and particulate control.

As clean air laws were amended to regulate additional pollutants, B&W PGG expanded its capabilities to include emissions control systems for nitrogen oxides ( $NO_x$ ), mercury, and other hazardous air pollutants. Recognizing the growing emphasis on reducing carbon dioxide ( $CO_2$ ) emissions from coal-fired boilers; B&W PGG began development of its oxy-combustion carbon capture technology in 2000.

In response to the requirements of existing utility power plants for partial  $CO_2$  capture capability, B&W PGG began development in 2005 of a post-combustion  $CO_2$  capture process. Since that time, B&W PGG's research and development efforts in PCC have led to the construction of a seven ton per day  $CO_2$  pilot plant (Figure 1).



Figure 1: B&W PGG's Post-Combustion Pilot Test Facility

Using a consistent and logical technology development roadmap will aid in accelerating the commercial deployment of PCC processes such as the RSAT system. B&W PGG's RSAT development process is shown in Figure 2, which has been conducted using a stage-gate approach. Solvent and process developments have been carried out in a deliberate step-by-step program to progress from discovery to commercial demonstration in the shortest reasonable time.

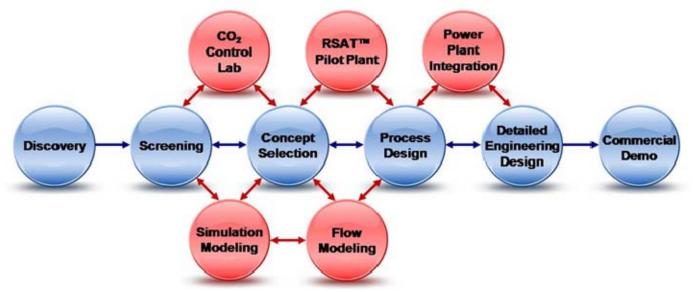


Figure 2: B&W PGG's RSAT Process Development Program

In 2005, B&W PGG began efforts to develop the RSAT process, and a team was assembled at Babcock & Wilcox' Research Center in Barberton, Ohio. The team initiated an in-depth technology review which included existing and developing solvent-based, PCC technologies, design methods, solvents, academic research, and other sources to establish a basis for development of the B&W PGG RSAT product. A dedicated  $CO_2$  control laboratory was built and outfitted with the latest equipment to screen candidate solvents and obtain physical and chemical data for the design of the RSAT system.

 $CO_2$  Control Laboratory. The CO<sub>2</sub> control laboratory is used to quickly assess potential solvents, which are evaluated with regard to their rate of absorption, capacity to hold CO<sub>2</sub>, ease of operation, and the energy required to regenerate the solvent. The lab contains two primary test facilities: a wetted-wall column for precise measurements of fundamental mass transfer and chemical kinetics data (Figure 3), and a fully integrated bench-scale RSAT simulator used to evaluate solvent and process design concepts (Figure 4). These laboratory-scale tools facilitate the characterization and selection of solvents and help to quickly and effectively evaluate process changes.

*Wetted-Wall Column.* The wetted-wall column (Figure 3) is a gas-liquid contactor in which  $CO_2$  absorption or desorption can be studied under precisely controlled conditions. Due to its simple geometry, the area of contact between the gas and liquid solvent is accurately known. The solvent flows upward through the tube in the center of the column, exits at the top, and flows over the outside surface of the tube in a thin film. The solvent is then contacted with a gas mixture containing  $CO_2$  which flows upward in the annular space around the tube.

Careful control of temperature, pressure, and gas and solvent concentrations produces high quality fundamental data on mass transfer, chemical reaction kinetics, and thermodynamic properties of the solvent. This

information is then used in computer simulation models to predict process performance in both the bench- and pilot-scale systems. These computer modeling tools have been utilized to size equipment and predict system performance and are continuously validated against actual data from lab, bench, and pilot-scale equipment.

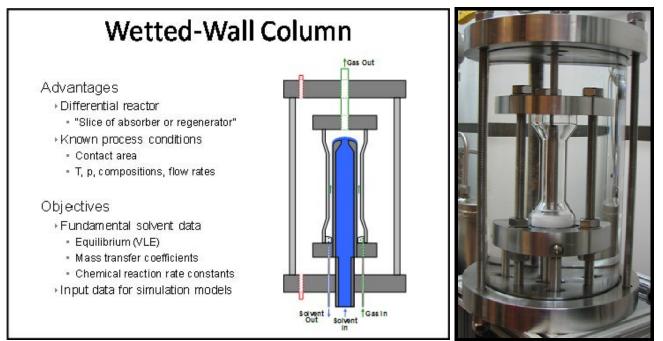


Figure 3: Wetted-Wall Column

**Bench-Scale RSAT Unit.** The bench-scale RSAT simulator (Figure 4) is a fully functional process test facility. The unit contains most of the equipment which would be included in a large-scale facility including the absorber column (left), the regenerator column (right), and the electrically heated reboiler (lower right). The bench-scale unit is designed to capture approximately one kilogram of  $CO_2$  per hour. The columns are of modular design and the process can be operated in a variety of modes which provide excellent flexibility for process analysis and development work. In addition, the unit provides an initial indication of the performance of a new solvent in an integrated system. This fully integrated bench-scale process also facilitates parametric studies of independent process variables and provides data for validating computer simulation models.



Figure 4: Bench-Scale RSAT Simulator

**RSAT Pilot Plant.** Following laboratory and bench-scale evaluations, the most promising solvents are tested at large scale in B&W PGG's RSAT pilot plant (Figure 5). Relative to the data provided by the CO<sub>2</sub> control lab, the RSAT pilot plant provides high quality, quantitative data which is representative of full-scale systems. Different process flow schemes which can affect CO<sub>2</sub> absorption rates and regeneration energy for a given solvent are tested and evaluated in the pilot unit with a focus on minimizing the overall energy consumption of the CO<sub>2</sub> capture process.

The RSAT pilot plant is installed in a building adjacent to B&W PGG's small boiler simulator (SBS). The SBS facility replicates a coal-fired power plant from fuel handling to the stack. The RSAT pilot plant can process approximately 3,100 lb of flue gas per hour and capture approximately 7 tons/day of  $CO_2$  (approximately 50% of the flue gas produced by the SBS). The pilot plant can also be operated in recirculation mode, wherein the captured  $CO_2$  is mixed with nitrogen and other gases to simulate actual flue gas from a coal-fired power plant before being recycled to the inlet of the absorber.



Figure 5: B&W PGG's RSAT Pilot Plant

Construction of the RSAT pilot plant began in June 2008. The plant installation was completed and commissioning of the facility began in January 2009. First operation on an amine solvent was achieved in June 2009. Baseline tests to characterize pilot plant performance were first run on a 30 wt% MEA solvent. Results of these tests serve as a basis for comparison to other solvents and were used to validate computer-based process simulation models. The most promising solvents identified in the laboratory by bench-scale testing and computer simulation modeling were then run through a series of test campaigns in the RSAT pilot plant.

### Solvent Selection

As a result of its extensive research test program, the BWRC team selected the most promising solvent candidate for more in-depth development and testing. The result is B&W PGG's OptiCap solvent, which has been tested extensively at lab and pilot scale.

Extensive lab and pilot testing of the OptiCap solvent at BWRC has shown favorable performance characteristics. Under similar test conditions, a lower reboiler heat duty was attained for the OptiCap solvent as compared to the 30 wt% MEA solvent. The minimum reboiler heat duty attained was comparable to the heat duty values claimed by other solvent and process providers of 1,200 - 1,275 BTU/lb CO<sub>2</sub>. Additional properties of the OptiCap solvent that were expected to provide additional savings in capital and operating costs have been verified in these campaigns and will be further quantified in future test campaigns.

The results described above are considered to be only an early indication of the potential of the OptiCap solvent. B&W PGG has simulated several process design cases which could further reduce the energy penalty of solvents by using heat integration with the power plant. Some of these design cases are specifically related to the unique properties of the OptiCap solvent – for example, the ability to regenerate at higher temperatures and pressures. Computer models have indicated that these process improvements are feasible, and projected energy requirements in the range of 1,000 to 1,100 Btu/lb  $CO_2$  are possible for the OptiCap solvent.

### **Solvent Benefits**

Below are some of the characteristics of the OptiCap solvent which were expected to be confirmed and further quantified as a result of testing at NCCC.

- **Resistance to Oxidative Degradation.** Most solvents degrade in the presence of high concentrations of oxygen, which can occur in coal combustion flue gas. Preliminary testing of the OptiCap solvent indicated a relatively high level of resistance to this phenomenon, which offers the potential for lower solvent make-up rates as well as lower solid waste generation rates.
- *Resistance to Thermal Degradation*. Testing thus far has shown the OptiCap solvent to be stable at operating temperatures up to 300°F. This attribute offers the potential for regeneration at higher operating temperatures and pressures, which could lead to significant CO<sub>2</sub> compression energy savings.
- *Ease of Reclaiming.* Results at BWRC indicated that thermal reclaiming is likely the primary technology for removing degradation species formed using the OptiCap solvent. Thermal reclaiming is a well-known technology which has been used successfully for decades for solvent regeneration.
- *Lower Volatility.* Compared to 30 wt% MEA, the OptiCap solvent showed decreased volatility. Lower volatility reduces solvent losses to the exhaust stack and decreases energy requirements for heat exchanger cooling in the solvent wash section of the absorber.
- Increased Mass Transfer Rate. The rate of absorption of CO<sub>2</sub> for the OptiCap solvent is approximately twice that of 30 wt% MEA. This kinetic advantage allows the absorber towers to be designed with less packing than towers designed for 30 wt% MEA. This characteristic offers capital cost savings with reduced absorber tower height, quantity of packing, structural steel, foundations, and installation cost. Also, reduced tower height results in auxiliary power consumption savings, due to decreased pressure drop through the absorber and decreased pump power required for solvent recirculation due to decreased head pressure. Approximately 75% of the electrical power required to operate the RSAT system is consumed by the fan or blower to move the flue gas through the flue gas cooler and absorber, so cost savings generated by decreased pressure drop through the absorber tower to move the flue gas through the substantial.
- *Increased CO<sub>2</sub> Carrying Capacity.* Because the OptiCap solvent can be loaded with approximately twice the amount of  $CO_2$  per unit of solvent, the solvent recirculation rate is decreased, saving not only the energy required to pump the solvent within the system, but also the energy required to heat and cool the solvent in the various process stages.

Testing under actual power plant flue gas conditions at NCCC was required in order to confirm the research performed in both the BWRC lab and pilot plant regarding the characteristics of the OptiCap solvent. In addition, phenomena such as solvent degradation, system corrosion, and waste stream formation must be studied across time periods which exceed the duration of most lab- or bench-scale test campaigns. Therefore, a three-month (~2,000 hour) test campaign was completed in the PSTU at NCCC during the Fall of 2011.

# **3.0 OBJECTIVES**

Along with confirming and quantifying the solvent benefits described above, the primary objectives of the test campaign were:

- Process Simulation Model Validation
- Effluent Streams Characterization
  - Stack Emissions
  - Liquid and Solid Waste Characteristics
- Solvent Degradation and Reclamation
  - Oxidative
  - Thermal
  - Acid Gas
- Corrosion Studies

To accomplish these objectives, as well as to provide a written guide to the operators and engineers of the PSTU, a comprehensive test plan was created which included (1) complete corrosion and solvent degradation programs, (2) checklists and procedures for solvent sampling and analysis as well as instrument calibration, (3) a test matrix of 58 different test conditions for purposes of gathering model validation data, and (4) important safety and handling information for the solvent.

Prior to the test campaign, B&W PGG personnel traveled to NCCC to meet with engineers and operators to discuss solvent handling and preparation – a process which ultimately led to modifications being made to the PSTU. Also, B&W PGG personnel witnessed and provided feedback on the MEA baseline tests. B&W PGG provided installation supervision and operator training for the corrosion probes and coupons, participated in HAZOP planning and equipment commissioning.

Prior to testing, B&W PGG performed a detailed evaluation of the technical risks involved with testing the OptiCap solvent in a coal-fired utility power plant. Operating scenarios of interest from this analysis included:

- Extended Planned Shutdown
- Introduction of Contaminants
- Low Flue Gas Temperature
- Piping Leaks and Other Equipment Failures
- Emergency Evacuation
  - Anhydrous Ammonia Alarm
  - Inclement Weather
- Black Plant
- Unplanned Shutdown

The list of corrective actions generated from the risk analysis included several different categories of actions, including more detailed investigation of certain solvent properties, additional operating procedures, and potential equipment modifications. In addition, B&W PGG and NCCC personnel began discussions regarding potential equipment modifications to the PSTU to address items arising from the risk assessment as well as items which were requested in order to increase the amount and / or quality of data which could be obtained from the pilot test campaign.

After a series of discussions, B&W PGG and NCCC personnel agreed upon a final list of modifications which would be made to the PSTU in preparation for testing the OptiCap solvent. These modifications, which will henceforth be referred to as "MOC" (management of change) modifications are summarized in Section 7.2.

# 4.0 COAL

During the OptiCap solvent test campaign, Gaston Unit #5 burned a mixture of eastern bituminous coals. Therefore, the chemical composition of the fuel slightly changed throughout each day, and thus the chemical composition of the flue gas changed accordingly.

# 5.0 **PSTU**

The NCCC is a post combustion capture facility that extracts a 3 megawatt (MW) slipstream of flue gas from Gaston Unit 5. The facility (referred to as PC4) is comprised of a 0.5 MW test unit (PSTU), a future 1 MW slipstream unit (PSTU 2), and four small bench scale bays. Refer to Figure 6 for further details.

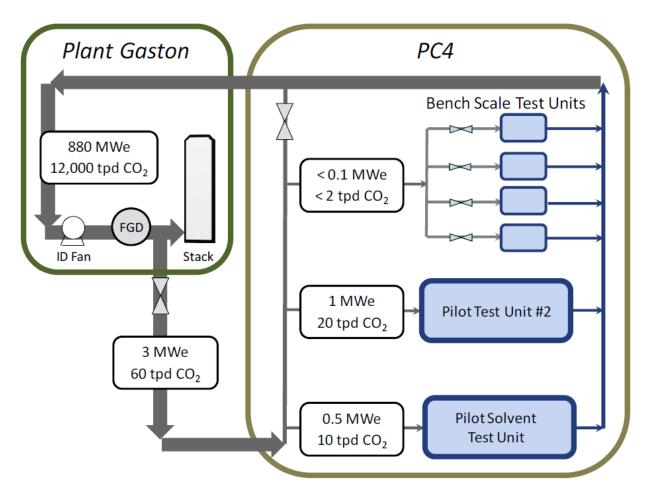


Figure 6: PC4 Layout

Construction of the facility was finalized in March 2011.

As shown in Figures 7, 8, and 9, the PSTU (section of PC4) is comprised of a sodium pre-scrubber (C101), direct contact cooler / condenser (C301), absorber tower (C401), cross heat exchanger (E404), flash tank (C501), regenerator (S601), reboiler (E602), reclaimer (E603), intercooler heat exchanger (E402), lean trim heat exchanger (E405), rich filtration (F401), lean filtration (F405), activated carbon and filtration (F402 - F404), lean storage tank (TK401), extra solvent storage (TK402, TK403), and a wash tower (C501). The column height and diameter details are listed in Table 1.

Column	Height	Outer Diameter	
	m (ft)	cm (in)	
Pre-Scrubber	14 (46)	76 (30)	
Cooler/Condenser/DCC	9.1 (30)	61 (24)	
Absorber	32.9 (108)	66 (26)	
Washing Tower	9.1 (30)	61 (24)	
Regenerator	23 (75)	61 (24)	

## Table 1: PSTU Column Sizes

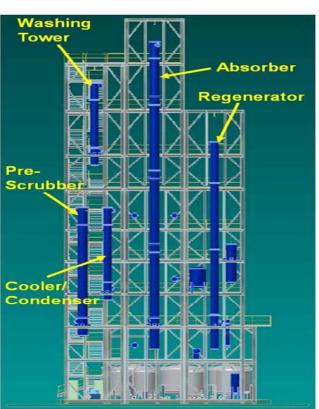


Figure 7: PSTU Representation

The pre-scrubber utilizes a caustic solution to reduce the concentration of  $SO_2$  in the inlet flue gas to <1 ppm. B&W PGG decided not to vary the outlet concentration of  $SO_2$  because it was previously known that all  $SO_2$  would react with the amine to form heat stable salts.

C301 is used to reduce the temperature in the flue gas and help control the water balance (further details are provided in Section 8). The outlet gas temperature was varied during the test campaign.

The absorber tower was significantly taller than what was required for the OptiCap solvent. The tower was designed to achieve 90% CO<sub>2</sub> removal for 30wt% MEA. Therefore, the tower had three (3) twenty-foot tall beds of Mellapak 252Y, 316L stainless steel structured packing. B&W PGG used only the bottom two beds during the OptiCap solvent test campaign. The injection locations for the intercooler sections were fixed and could not be optimized. Only the bottom intercooler was operated during the B&W PGG test.

The regenerator tower was significantly taller than what was required for the OptiCap solvent. The tower was designed to achieve 90%  $CO_2$  removal for 30wt% MEA. Therefore, the tower had two (2) twenty-foot tall beds of Mellapak 252Y, 316L stainless steel structured packing. Both beds were used, since this was the only available operating configuration. The regenerator was designed to operate up to 200 psig.

The wash tower had 10 feet of structured packing to help increase the contact area of the inlet gas and water. This was used to help control the water balance and to decrease solvent losses from the system.

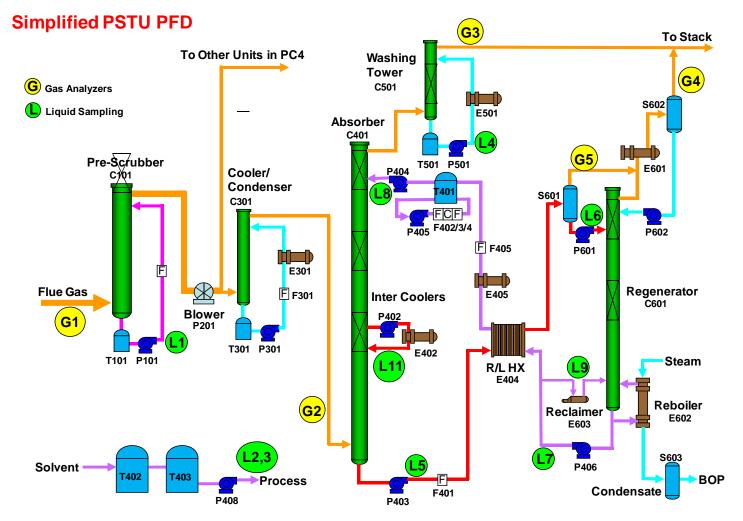
The heat exchangers used in the process were of shell and tube design, except the cross heat exchanger, which was of plate and frame design. Some design limitations were experienced during operation which did not allow further optimization. For example, the cross heat exchanger (E404) was not capable of achieving optimal approach temperature in many cases because it was not specifically designed for the OptiCap solvent. Similarly, the lean trim heat exchanger (E405) was not capable of cooling the solvent to optimal conditions.

The lean and rich filters were full flow, five micron cartridge filters. The purpose of the filters was to remove suspended solids in the circulating solution, which could increase solvent degradation rates.



Figure 8: PSTU Structure

## 5.1 PSTU PROCESS FLOW DIAGRAM (PFD)



**Figure 9: PSTU Process Flow Diagram** 

# 5.2 NCCC CHEMISTRY LAB EQUIPMENT

Processes such as the RSAT process are chemistry-based by nature, and research projects require specific knowledge of the inlet and outlet gas composition as well as a characterization of the liquid solvent. In order to operate this type of process in an ever-changing research environment, a dedicated "field" lab is required. The PC4 had two dedicated chemists and most of the necessary equipment to run a successful test campaign. The following analytical equipment was available:

Gas Sample ID	Location	Gases Measured	Device	
		SO2	Rosemount Xstream Enhance	
G1	PSTU Inlet	CO2	Rosemount Xstream Enhanced	
61		02	Fuji Electric ZFK (zirconia)	
		H2O	MAC125	
		SO2	Rosemount Xstream Enhanced	
G2	Absorber Inlet	CO2	Rosemount Xstream Enhanced	
62		02	Fuji Electric ZFK (zirconia)	
		H2O	MAC125	
		CO2, NO, NO2,		
	Wash Tower Outlet	H2O, O2,	Cormot ETIP System	
G3		Formaldehyde,	Gasmet FTIR System	
65		MEA, OptiCap, NH3		
		CO2	Rosemount Xstream Enhanced	
		02	Fuji Electric ZFK (zirconia)	
G4	Flash Tank Outlet	H2O	MAC125	
G5	Regenerator Knock Out Drum Outlet	H2O	MAC125	

## Table 2: Gas Analysis Equipment

## **Table 3: Liquid Analysis Equipment**

Liquid Sample ID	Location	<b>Component Measured</b>	Device
L5	Rich Stream	Amine Concentration	Metrohm 904 System, Applkon ADI2040 (online)
LJ	(Absorber Outlet)	CO2 Loading	Metrohm 904 System, Applkon ADI2040 (online)
L6	Rich Stream	Amine Concentration	Metrohm 904 System, Applkon ADI2040 (online)
LO	(Flash Outlet)	CO2 Loading	Metrohm 904 System, Applkon ADI2040 (online)
L7	Lean Stream	Amine Concentration	Metrohm 904 System, Applkon ADI2040 (online)
L7	(TK401 Outlet)	CO2 Loading	Metrohm 904 System, Applkon ADI2040 (online)
L11	11 Bottom Intercooler	Amine Concentration	Metrohm 904 System, Applkon ADI2040 (online)
	bottom intercooler	CO2 Loading	Metrohm 904 System, Applkon ADI2040 (online)

## 6.0 SOLVENT HANDLING AND PREPARATION

The OptiCap solvent for this test campaign was prepared at Babcock & Wilcox' Research Center (BWRC) in Barberton, Ohio. When the solvent arrived at NCCC via tanker truck, the solvent was already at the desired bulk concentration and a stable  $CO_2$  loading for ambient conditions. The solvent was stored in the spare solvent storage tanks with nitrogen blanketing until the beginning of the test campaign. Samples were taken during storage in accordance with the protocol provided by B&W PGG to periodically verify the  $CO_2$  loading and solvent concentration. No composition changes or solidification were experienced.

When the PSTU was started up for the OptiCap solvent campaign, the solvent was first transferred from the balance of plant (BOP) and spare storage tanks to the lean storage tank (TK401) in the PSTU. The recirculation loop around TK401 was activated to ensure thorough mixing and decrease the possibility of stratification. At the same time, the heat tracing was activated to emergency shutdown levels. This temperature was maintained for the length of an entire solvent inventory cycle before (1) intercooling started, (2) flue gas was introduced, or (3) steam was introduced into the reboiler for regeneration.

# 7.0 SOLUBILITY DISCUSSION

In addition to its many projected benefits, a differentiating property of the OptiCap solvent as compared to many other conventional amines being considered for post combustion  $CO_2$  scrubbing applications, is that precipitation of solids may potentially occur under some scenarios. This property of the solvent has been found to be dependent on both the temperature and  $CO_2$  loading of the solution (Figure 10).

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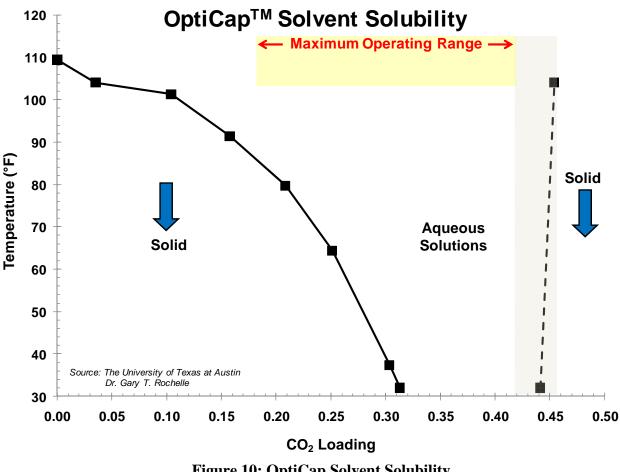


Figure 10: OptiCap Solvent Solubility

The overall subject of solvent solubility can be classified into two subcategories: lean precipitation (LP) and rich precipitation (RP) events. During normal operation, LP could occur in areas of the process where lower (leaner) concentrations of CO<sub>2</sub> exist, such as in the piping from the regenerator liquid outlet to the absorber inlet. RP may occur in areas of the process where the solvent is laden with CO<sub>2</sub>, such as piping and equipment between the absorber outlet and regenerator inlet.

LP is generally controllable and predictable during normal operation. The lean loading is primarily a function of a combination of (1)  $CO_2$  removal efficiency, (2) liquid to gas flow ratio in the absorber (L/G), and (3) inlet concentration of CO<sub>2</sub> in the flue gas. As CO<sub>2</sub> removal efficiency increases, L/G decreases, or as the inlet gas concentration of CO<sub>2</sub> decreases, the lean loading will decrease. Therefore, using a combination of these variables, the engineer can predict the temperature where LP may begin to occur. Since the operator has direct control of the inlet gas temperature, steam flow rate, lean temperature and intercooler temperature, a significant amount of flexibility and control exists during normal operation.

Above a specific temperature, no LP is expected to form regardless of the  $CO_2$  loading. This means that the lean loading can theoretically decrease to zero with minimal risk, provided that the stored solvent is maintained at or above the specified temperature. However, at times it may be desirable to operate parts of the process below this temperature; therefore, a thorough understanding of the relationship between  $CO_2$  loading and temperature is essential to smooth operation with the OptiCap solvent.

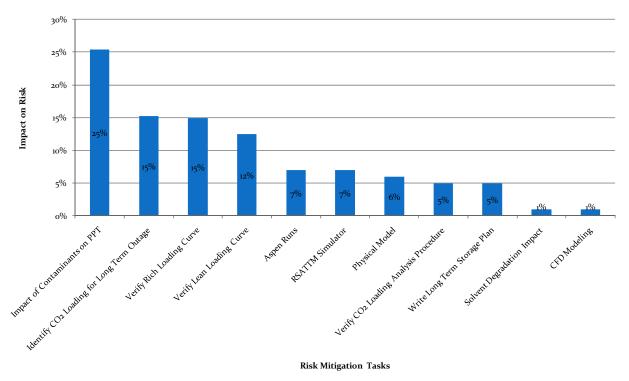
# 7.1 RISK ANALYSIS

Although laboratory and simulation model predictions have indicated that, during normal plant operation, the test conditions from the original test matrix did not require the OptiCap solvent to operate in a  $CO_2$  loading range where it would be expected to precipitate, the PSTU is connected to a utility power plant, and upsets do occur. During upset conditions, both temperatures and  $CO_2$  loadings can become compromised. Therefore, B&W PGG performed a detailed evaluation of the technical risks involved with testing the OptiCap solvent in a coal-fired utility power plant.

Risk scenarios were identified that had the potential for resulting in a precipitation event at the NCCC. These scenarios are as follows:

- Extended Planned Shutdown
- Contaminants
- Low Flue Gas Temperature
- Piping Leaks and Other Equipment Failures
- Emergency Evacuation
  - o Anhydrous Ammonia Alarm
  - o Inclement Weather
- Black Plant
- Unplanned Shutdown

A list of mitigation strategies was created to reduce risk to acceptable levels. The list included areas for further solubility testing, additional operating procedures and potential equipment modifications. Each risk mitigation strategy was quantitatively evaluated using a composite score based on probability and impact to determine a forced ranking of the various strategies being considered. The result of this evaluation is shown in Figure 11.



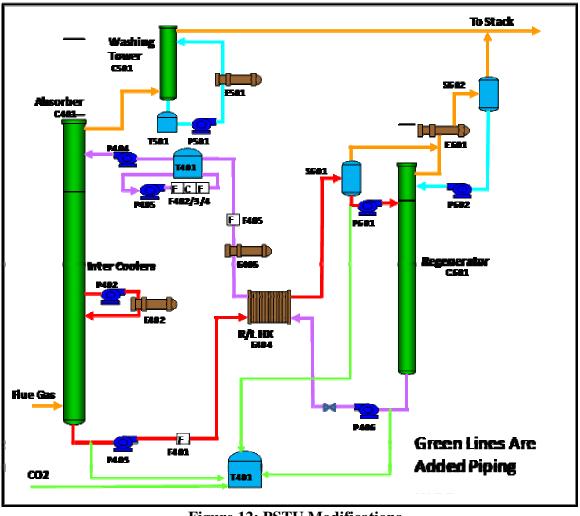
**Figure 11: Risk Mitigation Strategies** 

Based on the results shown in Figure 11, it was determined that the risk mitigation strategies which would most effectively lower the solvent precipitation risk were to (1) better understand the impact of contaminants on precipitation, (2) identify the  $CO_2$  loading where the solvent should be stored during long term outages, (3) verify the rich loading curve, and (4) verify the lean loading curve. In addition to these objectives, B&W PGG evaluated the PSTU to determine if equipment modifications should be made to further decrease risk.

## 7.2 PSTU EQUIPMENT MODIFICATIONS

One of the highest-ranking scenarios in the risk assessment was a black plant condition. Although the probability of a black plant scenario was very low, the magnitude of the potential impact could be significant. During a black plant scenario, steam, flue gas, and compressed air are all unavailable. Based on the original PSTU design, a scenario such as this would leave the OptiCap solvent distributed throughout the entire process (vessels and piping). If precipitation were to occur due to cooling, the entire process could require cleaning. The existing process did not include a means to address this situation. B&W PGG recommended adding piping with manual drain valves to the piping upstream of the pumps following the absorber, regenerator, and flash tank sumps to the top of TK401 (refer to Figure 12). This would allow for the sumps of these vessels to drain to a single location via gravity, as the vessel sumps were elevated and TK401 was located at grade.

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**Figure 12: PSTU Modifications** 

The piping which was actually installed is shown in Figures 13 and 14. The header which collects the streams from the various vessel sumps is shown in Figure 13 was installed at grade. The header terminates at TK401, and enters into the bottom of the tank as shown in Figure 14. While this configuration does allow the absorber, regenerator, and flash tank sumps to drain to TK401, the installed piping itself will not gravity drain since it is located below the liquid level in the tank.



Figure 13: Vessel Drain Header at Grade



Figure 14: Vessel Drain Header Outlet Connection to TK401

Experience from the BWRC OptiCap solvent test campaign and laboratory work at BWRC indicated that any precipitate that formed could be dissolved by adding heat. This led to the B&W PGG recommendation to add a portable hot water heater (Figure 15) and water nozzle connections at each pump. This allowed for the injection of hot water directly to any area where precipitation may occur.



**Figure 15: Portable Hot Water Heater** 

The only piping in the PSTU which could not be drained via the recommendations shown in Figure 12 was the piping directly surrounding the cross heat exchanger (CHX). B&W PGG requested that drains be added to the CHX for emergency situations. These drains are shown in Figure 16.



**Figure 16: Cross Heat Exchanger Drains** 

Along with controlling temperature, another mechanism which is available to prevent precipitation is to control the  $CO_2$  loading of the solvent. If the bulk  $CO_2$  loading is on the lean side – which was always the case in the PSTU because the bulk of the solvent inventory is stored in TK401, which is located in the lean stream – then  $CO_2$  can be injected into the solvent to increase the bulk solvent loading. To allow injection of additional  $CO_2$  if required, B&W PGG recommended installing a temporary  $CO_2$  dewar and injection nozzle system (refer to Figure 17), with an induction nozzle to promote mixing.



Figure 17: CO<sub>2</sub> Injection Nozzle on TK401

In addition to the above items, B&W PGG also requested that some instrumentation and nozzles be added to the system, in order to facilitate gathering of information and data. For example, local gauges for temperature indication were added to the cooling water outlets of several heat exchangers. Also, nozzles were added to several vessels for installation of ER probes and weight loss WL coupons so that corrosion information could be gathered throughout the campaign (Figure 18).



Figure 18: Electrical Resistance Probe (Top) and Retractable Coupon Holder (Bottom)

## 7.3 RISK MITIGATION

A set of operational guidelines including stepwise instructions was generated by B&W PGG and provided to the PSTU operators to address any upset which could occur (refer to Section 7.1). Depending on the risk scenario (black plant, loss of flue gas, boiler outage, etc), an appropriate series of steps was recommended. Implementation of these protocols worked well during the test campaign, as no solvent precipitation events were encountered in the circulating system despite experiencing many of the associated risk scenarios. Some changes were made to these guidelines after the test campaign to reflect knowledge gained at NCCC.

An important finding from the B&W PGG test campaign was that the solvent will stay in liquid form as long as it is kept warm. This campaign showed that the risk of operating with the OptiCap solvent is manageable as long as heat is available. Heat tracing proved to be a valuable tool, but was not as effective as flowing steam to the reboiler. Also, the solvent seems to precipitate much more slowly on the rich side, as rich samples were refrigerated throughout the campaign (some for several weeks), with no observed precipitation.

## 8.0 WATER BALANCE

Because the RSAT process is cyclical, solvent inventory and water management are important operating parameters. Solvent inventory is managed by limiting solvent volatility and degradation (which is discussed further in Section 14). However, water balance it is primarily a function of solvent selection as well as the selection of various process parameters.

Water balance is controlled by process management through balancing the water entering the absorber via the flue gas with the water leaving the wash tower to the stack, via the regenerator condenser knock-out drum, and

via the regenerator reflux purge stream. All of these streams are saturated, so the water balance is proportional to the temperature leaving each vessel. If the temperatures leaving each of these vessels are balanced, the water mass balance will most likely balance. However, due to the combination of the purge stream leaving the reflux loop and water entrainment, some small adjustments are often required.

Water management is an important concept for two reasons. The first reason is that, if the process is condensing water, the overall system will begin to accumulate water, causing the solvent to dilute. From a positive perspective, this will expand the solvent solubility window which will slightly lower the lean loading where precipitation could occur. The viscosity will decrease slightly, equating to an increased heat transfer coefficient across the CHX. However, if the liquid flow rate is not correspondingly increased, there will be less available solvent to react with the  $CO_2$ , which may decrease the  $CO_2$  removal efficiency at low L/G flow ratios. In order to achieve 90% removal, the reboiler will be required to over-strip the solvent, thus decreasing the lean loading, which may increase the solubility risk. In addition, since water has a higher heat capacity than the OptiCap solvent, more steam will be required to the reboiler to overcome the sensible heat requirements.

The second reason that water balance is important is that, if the process is not condensing a sufficient amount of water, the water will vent from the overall system, causing the solvent to concentrate. This is a more significant issue than diluting the solvent, as the solubility window tends to narrow more significantly on the rich side. In addition, the solvent viscosity increases, which equates to a decreased heat transfer coefficient across the CHX.

Both instances of over- and under-concentrating the solvent were experienced at NCCC. Both were addressed without experiencing precipitation issues in the circulating solution by maintaining process temperatures and making the appropriate process adjustments to remedy the water balance issue.

Water balance control was more challenging in the PSTU than would be the case for a typical operating plant. B&W PGG's objectives required changing test conditions on at least a daily basis, which also changed both the degree of and location where water was condensing in the process. Some reasons that water balance issues were experienced include: (1) the original PSTU control scheme included instructions for closing the water balance differently, (2) the regenerator reflux pump was undersized for high pressure operation, (3) high liquid flow rates, and primarily, (4) operator inexperience.

The original design of the PSTU control scheme (which was written by NCCC) required balancing the water around the entire PSTU including the pre-scrubber (C101) and direct contact cooler (C301). This meant that water leaving the wash tower and knockout drum had to be approximately 130°F. Water condensed in C301 was fed to the wash tower storage tank (TK501), and then into the lean solvent storage tank (TK401).

The design control scheme was such that, when the level in TK401 fell below the low level set point, the valve in the piping connecting TK501 to TK401 would open, filling TK401 to the high level set point. In addition, when the level in TK501 fell below its low level set point, the valve in the piping connecting TK301 (direct contact cooler circulating tank) to TK501 would open and fill TK501 to its high level set point. The water balance on the regenerator side of the process was controlled in a similar fashion. When the level in S602 (regenerator knock-out drum) reached its high level set point, the reflux pump would start and pump water into the regenerator as reflux in a batch mode. This control scheme was not in accordance with B&W PGG's recommendations regarding adjustment of the system water balance.

B&W PGG's recommendations required balancing the water from the absorber inlet (C401) to the outlets of the wash tower (C501) and regenerator knock out drum (S602). B&W PGG does not recommend that C301 should be included in the water balance for a PCC system such as the PSTU, as there will be calcium and sodium

carryover from the WFGD and pre-scrubber. These chemical species would be contaminants for any PCC solvent. Both species will react with  $CO_2$  and possibly precipitate in piping or other areas of the process. The water contained in TK301 should instead be combined with the WFGD make-up water to reduce water make-up requirements in the WFGD system.

By not including C101 and C301 in the control scheme, the overall PSTU water balance control is simplified. Since the PSTU was not originally designed in this manner, some changes were made to the control scheme which took some time to fully implement. To control the water balance, the level in TK401 was allowed to float within a 1% range. If the level reached the low set point, the valve in the piping connecting TK501 to TK401 would automatically open and increase the level by 1% to the high set point. The level in TK501 was maintained by adjusting the outlet temperature of the wash tower. Due to the significant variation in test conditions B&W PGG was running, the outlet temperature leaving the wash tower was always kept slightly lower than required to build up water inventory in TK501 for cases where water balance might be challenging.

Due to operator inexperience with the revised water balance control scheme, there was some difficulty in operating test cases with high liquid to gas flow ratios (L/G). High L/G cases pushed the temperature bulge to the bottom of the absorber, meaning that the outlet gas temperature from the absorber was lower than the inlet gas temperature. This resulted in a dilution effect. To correct this issue, the flue gas temperature leaving C301 must be simultaneously decreased. However, this requirement was not always identified quickly enough, and solvent dilution sometimes occurred. In a commercial plant, operating conditions will be verified during the commissioning process, and gas temperatures will be specified appropriately to control the water balance.

High regenerator operating pressure cases were also challenging due to PSTU equipment limitations. The reflux pump was undersized for high pressure operation and was not able to overcome the backpressure from the regenerator. Therefore, water would accumulate in S602 and consequently concentrate the solvent. Since this was a large tank and the auto titrator only took a sample every thirty minutes, this condition was often not noticed quickly. To resolve this issue, the wash tower outlet exit temperature set point was decreased and the inlet flue gas temperature increased, or if excess water had accumulated in TK501, it was allowed to flow into TK401 to offset the water difference.

Neither of these challenges would be expected to be problematic in a PCC process specifically designed for the OptiCap solvent, since the process equipment would be adequately sized for the appropriate process conditions.

## 9.0 PARAMETRIC TEST MATRIX

Using Design for Six Sigma tools, B&W PGG engineers assembled a test matrix to analyze the impact of various key operating parameters on system performance,  $CO_2$  removal, and regeneration energy. The primary objective of the initial test matrix was to gather a wide range of data over possible operating regions to verify the predictions of the B&W PGG simulation model.

The independent test parameters which were varied during the test campaign were:

- L/G
  - o Liquid Flow Rate (L)
  - o Gas Flow Rate (G)
- Regenerator Pressure and Temperature
- Wash Section Outlet Temperature
- Lean Amine Inlet Temperature to Absorber
- Flue Gas Inlet Temperature to the Absorber
- Use of the Intercooler between 1<sup>st</sup> and 2<sup>nd</sup> Packed Beds
- Intercooler Liquid Outlet Temperature
- CO<sub>2</sub> Removal
- Reflux Location

All test campaigns varied the steam flow to the reboiler to achieve a desired  $CO_2$  removal efficiency. In most cases, the targeted removal efficiency was ninety percent (90%) removal of  $CO_2$  which was calculated using the following two equations.

#### Equation 1: CO<sub>2</sub> Removal (Volume Basis)

% CO2 removal = 100 \* 
$$(1 - \frac{A^{out} * (1 - \frac{A^{ln}}{100})}{A^{ln} * (1 - \frac{A^{out}}{100})})$$

Where:

 $A^{out}$ : outlet CO<sub>2</sub> volume percentage as measured by the gas analyzer  $A^{In}$ : inlet CO<sub>2</sub> volume percentage as measured by the gas analyzer

#### Equation 2: CO<sub>2</sub> Removal (Mass Basis)

% CO2 Removal = 
$$(1 - \frac{A^{out}}{A^{in}}) * 100$$

Where:

 $A^{out}$ : pounds per hour of  $CO_2$  leaving the wash tower  $A^{In}$ : pounds per hour of  $CO_2$  entering the absorber

Note that twelve (12) replicate test conditions were included in the original test matrix. These were included to help identify any variables which could impact the performance of the system over time, and they were useful in comparing the first completed test to the last. These runs provided important insight into the performance/life of the solvent.

The order in which the various tests IDs were completed was changed during the test campaign. At approximately four weeks into the campaign, various plant upsets caused the test program to become more than a week behind schedule. Therefore, in an effort to achieve all of the goals of the test program, multiple test conditions were completed on the same day and the order of tests was adjusted to minimize transition time for

the PSTU equipment. It was discovered during this time that L/G and regenerator pressure changes took much longer to achieve steady state conditions, and thus these transitions were minimized as much as possible.

## **10.0 OPERATIONAL VARIANCES**

Since the PSTU was operated on actual coal flue gas generated by a utility power plant, maintaining some of the original operational variances listed in Table 4 proved to be challenging.

## **Table 4: Operational Variances**

Parameter	Variation	Target		
Flue Gas Flow to Absorber	± 100	-	lb/hr	(± 50 if possible)
Flue Gas Temperature to Absorber	± 2°F	-	°F	
Inlet SO2 to Absorber		1	ppm	
Lean Solvent Flow to Absorber	± 200	-	lb/hr	
Lean Solvent Temperature to Absorber	± 2°F	-	°F	
Regenerator Pressure	± 0.5	-	psig	
Intercooler Outlet Temperature to Absorber	± 2°F	-	°F	
OptiCap Solvent Concentration	± 1 wt%	40	wt%	
CO₂ Removal	± 1%	90	%	

Due to current economic conditions, low natural gas prices, and a power demand schedule where energy conservation is critical, wind turbine power must be utilized whenever available, and so many large power generation stations which were once base loaded units have started to cycle frequently. Even though the design flue gas rate to the PSTU can always be supplied despite load cycling, Figure 19 shows that this also changes the mass flow rate of  $CO_2$  to the absorber in the inlet flue gas. In addition, boiler load cycling changes the  $CO_2$  rich loading equilibrium due to a decrease in the driving force for  $CO_2$  absorption, and this requires a corresponding adjustment in steam flow. When this situation is combined with the need to maintain steady state for three to four hours plus the time for the total solvent inventory to cycle through the PSTU (1 to 2.5 hours, depending on liquid flow rate), it can be extremely challenging to achieve the targeted variances. Therefore, the decision was made on a few test conditions to run at a slightly increased variance in solvent concentration or  $CO_2$  removal, and to adjust the data for the simulation models accordingly.

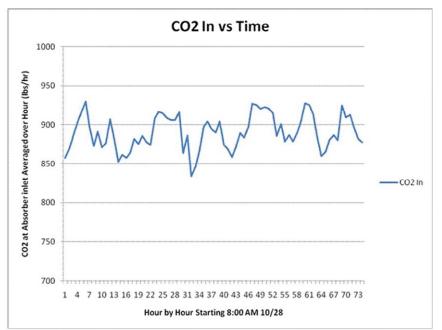


Figure 19: Example of Change in CO<sub>2</sub> Inlet Gas Flow over Three Days

## **11.0 REGENERATION ENERGY**

When comparing advanced solvents for post combustion carbon capture, one of the primary metrics by which solvents are frequently compared is regeneration energy. Although not the only important measurement, regeneration energy is one of the most significant drivers in terms of parasitic power requirements. Lower regeneration energy directly equates to a lower required steam flow to regenerate the captured  $CO_2$ , which must be extracted from the boiler turbine or generated separately.

A short test campaign was completed in order to optimize the regeneration energy for the OptiCap solvent in the PSTU. It is important to note that several factors limited the ability to obtain a true optimal value, including:

- An oversized back pressure valve (PI20231)
- Shell and tube design for most heat exchangers
- Absorber level control fluctuations at low solvent recirculation rates

The back pressure valve was oversized because it was designed to operate in conjunction with a 10°F CHX approach for 30wt% MEA. At these conditions, a design back pressure of 100 psig is sufficient to suppress vaporization because the reboiler for a MEA process operates at  $<250^{\circ}$ F. This is the maximum operating temperature, because higher temperatures quickly increase the thermal degradation rate and the operating expense of a MEA capture facility. At these low temperatures, the hot lean stream enters the CHX between 235°F and 250°F. If the CHX is able to achieve a 10°F approach, the outlet rich stream will be 230°F to 240°F. At these temperatures, a backpressure between 50 and 100 psig is sufficient to suppress vaporization. Therefore, when PI20231 was designed, the maximum backpressure to which the valve would control was 125 psig. When operating at 125 psig, the valve was less than 10% open and small changes in valve position caused the absorber sump level to oscillate, which made it difficult to maintain a steady rich flow.

Many advanced solvent developers are investigating increased regenerator pressure in order to lower LCOE as compared to a typical MEA process. To operate safely and economically at higher pressures, the solvent must

be thermally stable at increased temperatures. Thermal stability is an advantage of the OptiCap solvent which B&W PGG sought to validate at NCCC. However, when regenerator temperature is increased, this also increases the inlet lean temperature to the CHX. When the inlet lean temperature is increased, the hot rich outlet stream temperature must increase accordingly to achieve the same approach temperature. However, when the temperature is increased, this also increases the required backpressure to suppress vaporization. This valve therefore limited the maximum regenerator pressure which could be achieved with the OptiCap solvent.

## **11.1 REGENERATION ENERGY RESULTS**

Although an optimization study was completed for the OptiCap solvent at NCCC, minimum regeneration energy values could not be achieved for reasons as described in Section 11.0. However, despite these limitations, the solvent was still able to achieve regeneration energy values as low as 1,098 Btu/lb  $CO_2$ , which is one of several factors that made the OptiCap solvent test campaign very successful.

B&W PGG was present at NCCC during the 30wt% MEA commissioning test of the PSTU. This test was beneficial in helping B&W PGG to understand some of the limitations of the PSTU equipment. In addition, NCCC personnel shared the performance data from the test with B&W PGG. Table 5 shows a comparison of the regeneration energy values gathered from B&W PGG's OptiCap solvent test, the 30wt% MEA commissioning test, and the 40wt% MEA test at the PSTU. It is important to note that NCCC operated the MEA tests differently from the B&W test. For example, the MEA tests did not target 90% CO<sub>2</sub> removal. Test conditions and steam flows were set, allowing the process to stabilize at the resultant removal efficiency without adjustment. The process was then allowed to run overnight. No process adjustments were made for changes in load or to maintain CO<sub>2</sub> removal. This made it more difficult to directly compare the test results.

Solvent	$\Delta H_{Regen}$	CO <sub>2</sub> Removal
30% MEA	1507 Btu/lb CO <sub>2</sub>	86%
40% MEA	1245 Btu/lb CO <sub>2</sub>	82%
OptiCap	1098 Btu/lb CO <sub>2</sub>	90%

Table 5: PSTU Regeneration Energy Comparison

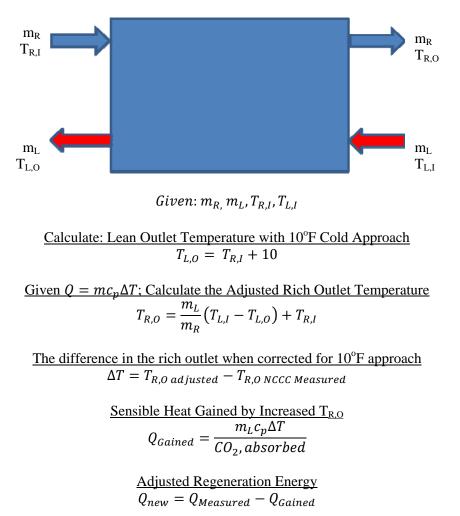
Table 5 shows that the lowest MEA regeneration energy  $(1,245 \text{ Btu/lb } \text{CO}_2)$  case occurred while running 40wt% MEA, as expected. However, this case was run at CO<sub>2</sub> removal efficiency less than 90%. Based on data gathered at the PSTU for the OptiCap solvent, it was observed that regeneration energy values are lower at reduced removal efficiencies. B&W PGG predicts that this particular test case would result in a measured regeneration energy value of approximately 1,300 Btu/lb CO<sub>2</sub> at 90% removal. The lowest OptiCap solvent regeneration energy measured was 1,098 Btu/lb CO<sub>2</sub>, which was achieved at 90% CO<sub>2</sub> removal.

# **11.2 CORRECTED REGENERATION ENERGY RESULTS**

The measured regeneration energy values at NCCC were not fully optimized for the OptiCap solvent, as described in Section 11.0. The CHX was not able to achieve the designed approach temperatures during OptiCap solvent operation since the PSTU was not designed specifically for the OptiCap solvent (primarily in terms of solvent viscosity).

As part of a separate effort prior to testing at NCCC, B&W PGG had invested significant resources into design of a PCC reference plant. Working with vendors to design the necessary equipment for the RSAT process was a significant part of this effort. During this process and subsequent conversations, B&W PGG learned that the CHX for an OptiCap solvent test can safely be designed to achieve the same CHX approach temperatures as for MEA. In light of this, B&W adjusted the measured regeneration energy values to meet this requirement.

The measured regeneration energy values were adjusted to meet the 10°F approach temperature as follows:



#### **Equation 3: Adjusted Regeneration Energy Calculations**

Using this calculation method, several cases with regeneration energy values below 1,050 Btu/lb CO<sub>2</sub> would have been measured at NCCC had the CHX been designed specifically for the OptiCap solvent.

### **12.0 MANUAL SAMPLING**

Since the objectives of the OptiCap solvent test at NCCC included understanding solvent degradation and corrosivity, frequent withdrawal of manual liquid samples from the PSTU was a significant portion of the test

plan. The liquid sampling plan required extraction of 40mL, 60mL, and 1000mL samples at least weekly throughout the test campaign.

The liquid samples were drawn from a sample line inside the chemical laboratory. The manual sampling system was designed to extract liquid samples from most of the pumps in the process (refer to Figure 9). The green circles labeled L1, L2, etc. were the locations where manual samples could be extracted. When the solvent sampling valve was opened, the solvent would flow through a cooler ( $80^{\circ}$ F) to limit CO<sub>2</sub> vaporization, and then through a series of plastic tubing and into a sink. The solvent would be allowed to drain into the sink for five minutes before a liquid sample was collected into a glass vial, capped and labeled.

At least once per day, 40mL samples were taken in clear vials from four different locations (L5, L6, L7, and L8) in the process. The original intent of these vials was to provide a daily check of the auto titrator. After the samples were taken, the on-site chemist would run a manual titration in the laboratory for both  $CO_2$  and solvent concentration. These values would then be checked against the automatic titrator readings from the same time period. Shortly after starting the test campaign, it was determined that there were issues with the automatic titrator readings at L6 (regenerator inlet) and L7 (regenerator outlet). These were the two highest temperature locations in the process and air bubbles were frequently present in these sample lines. Due to these issues, the auto titrator was not used to analyze these two locations. Instead, the lab was used for these measurements.

Once per week (except during the thermal reclaimer run), 60mL samples were taken in amber vials from both the rich (L5) and lean (L7) sampling locations in the process. Amber vials were used for storing these liquid samples because one of the primary chemical species of interest in the liquid analysis was mononitroso-OptiCap (MNOC), which is known to decompose when exposed to certain UV wavelengths. After these samples were taken, the samples were refrigerated to reduce the risk of any continuing reactions which might form additional or different degradation species or decay the MNOC. After completion of the test campaign, these sample vials were shipped for solvent degradation characterization including nitrosamines. Metals analysis using inductively coupled plasma optical emission spectroscopy (ICP-OES) was also part of this analysis.

Also, once per week at the same time as the 60mL samples were withdrawn, one or more 1000mL sample(s) were taken in clear bottles from location L5 using the same method as above. The samples were then stored in the refrigerator to inhibit further reactions in the liquid phase. These samples were shipped to BWRC in two shipments (one in the middle and one at the completion of the test campaign), due to lack of refrigeration space. These samples were taken for two purposes. The first was to determine the change in corrosivity of the solvent over time via electrochemical testing. The second set of 1000mL samples was taken periodically during the test to characterize how the vapor-liquid equilibrium (VLE) of the solvent was changing over time.

The thermal reclaimer was one of the unit operations that was expected to have the greatest impact on the composition of the circulating solution. The thermal reclaimer process raises the temperature of a slipstream in an attempt to boil the volatile compounds and achieve a concentrated heel of heat stable salts. Then, a small amount of NaOH is added to break the heat stable bonds and recover the base OptiCap solvent molecule. This technique, in conjunction with the use of elevated temperatures to concentrate the heel, can alter the thermal degradation rate of the slipstream. Based on this, 60mL liquid samples of the rich and lean streams were extracted on a daily basis during the week of thermal reclaimer operation. Also, samples were taken of the concentrated heel in between test condition changes. All samples were submitted for analysis.

## **13.0 CORROSION PROGRAM**

Prior to the NCCC test campaign, the corrosivity the OptiCap solvent was a subject on which only a limited amount of (mostly laboratory scale) data existed. Published industry reports indicated that a process such as the RSAT process may require a design using either stainless steel throughout the entire process or the use of corrosion inhibitors. Designing the entire process using stainless steel 316L (note that 304L is not an option due to  $CO_2$  pitting) requires a significantly higher initial capital investment and slightly higher LCOE than construction using carbon steel. Using corrosion inhibitors would decrease the initial capital expense, but their use would likely increase operating costs as well as possibly increasing both solvent degradation rates and surface tension (which can lead to foaming). Also, many inhibitors can be removed by thermal reclamation.

Preliminary bench scale electrochemical tests completed at BWRC as part of the NCCC preparation activities predicted that the corrosivity of the OptiCap solvent was expected to be less than 30wt% MEA, but this data was not sufficient to definitively specify the materials of construction. In order to better understand OptiCap solvent corrosivity and how this parameter would change over time with an increase in degradation species, the following corrosion program was implemented at NCCC.

The team decided to implement a corrosion program which used a combination of both ER probes and corrosion WL coupons. The initial plan was to extract both the WL coupons and ER probes from the process on a weekly basis to visually inspect the elements for  $CO_2$  pitting, surface color change, evidence of an oxide layer, material loss, and other signs of corrosion in order to document how these changed over time. However, when the PSTU was started up, some of the probes were observed to be leaking. To address the leaks, all of the threaded connections were welded. However, due to some issues which occurred during the welding process, some of the elements could not be removed for inspection until the completion of the test campaign. Despite this minor issue, sufficient data was collected to determine an overall corrosion rate for the OptiCap solvent during the NCCC campaign. Pictures of the ER probes and WL coupons are shown in Figures 20 and 21.



Figure 20: Typical ER Probe

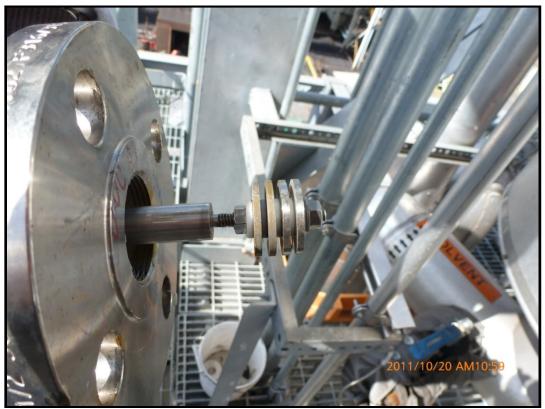


Figure 21: Typical Weight Loss Coupon Assembly

ER probes measure the electrical resistance of the probe element, which changes over time and can be utilized to calculate the corrosion rate. The probes were expected to provide the advantage of providing an instantaneous corrosion measurement that could be documented in the control room and compared for each test condition. However, due to the lower than expected OptiCap solvent corrosion rate, the ER probe response time was not sufficiently long during a three-month test campaign to observe significant differences in corrosion rates using the ER probe technique.

B&W PGG installed WL coupons at twelve locations in the PSTU, while ER probes were installed at seven locations in an effort to characterize the different corrosion mechanisms in different areas of the process. Refer to Figure 23 for detailed location information. At each location where a weight loss coupon holder (Figure 21 and 22) was installed, two carbon steel 1018 (coupons 1 and 2) and two stainless steel 316L (coupons 3 and 4) coupons were utilized. At each location where an ER probe was mounted, only one probe material was selected. Location ER6 included a SS316L probe, and all other locations utilized CS1018 probes.

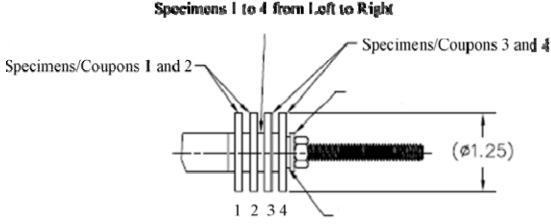


Figure 22: WL Coupon Arrangement

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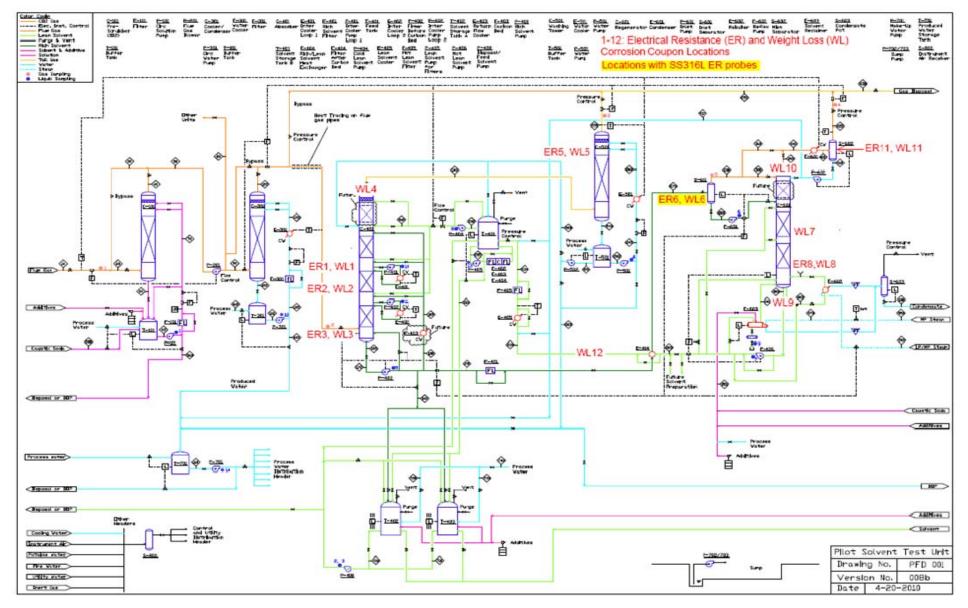


Figure 23: Corrosion Probe / Coupon Locations

# **13.1 CORROSION EQUIPMENT and TECHNIQUES**

### Weight Loss

Weight loss coupons were selected for use in the NCCC corrosion program for the following reasons:

- WL coupons are simple to use and do not require sophisticated instrumentation to obtain results.
- A direct measurement is obtained with no theoretical assumptions or approximations.
- WL coupons are applicable to all environments and provide information on all forms of corrosion.
- Corrosion measurements using WL coupons are reliable as they are purely a metal loss measurement.

WL corrosion measurements are commonly used as calibration standards for other means of corrosion monitoring, such as electrical resistance. In cases where slow response and averaged data are acceptable, WL monitoring is the preferred technique.

In the NCCC study, WL collected data is presented as the most reliable measurement. Both electrical resistance measurements and electrochemical testing of OptiCap solvent samples were analyzed considering limitations associated with each technique.

### ER Probes

ER probes provided the advantage of measuring an online metal loss which could be converted to a corrosion rate. This provided the ability to measure a relative corrosion rate for each process condition.

### Laboratory Electrochemical Testing

The advantage of using the electrochemical technique is the ability to determine an instantaneous corrosion rate, since the corrosion process is accelerated by the application of electricity. Thus different environments and a multitude of test conditions can be quickly studied and understood. Specifically, the technique known as Linear Polarization Resistance (LPR) provided corrosion rates for each OptiCap solvent sample extracted from the PSTU on a weekly basis. This analysis allowed an evaluation of how the solution corrosivity changed over the course of the test campaign, and thus provided information on the impact of solvent degradation products.

# **13.2 NCCC INSPECTION / ANALYSIS / RESULTS**

WL corrosion coupons (CS1010 and SS316L) were installed at twelve different locations in the PSTU in order to evaluate the corrosion behavior of two potential materials of construction, and were subjected to typical OptiCap solvent test conditions. Figure 24 shows a photo of one of the installed locations.

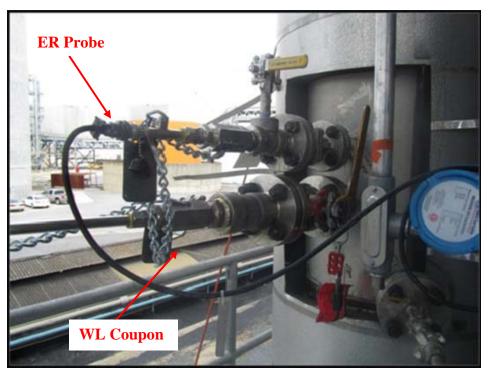


Figure 24: Typical ER Probe (Top) and WL Coupon (Bottom) Installation

Weight loss analysis is the simplest and most well-established method of estimating corrosion losses. A specimen/coupon of the metal or alloy under consideration with finite surface area is initially weighed and introduced into the process. After the coupon is exposed to the process for a reasonable time interval (minimum of 30 days), the specimen is chemically cleaned of all corrosion products and re-weighed. The weight loss is then converted to a corrosion rate (CR) or metal loss (ML), as indicated by Equations 4 or 5 below:

#### **Equation 4: Corrosion Rate Calculation for WL**

$$CR = \frac{WL \times K}{\rho \times A \times t}$$

#### **Equation 5: WL Calculation**

$$WL = (W_1 - W_2)_{Coupon_{Exposed}} - (W_1 - W_2)_{Control Coupon_{Cleaned}}$$

Where:

- CR: Corrosion Rate (mils per year, mpy)
- WL: Weight loss (g)
- K: Conversion factor
- $\rho$ : Alloy density (g/cm<sup>3</sup>)
- A: Exposed area  $(cm^2)$
- t: Exposure time to the process (hr)

Throughout the OptiCap solvent test program, the ER probes were extracted from the process on a weekly basis. In addition, a few of the corrosion coupons were periodically removed for inspection of the change in appearance over time. Figure 25 below illustrates in sequential order the appearance of coupons at location WL3 when extracted for inspection. This figure shows the corrosion of the WL coupon on 9/16/11 after exposure to water for one week and air for another week. In addition, it can be seen that the CS1010 appearance did not dramatically change over the reported period after exposure to water and air.

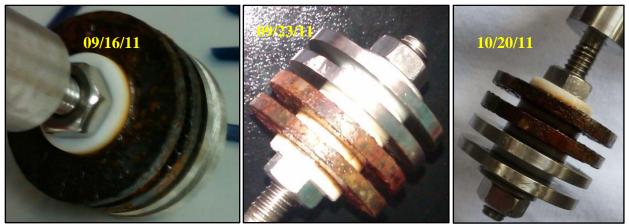


Figure 25: WL3 Visual Inspection Changed Over NCCC Test

In general, all carbon steel coupons exhibited rust with colors varying from orange to brown, red, grey, and black. The morphology of the oxide layer of these coupons varied. Most of the rust formed on the coupon surfaces was homogeneous except the oxide layer of WL5 at the wash tower.

Based on the reported CR values, there was 96% reproducibility in the corrosion program. One coupon was considered an outlier (CS-7.2) and one coupon was considered not reproducible (SS-9.2) based on the non-replication of results with their respective adjacent specimens.

The highest carbon steel corrosion rate of seventeen mils per year was observed in the regenerator tower, as expected. Outside of the regenerator, the measured carbon steel corrosion rates were less than 10 mpy. However, some instances of mild  $CO_2$  pitting were observed.

After a detailed analysis of the WL stainless steel coupons, results indicated that CRs ranged from 0 to 5 mpy. The highest corrosion rates were observed in the bottom of the regenerator where the highest process temperatures existed.

In summary, CS coupons exhibited a greater CR than SS coupons. Both materials exhibited excellent to good corrosion across all tested plant locations. However, some areas of the plant may still require stainless construction due to the observation of mild  $CO_2$  pitting. This subject must be evaluated further during a longer test campaign with more optimal test conditions.

### ER Probes

ER probe analyses, despite providing a continuous metal loss measurement during the test program, did not show significant changes in CR over the full length of the test program. An absolute determination of CR was not possible from the given results. It is believed that, due to the lower than expected OptiCap solvent corrosion rate, the response time was not sufficiently long during a three-month test campaign to observe significant differences in corrosion rates using the ER probe technique.

## **13.3 ELECTROCHEMICAL TESTING**

Electrochemical corrosion testing was performed on OptiCap solvent samples extracted from the PSTU to explore the corrosive behavior of the OptiCap solvent under different process conditions, to facilitate future material selection. Variables studied included: process temperatures (similar to regenerator and absorber conditions), fresh OptiCap solvent solutions (after preparation) as well as degraded solutions (subjected to both rich and lean CO<sub>2</sub> loading conditions), and dissolved metals concentration.

Analyses consisted of electrochemical corrosion screening tests using carbon steel, C1010, in order to evaluate the possibility of utilizing this material in areas of the PCC plant. In addition, evaluating OptiCap solvent solutions at different time intervals provided an understanding of how degradation and dissolved metal concentrations impacted the corrosivity of the material. The analyses conducted included Open Circuit Potential, Potentiostatic Scans, and Linear Polarization Resistance (LPR). The LPR technique provided corrosion rates allowing the evaluation of different process environments, which were characterized by OptiCap solvent samples taken over time intervals of approximately one week, to be compared amongst one another.

To calculate corrosion rates from polarization resistance data, a series of calculations is conducted according to ASTM Standard Designation G102, Standard Practice for Calculation of Corrosion Rates and Related Information from Electrochemical Measurements. The common unit of corrosion rate measurement is mils per year.

The primary objective of this study was the evaluation of carbon steel corrosivity in the presence of OptiCap solvent solutions under different degradation stages which will occur in  $CO_2$  scrubbing systems. The corrosion study was fundamentally based on electrochemical techniques which in essence are the study of chemical reactions when electrical energy is either present or not in the environment where the reactions are occurring.

The electrochemical corrosion study focused on collecting reliable data under conditions which were as representative of the RSAT process as possible. This was achieved by (1) conducting corrosion tests at critical temperatures typically represented by the regeneration process (one test was conducted at absorption temperature); (2) using characteristic  $CO_2$  loadings for the OptiCap solvent samples which were taken during the NCCC test program (primarily rich samples); (3) creating maximum possible  $CO_2$  loadings for each of the OptiCap solvent solutions which were prepared in the laboratory as fresh solutions; and (4) using constant simulated flue gas conditions.

The corrosion study included sixteen different OptiCap solvent samples which were drawn from the bulk solvent inventory during the NCCC test program. Test conditions included (1) samples with increasing levels of degradation concentration since they were extracted from the PSTU over time; (2) continuous injection of

simulated flue gas; (3) carbon steel; and (4) rich and lean  $CO_2$  loadings. Figure 26 shows these results in order to study the primary differences between the evaluated parameters as well as to establish trends and effects.

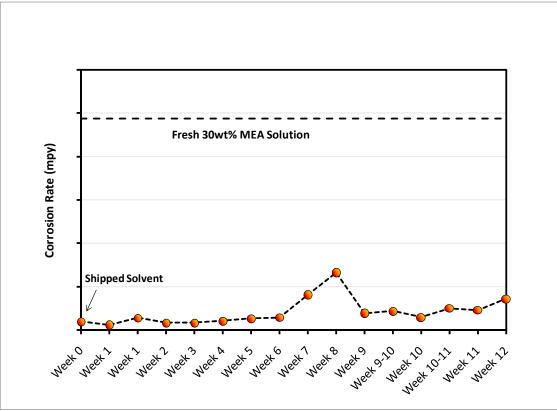


Figure 26: NCCC Sample Corrosion Rates for CS1010 Using LPR

Figure 26 shows that the CR of CS1010 did not significantly change as a function of time, with the exception of weeks 7 and 8, when a process change which was made which was expected to increase the CR. Overall, there was no significant difference between the baseline (shipped) sample (which was not exposed to the process) and subsequent degraded samples extracted over the 12 weeks of the OptiCap solvent test program at NCCC.

Overall, the degraded and non-degraded OptiCap solvent solutions provided more corrosion resistance to carbon steel than 30wt% MEA which resulted in at least five times more corrosion using the same test method and materials.

A second analytical method, ICP-OES (discussed in Section 14.1), was used to determine the dissolved metal concentration as a function of time. The identified metals from the ICP-OES were characteristic of corroded stainless steel (Fe, Cr, and Ni), as expected since the PSTU was constructed from stainless steel throughout. Figure 27 shows a comparison of the ICP-OES and electrochemical results. The y-axis is represented as the change in the dissolved metal concentrations with respect to their immediate value in order to correlate the true change for each data point. The same trends are observed in the increase in electrochemical corrosion rate versus the change in dissolved metals concentration.

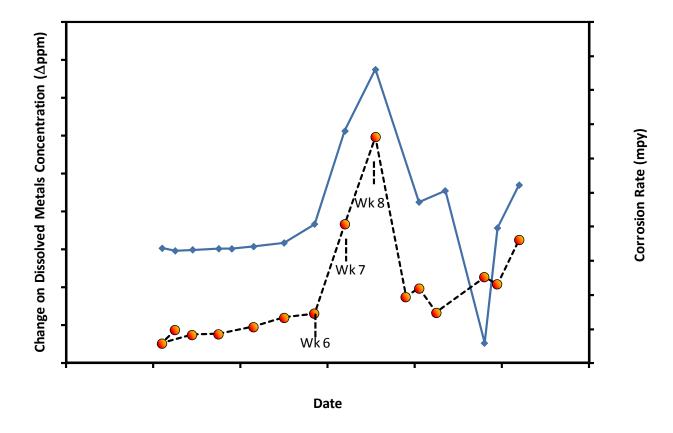


Figure 27: Comparison of Electrochemical Corrosion and ICP-OES Results

### **14.0 SOLVENT DEGRADATION PROGRAM**

The degradation of the OptiCap solvent had been studied in a laboratory setting, and the solvent showed enhanced resistance to both thermal and oxidative degradation as compared to MEA. However, the NCCC test campaign provided the first opportunity to characterize the performance of the OptiCap solvent on coal-fired flue gas, as well as to understand how the chemical composition of the liquid changed throughout the test.

One of the primary objectives of the B&W PGG test program was to understand how the solvent changed over time, as well as the associated impact on performance. To accomplish this goal, liquid samples were taken on a weekly basis as well as before and after test conditions which may have a significant impact on the bulk chemical composition. The samples were refrigerated in an effort to minimize any continued chemical reactions until the samples were analyzed.

Analytical Method	Typical Molecules Quantified
Anion IC	Carboxylate Ions (Formate,
	Acetate, Oxalate)
Cation IC	Amines (OptiCap, MEA, Ammonia)
	Amides (N-Formyl OC)
HPLC	Nitrosamines (MNOC)
IC-MS	All
ICP-OES	Heavy Metals
LC-MS	All

### Table 6: Analytical Chemistry Descriptions

Several analytical procedures were used in an effort to better classify the chemical make-up of the solvent over time due to various degradation pathways. OptiCap solvent degradation can occur via three different known mechanisms: (1) oxidative, (2) thermal, or (3) introduction of contaminants such as acid gases.

Oxidative degradation is the process of oxygen from the inlet flue gas reacting with the amine molecule to create products such as formates, acetates, amides, etc. This process has generally been expected to occur primarily in the absorber. However, recent experiments by Fred Closmann of the University of Texas at Austin (UT) have shown that, if dissolved or entrained oxygen is allowed to flow with the solvent to the cross heat exchanger, the combination of elevated temperatures and oxygen will significantly accelerate degradation. Therefore, the affinity of the OptiCap solvent to react with  $CO_2$  as opposed to  $O_2$  – and thus, its resistance to oxidative degradation – was a significant driver for B&W PGG to investigate the OptiCap solvent at NCCC.

Thermal degradation occurs when the solvent is exposed to elevated temperatures, creating an environment where the kinetics are favorable for the OptiCap solvent molecule to undergo additional types of reactions. In advanced systems, thermal degradation will occur in the regenerator, reboiler, rich piping from CHX to regenerator, or the lean piping from the regenerator to the CHX. Therefore, thermal degradation is a key variable which will differentiate advanced solvents because solvents with a higher resistance to thermal degradation will have the capability to be regenerated at higher temperatures and thus higher pressures. This helps to lower the LCOE of a PCC process by decreasing the  $CO_2$  compression work.

The last degradation mechanism occurs through the presence of dissolved metals from corrosion or impurities which enter the system through the inlet flue gas. The only species created via this mechanism which was evaluated at the PSTU was nitrosamines, which are discussed in Section 16.

# **14.1 DEGRADATION RESULTS**

One of the primary goals of the OptiCap solvent test campaign at NCCC was to validate the laboratory findings showing low degradation rates for the OptiCap solvent. Liquid OptiCap solvent samples were taken from the process on a weekly basis as described in Section 12. Rich solvent samples from the first seven weeks of testing and the baseline solvent are shown in Figure 28.



**Figure 28: Solvent Color Change** 

As shown in Figure 28, the color of the solvent changed throughout the test campaign which can be a sign of solvent degradation. The primary color change occurred during the first seven weeks after which the solvent maintained a dark brown/black color. The compositions of all of these samples were analyzed using multiple analytical techniques.

### High- Performance Liquid Chromatography (HPLC)

Results from the HPLC are indicated in Figure 29. The graph shows overlapped spectra of some of the liquid samples taken during the course of the campaign from September  $15^{\text{th}}$  to December  $7^{\text{th}}$ .

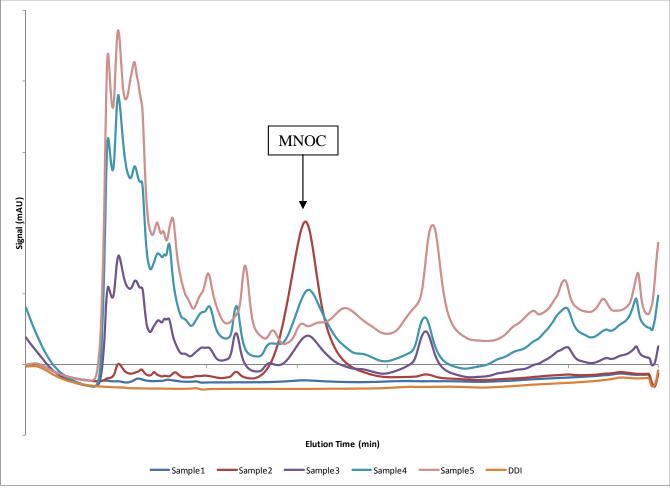


Figure 29: HPLC Results

The concentrations of most of the degradation species observed in Figure 29 are shown to increase over time, with the exception of one peak. This peak was identified as mononitroso-OptiCap (MNOC). A detailed discussion of the formation and thermal decay of this species is provided in Section 16.1.

The concentration of degradation species in Figure 29 are shown to remain low for the first month of the test program, indicating a gradual increase in degradation species over time. As time increases, the number and concentration of species increases, as predicted.

At the time of writing, none of the peaks besides the MNOC peak have been identified. Therefore, a definitive statement on degradation concentrations and rates cannot be made at this time. Further work is being completed in an effort to identify the other compounds present in the liquid solution.

### Anion IC

A second analytical technique used to analyze the NCCC liquid samples was anion IC. Figure 30 shows how the liquid composition of anions changed over the course of the test campaign. The graph shows overlapped spectra of some of the liquid samples taken during the course of the campaign from September 15<sup>th</sup> to December 7<sup>th</sup>.

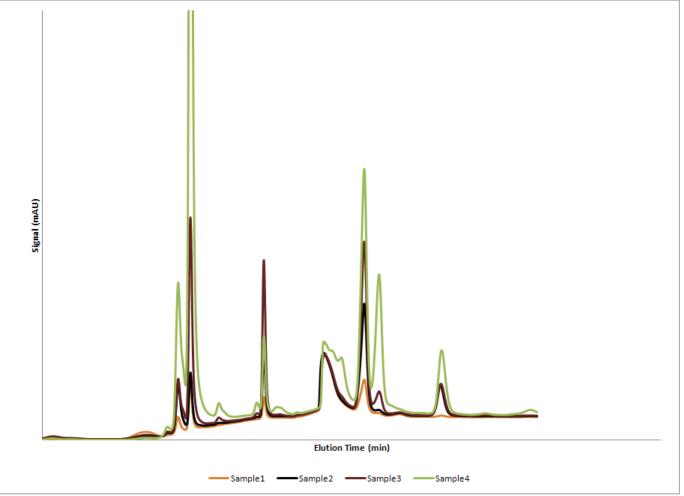
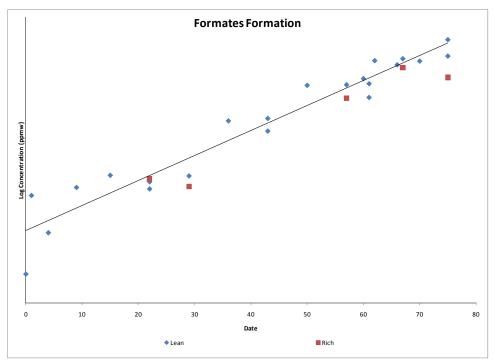


Figure 30: Anion IC Results

Two of the identified degradation peaks from the Anion IC spectra are formate and acetate. Lab studies have indicated that formate is one of the primary degradation products for the OptiCap solvent. Figures 31 and 32 indicate that the formation of both of these species can be predicted. Both graphs show the data represented on a log-linear plot.



**Figure 31: Formate Formation** 

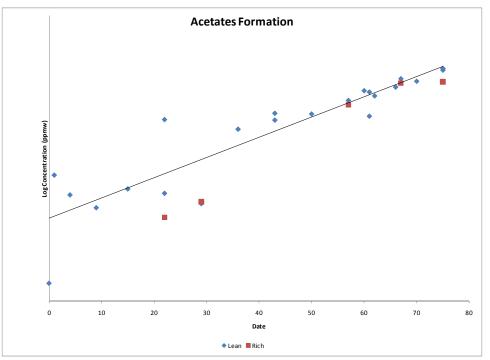


Figure 32: Acetate Formation

All anion species identified on the anion IC to date have previously been observed in laboratory studies including sulfate, glycolate, nitrate, and oxalate. Additional work is being performed to identify other anions observed on the anion IC.

### Cation IC

Another analytical technique used to analyze the liquid samples from NCCC was cation IC. The highest peak observed on the cation IC was the OptiCap solvent. The second highest identified peak is n-formyl OptiCap. Results for the change in n-formyl OptiCap concentration throughout the test period can be found in Figure 33.

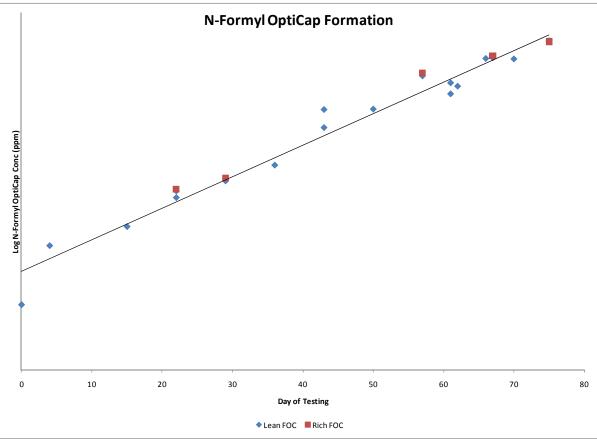


Figure 33: N-Formyl OptiCap Formation

The formation of n-formyl OptiCap is represented on a log-linear plot. The change in n-formyl OptiCap concentration was found to follow a linear trend.

Two other cation degradation components observed during the NCCC data analysis were aminoethyl-OptiCap (AEOC) and hydroxyethyl-OptiCap (HEOC). Both species were observed to achieve apparent equilibrium during the testing, indicating that they are intermediate species.

As expected, the OptiCap solvent did experience low levels of degradation during the NCCC test campaign. Despite solvent degradation, solvent performance was observed to actually improve over the course of the test campaign. This was evident when evaluating the replicate test conditions, which were run in order to understand how the presence of solvent degradation products impacted the solvent performance over time. One explanation for the improvement in performance is that the identified degradation products to date still have the capability to absorb CO<sub>2</sub>, which is another benefit of the OptiCap solvent.

## **15.0 GAS ANALYSIS PROGRAM**

A RSAT process is used to capture  $CO_2$  in the flue gas which would typically be vented to the atmosphere. During the process of capturing the  $CO_2$ , it is important that additional contaminants are not released to the environment in place of  $CO_2$ . Therefore in order to characterize the chemical composition of the gas stream exiting the RSAT process, it is important to have a reliable gas analysis program.

The existing PSTU facility was equipped with a Fourier transform infrared (FTIR) spectrometer and separate, backup  $CO_2$  and  $O_2$  analyzers. The FTIR was installed to characterize the gas stream for ammonia, formaldehyde, OptiCap solvent, water, MEA, nitrogen oxide (NO), and nitrogen dioxide (NO<sub>2</sub>). The levels of NO and NO<sub>2</sub> were expected to be below detectable limits, but the FTIR was expected to be able to characterize the concentration of the other species well. However, the FTIR was unreliable throughout the entire test campaign and was therefore operated for only a portion of the test program. Thus, B&W PGG was not able to adequately characterize the gas stream leaving the wash tower.

### **15.1 FTIR ANALYSIS**

During the B&W PGG test, condensate was repeatedly observed in the gas sample line to the FTIR. Because of this issue, coupled with insufficient experience using FTIR to analyze flue gas from a post combustion capture process, B&W PGG engineers were not always able to gather continuous, online analysis data for the flue gas leaving the wash tower. However, the FTIR unit was still gathering and storing data (spectra files) daily, unless it was being serviced or offline. SCS supplied this data to B&W PGG at the completion of the test campaign.

Several days of FTIR data were analyzed to determine the optimal range of wavelengths at which to gather concentration data for the various species of interest. The primary objective was to find wavelength ranges where major components such as water and  $CO_2$  did not overlap the species of interest (refer to Table 7). The wavelength ranges selected for data analysis for all samples are indicated in Table 7.

	Range 1 Range 2				Denge 2	
	Ran	ge I	Ran	ge z	Range 3	
Water	3157	3477				
CO2	910	1129				
N2O	2123	2224	2505	2628		
NO	1875	2150	2503	2593		
Other Amine	2500	2893				
NH3	3144	3405	915	988	2423	2560
OptiCap	XX	XX	XX	XX		

 Table 7: FTIR Measurement Ranges

Minitab<sup>®</sup> statistical analysis software was used in an effort to predict the OptiCap solvent FTIR emissions created during the NCCC test program. One of the variables which was found to be statistically significant in terms of impacting OptiCap solvent emissions was Gaston Unit 5 boiler load.

The conclusions from the regression were:

- The total measured OptiCap solvent emissions were higher than predicted by modeling and laboratory work. Aerosols are hypothesized to be a contributing factor to this increase.
- The factor which most significantly increased OptiCap solvent emissions was Gaston Unit 5 operating load. At lower boiler loads, the OptiCap solvent emissions decreased. Based on B&W PGG experience, as boiler load decreases, aerosol concentration in the flue gas decreases. Since the flue gas slipstream total mass flow rate entering the PSTU was constant during the NCCC testing, fewer aerosols would have entered the absorber at lower boiler loads, equating to lower OptiCap solvent emissions.
  - Gaston Unit 5 has a hot-side ESP and uses an additive to decrease  $SO_3$  emissions. On a new plant, B&W PGG would install hydrated lime injection and a fabric filter (without ESP) to further reduce  $SO_3$  aerosols.
  - Another source of aerosols which would have been present during NCCC testing is ammonium. Ammonium chloride can be formed when SCR catalyst issues are encountered. Ammonium is also formed as a byproduct of thermal degradation reactions.
  - This trend was also observed by TNO during their pilot test at Maasvlakte using MEA.
- OptiCap solvent emissions were observed to increase with lower exit flue gas temperatures at the wash tower exit. This supports observations made by B&W PGG onsite engineers and SRI data collection, which are indicative of a possible fogging or aerosol impact on emissions.

The relationship between OptiCap solvent emissions and aerosol concentration is not thoroughly understood, and thus further research should be conducted in this area.

## **15.2 SRI GAS ANALYSIS**

Due to the importance of understanding the gaseous emissions leaving a RSAT process, B&W PGG worked with SRI to conduct a series of seven gas stream analysis tests at three different locations (absorber flue gas inlet, wash tower outlet, and regenerator outlet) in the process. SRI used a combination of industrial hygiene procedures and components of the EPA Modified Method 5 to build a mobile sampling system to collect both entrained liquid emissions as well as vapor phase compounds. To collect a representative sample, the samples were extracted isokinetically from the process. Figure 34 shows a schematic of the sampling system.

After gas samples were isokinetically extracted, the sample flowed through a condenser with ice water to collect entrained droplets (condensables). The collected liquid was gathered, weighed, and analyzed using standard EPA methods. Some results from the wash tower outlet are represented in Table 8.

A portion of the remaining vapor sample flowed to a set of parallel sorbent tubes coated in specially-treated resins designed to capture specific compounds. The tubes were analyzed by separate laboratories using NIOSH/OSHA analytical methods. Some results from the wash tower outlet are represented in Table 9.

To insure sample integrity, the clear sampling train was covered with cardboard during sample collection. The sorbent tubes, which were designed to capture nitrosamines, were shipped to their respective laboratories. The samples were shipped in amber vials or wrapped in aluminum foil to inhibit possible UV degradation.

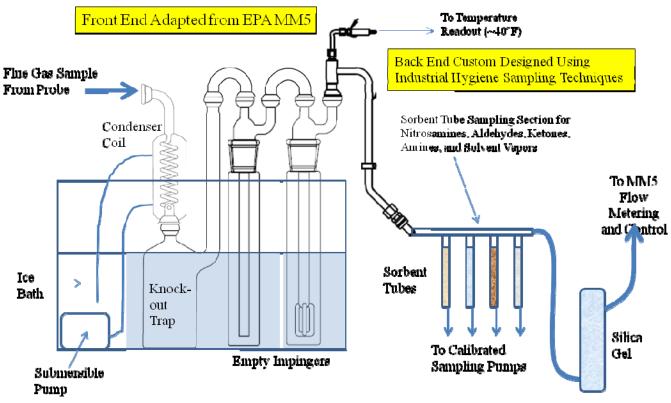


Figure 34: SRI Gas Sampling System

The primary objective of the gas sampling campaign was to understand which species were passing through or being created by the RSAT process and emitted to the atmosphere. The analytes for which SRI evaluated their gas samples were:

- Aldehydes
- Amines including the OptiCap solvent
- Ammonia
- Aminoethyl-OptiCap
- Hydrocarbons
- Nitrosamines

tubie of bitt dus finalysis Results - rupor Entrainment (Enquite i nus					
Location	Wash Tower Outlet				
Date Sampled	9/21/2011	11/8/2011	12/1/2011	12/5/2011	
Analyte	ppbv	ppbv	ppbv	ppbv	
N-Nitrosodimethylamine	< 0.0092	< 0.0043	< 0.0049	0.0116	
N-Nitrosomethylethylamine	< 0.0078	< 0.0036	< 0.0041	< 0.0019	
N-Nitrosodiethylamine	< 0.0067	< 0.0031	< 0.0035	< 0.0017	
N-Nitrosodi-n-propylamine	< 0.0053	< 0.0025	< 0.0028	< 0.0013	
N-Nitrosodi-n-butylamine	< 0.0043	< 0.0020	< 0.0023	< 0.0011	
N-Nitrosopiperidine	< 0.0060	< 0.0028	< 0.0032	< 0.0015	
N-Nitrosopyrrolidine	< 0.0068	< 0.0032	< 0.0036	< 0.0017	
N-Nitrosomorpholine	< 0.0059	< 0.0028	< 0.0031	< 0.0015	
N-Nitrosodiethanolamine	< 0.0051	< 0.0024	< 0.0027	< 0.0013	
	ppmv	ppmv	ppmv	ppmv	
Semi-Volatile Organics	*No Lower Limit Available	*Not Tested	*No Lower Limit Available	*Not Tested	
Volatile Organics	*No Lower Limit Available	*Not Tested	*No Lower Limit Available	*Not Tested	
Approximate Temperature	104	105	100	96	

### Table 8: SRI Gas Analysis Results - Vapor Entrainment (Liquid Phase)

### Table 9: SRI Gas Analysis Results - Vapor Phase

Location Wash Tower Outlet				
Location	VVd		:'L	
Date Sampled	9/21/2011	11/8/2011	12/5/2011	
Analyte	ppmv	ppmv	ppmv	
Total Hydrocarbons	*No Lower Limit Available	*Not Tested	*No Lower Limit Available	
	ppbv	ppbv	ppbv	
N-Nitrosodimethylamine	< 0.0186	< 0.0275	< 0.0254	
N-Nitrosomethylethylamine	< 0.0157	< 0.0231	< 0.0213	
N-Nitrosodiethylamine	< 0.0134	< 0.0199	< 0.0184	
N-Nitrosodi-n-propylamine	< 0.0110	< 0.0156	< 0.0144	
N-Nitrosodi-n-butylamine	< 0.0082	< 0.0129	< 0.0119	
N-Nitrosopiperidine	< 0.0123	< 0.0178	< 0.165	
N-Nitrosopyrrolidine	< 0.0136	< 0.0204	< 0.0188	
N-Nitrosomorpholine	< 0.0114	< 0.0175	< 0.0162	
N-Nitrosodiethanolamine	< 0.0051	< 0.243	< 0.244	
Approximate Temperature	104	105	96	

The red arrows in Figure 35 indicate the three locations where gas samples were extracted by SRI.

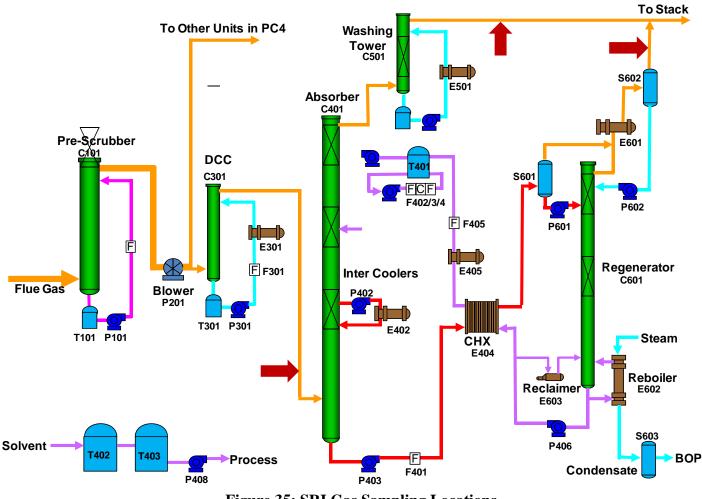


Figure 35: SRI Gas Sampling Locations

Some conclusions from the SRI gas sampling test include:

- Nitrosamines were observed in only one sample. N-Nitrosodimethylamine was observed in the entrained condensed liquid, but at a concentration well below 0.1 ppbv.
- Aminoethyl-OptiCap (AEOC) was not observed in any of the gas samples, despite being observed in the liquid phase.
- Few species were identified in either the entrained droplets or vapor phase after the first week of testing. The only species observed after the first set of tests were: (1) acetaldehyde, (2) formaldehyde, (3) ammonia, (4) OptiCap solvent, and (5) butyl amine.
- The highest measured emission rates were for the OptiCap solvent and ammonia.
- Total OptiCap solvent emissions appear to increase with lower wash section outlet temperatures. This was observed in the SRI test data and by B&W PGG engineers during the testing. The presence of increased emissions at lower outlet temperatures indicates a possible fogging or aerosol phenomenon.

This theory requires further evaluation before definitive conclusions can be made. If entrained aerosol droplets are found to be absorbing the OptiCap solvent, some potential process improvements which should be evaluated include:

- Utilizing random packing in the wash tower in place of the structured packing as originally installed in the PSTU. While random packing will slightly increase gas pressure drop and thus power requirements of the inlet blower, this will also create a more tortuous path for the gas flow and promote entrainment separation on the packing surface. This may further reduce solvent emissions with limited capital investment.
- Investigate using multiple stages or higher efficiency mist eliminators. The NCCC was equipped with a five micron wire mesh pad.
- Additives could be introduced into the flue gas upstream of the absorber in an effort to reduce the concentration of aerosol compounds.

### **16.0 NITROSAMINE DISCUSSION**

Nitrosamine generation from amine solvent PCC facilities is an important topic for CO2 capture. Nitrosamines are generated by the reaction of nitrite (anion of nitrogen dioxide [NO2]) with a secondary amine (such as the OptiCap solvent) in the absorber vessel. This reaction is expected to achieve one hundred percent conversion in a PCC process.

### **Equation 4: Generic Nitrosamine Reaction**

### Secondary Amine + $NO_2 \rightarrow Nitrosamines$

However, secondary amines (organic compound where two hydrogen atoms of an ammonia derivative have been replaced by organic functional groups) are not the only amines expected to generate nitrosamines because secondary amines are known degradation products of most amines. Thus, most amines will have the potential to produce nitrosamines although possibly at lower concentrations.

Recent laboratory research at the University of Texas has shown that nitrosamines may gradually thermally decay in the regenerator of an RSAT process if high enough operating temperatures are used. The overall proposed nitrosamine reaction pathway for the OptiCap (OC) solvent is shown in Equation 5.

### **Equation 5: MNPZ Proposed Reaction and Degradation**

$$OC + NO_2 \xrightarrow{k_1} Nitrosamine \xrightarrow{k_2} NO + OC^-$$

In addition to the possibility of nitrosamines being decomposed in the regenerator, nitrosamines are also known to be degraded by ultraviolet (UV) light. Therefore, when sampling for nitrosamines, amber sampling vials were used to limit the decomposition of these species.

Based on the importance of the formation of nitrosamines in the current  $CO_2$  capture environment, a dedicated sampling and testing program was employed for the NCCC test program to help develop a better understanding of the overall nitrosamine subject. B&W PGG extracted 60mL liquid samples from the rich and lean streams once per week throughout the NCCC test campaign, as well as daily throughout the thermal reclaimer test. These samples were stored in amber vials and refrigerated to preserve the integrity of the solvent composition until the samples were analyzed after the completion of the test program.

In addition, Southern Research Institute (SRI) completed a series of four gas phase sampling tests at the wash tower outlet in an effort to characterize the composition of the effluent gas stream. One of the primary groups of compounds for which SRI analyzed was nitrosamines. For details on the procedure used by SRI, refer to Section 15.1. Appropriate precautionary methods were used to ensure that UV rays did not destroy any nitrosamines present in the samples.

## **16.1 NITROSAMINE RESULTS**

The rich and lean solvent samples were shipped in amber vials for analysis of the liquid nitrosamine concentrations. All samples were analyzed using a high performance liquid chromatography (HPLC) method for nitrosamine analysis. Multiple HPLC runs were completed.

The measured concentration of mononitroso-OptiCap (MNOC) was similar in both the rich and lean phases. A few more data points were collected for the lean stream because these were expected to be more accurate due to lower  $CO_2$  loadings and decreased probability of degassing from the sample.

The data showed a significant spike in MNOC concentration after the first week of operation before the concentration decreased to what appeared to be an equilibrium concentration. Significant resources were directed towards understanding the reason for the peak at the beginning of operation. Several possibilities were evaluated, including:

- Higher NO<sub>2</sub> concentration in the inlet flue gas to the PSTU.
- A substantial volume of fresh solvent was added to the bulk inventory approximately one week after the start of the campaign. This would have diluted the concentration of reaction species such as MNOC.
- An unplanned shutdown and subsequent two-day outage occurred before the start of the concentration spike. It is possible that the SCRs were not immediately brought back online after the outage. SCS provided SCR operation data.
- Higher regenerator temperatures are expected to have a greater impact in reducing the concentration of nitrosamines in the liquid phase. Daily average regenerator sump temperatures were evaluated to determine whether a correlation existed.

Operating data was analyzed which showed that the change in MNOC concentration was not related to a dilution or concentration phenomenon. In addition, the change in MNOC concentration was compared to the upsets observed within the PSTU or due to Gaston Unit #5. The early unplanned plant shutdown and subsequent outage did not appear to have a significant impact on the concentration of MNOC. However, the sizeable increase in concentration did begin immediately following the outage. This indicated that the SCRs may not have been immediately brought online following the event, which may have increased the inlet concentration of NO<sub>2</sub> to the PSTU.

Due to equipment limitations, B&W PGG was not able to directly measure the concentration of inlet  $NO_2$  or  $NO_x$  continuously during the campaign. After the campaign, SCS provided B&W PGG engineers with the daily average total  $NO_x$  values (upstream and downstream of SCR) from September 15<sup>th</sup> to December 7<sup>th</sup>. When the inlet  $NO_x$  values and MNOC concentration were compared, it was determined that a correlation between the two variables did exist, as expected.

At one point in the data trend, a spike in inlet  $NO_x$  was observed, followed by an increase in MNOC concentration. However, the concentration of MNOC remained elevated for an extended period following the peak in inlet  $NO_x$ , indicating that an additional phenomenon existed. Both the inlet  $NO_x$  and MNOC concentrations were observed to approach to an apparent "equilibrium" value, thus indicating that the MNOC concentration was directly dependent on the concentration of inlet  $NO_x$ .

To fully explain the MNOC peak, an assumption was made that 2.5% of the inlet total  $NO_x$  was  $NO_2$ . Since one mole of OptiCap solvent reacts with one mole of nitrite to form one mole of MNOC, and assuming 100% conversion of the nitrite to MNOC, the resultant MNOC concentration was calculated. Using equation 6 below, the daily rate constant for the thermal decay of the MNOC was calculated, accounting for the various regenerator pressures and temperatures. By calculating each rate constant, the daily concentration of MNOC was calculated.

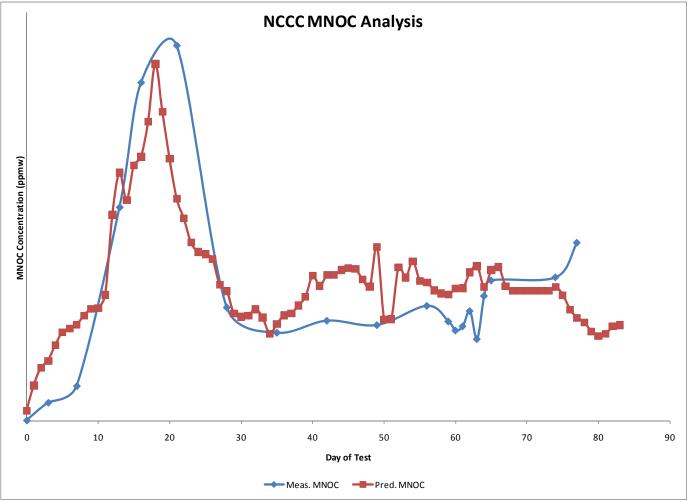
#### **Equation 6: MNPZ Thermal Decay Reaction Rate Constant**

$$k = k_1(T_1) \exp[\frac{E_a}{R} \left(\frac{1}{T_1} - \frac{1}{T}\right)]$$

Where:

- k : reaction rate constant for given temperature
- $k_1$  : reaction rate constant for reference temperature
- E<sub>a</sub> : activation energy
- R : ideal gas constant
- $T_1$  : reference temperature
- T : given temperature of reboiler sump

Figure 36 shows the predicted MNOC concentration in the liquid phase compared to the measured values from the HPLC.



**Figure 36: Thermal Decay Impact on MNPZ Concentration** 

The MNOC peak concentration can be predicted using this approach as well as the slope of the MNOC decay and a similar equilibrium value. The difference in the concentration at day twenty-one (21) may be due to a higher actual concentration of  $NO_2$  than the assumed value, or to a small error in the measured activation energy or reaction rate constant. However, this prediction method shows that a combination of thermal decay and inlet  $NO_2$  concentration can be used to predict the MNOC concentration in the circulating solution.

In addition to speculation that nitrosamines could be present in the liquid phase, it has been suggested that nitrosamines may be present in the gas phase or entrained droplets. SRI collected four separate samples at the wash tower outlet and two at the regenerator knock out drum outlet to analyze the vapor phase and any entrained droplets for nitrosamines. Tables 10 and 11 indicate that any nitrosamines present at these locations were at lower than detectable limits except for one sample at the wash tower outlet on 12/5. On 12/5, the sample taken at the wash tower outlet was found to contain 0.0116 ppbv N-nitrosodimethylamine entrained.

Location	Wash Tower Outlet			
Date Sampled	9/21/2011	11/8/2011	12/5/2011	
Analyte	ppmv	ppmv	ppmv	
N-Nitrosodimethylamine	< 0.0186	< 0.0275	< 0.0254	
N-Nitrosomethylethylamine	< 0.0157	< 0.0231	< 0.0213	
N-Nitrosodiethylamine	< 0.0134	< 0.0199	< 0.0184	
N-Nitrosodi-n-propylamine	< 0.0110	< 0.0156	< 0.0144	
N-Nitrosodi-n-butylamine	< 0.0082	< 0.0129	< 0.0119	
N-Nitrosopiperidine	< 0.0123	< 0.0178	< 0.165	
N-Nitrosopyrrolidine	< 0.0136	< 0.0204	< 0.0188	
N-Nitrosomorpholine	< 0.0114	< 0.0175	< 0.0162	
N-Nitrosodiethanolamine	< 0.0051	< 0.243	< 0.244	

### Table 10: SRI Nitrosamine Vapor Emissions Results

#### **Table 11: SRI Nitrosamine Entrainment Emissions Results**

Location	Wash Tower Outlet				
Date Sampled	9/21/2011 11/8/2011 12/1/2011 12/5				
Analyte	ppbv	ppbv	ppbv	ppbv	
N-Nitrosodimethylamine	< 0.0092	< 0.0043	< 0.0049	0.0116	
N-Nitrosomethylethylamine	< 0.0078	< 0.0036	< 0.0041	< 0.0019	
N-Nitrosodiethylamine	< 0.0067	< 0.0031	< 0.0035	< 0.0017	
N-Nitrosodi-n-propylamine	< 0.0053	< 0.0025	< 0.0028	< 0.0013	
N-Nitrosodi-n-butylamine	< 0.0043	< 0.0020	< 0.0023	< 0.0011	
N-Nitrosopiperidine	< 0.0060	< 0.0028	< 0.0032	< 0.0015	
N-Nitrosopyrrolidine	< 0.0068	< 0.0032	< 0.0036	< 0.0017	
N-Nitrosomorpholine	< 0.0059	< 0.0028	< 0.0031	< 0.0015	
N-Nitrosodiethanolamine	< 0.0051	< 0.0024	< 0.0027	< 0.0013	

While nitrosamines were not observed in the gas phase during the OptiCap solvent test campaign, further and more detailed research should be completed to verify these findings, as liquid phase analysis showed that MNOC was present in the circulating solvent. In addition, data analysis also showed that MNOC concentration was impacted by a combination of  $NO_2$  concentration and regenerator temperature. If the regenerator sump were operated at lower temperatures, the probability of finding nitrosamines in the gas phase would be expected to increase.

B&W PGG recommends implementation of the following nitrosamine analysis program in the future:

- Measure NO<sub>2</sub> concentrations at the absorber inlet and wash section outlet continuously.
- Collect 40mL lean solvent samples twice per week for liquid nitrosamine concentration analysis.
- Collect gas samples weekly at the wash section outlet using a sampling system similar to that shown in Section 15.2.
- Store all samples in amber sample vials.
- Collect regenerator sump temperature data on a continuous basis.

### **17.0 OPERATIONAL EXPERIENCE**

The NCCC test was the first opportunity to operate the OptiCap solvent on coal flue gas. Most previous operating experience had been completed in a laboratory setting or on synthetic gas. While laboratory experiments provide the advantage of having control over inlet parameters and process conditions, a commercial RSAT process will be installed in an operating power facility where unexpected upsets can and will occur at any part of the process. To design and safely operate a  $CO_2$  capture process, operating experience at an actual utility plant is crucial.

## **17.1 PLANT UPSETS**

A unique characteristic of the OptiCap solvent is the relationship between temperature, CO<sub>2</sub> concentration in the liquid, and precipitation. Due to this relationship, B&W PGG engineers took time to thoroughly consider possible operational issues both from the upstream power facility and within the PSTU. B&W PGG created operating procedures which were distributed to the PSTU engineers and operators prior to the test campaign to safely handle these upset situations. For more detailed information, refer to Sections 7.0 through 7.3.

During the three-month test period at NCCC, B&W PGG engineers experienced and successfully managed several upsets typical of those associated with operating a coal-fired power plant. Experiencing these upsets, the operator reactions, and the solvent response will be instrumental in designing a successful system.

Most of the upsets experienced by B&W PGG engineers fell into two categories: (1) loss of flue gas (steam for the reboiler was available), and (2) loss of both flue gas and reboiler steam (heat tracing was available). Both types of events will inevitably occur during commercial operation of a PCC facility and will provide different challenges; therefore, having the opportunity to develop hands-on experience was important.

When reboiler steam is available, the PCC facility should be placed into "warm" recycle mode. The solvent inventory should be continuously circulated between the absorber and regenerator while flowing steam to the reboiler in order to maintain a specified bulk temperature. Precipitation issues should not occur as long as the solvent is circulated and kept warm.

If steam is not available, but the plant is designed with heat tracing around the circulating piping, the solvent should be continuously circulated between the absorber and regenerator with heat tracing activated. At NCCC, this practice was sufficient to prevent precipitation.

One major type of upset B&W PGG did not experience was a black plant scenario where all power, heat, compressed air, etc. is unavailable. Engineering design considerations will be used to address this situation.

# **17.2 KEY LESSONS LEARNED**

Experiencing several excursions from normal operation allowed B&W PGG engineers to test the protocols that were developed to handle the various possible upsets while operating a PCC facility. All of the protocols which were used worked effectively and allowed the system to quickly return to normal operation when the upset was resolved, without experiencing any precipitation in the circulating loop. In addition, B&W PGG was able to learn many important lessons which should be incorporated into the design of a commercial plant to assist operators during an upset. Some important findings related to addressing upsets, as well as suggestions for designing a commercial plant, are:

- Alarms for low CO<sub>2</sub> and high O<sub>2</sub> concentrations should be installed on the flue gas stream entering the polishing scrubber. This will proactively warn the operator of the PCC facility if a trip has occurred in any equipment upstream of the PSTU such as a boiler tube leak or scrubber outage.
- A high level alarm should be included for the PCC system inlet SO<sub>2</sub> concentration. Essentially all of the SO<sub>2</sub> will react with the amine to form heat stable salts, which may lead to solvent degradation. Depending on plant operating constraints, it may be advisable to bypass the PCC facility until the cause of the high SO<sub>2</sub> inlet concentration is remedied.
- A MicroMotion<sup>®</sup> (or equivalent) density meter should be installed on the cold, lean solvent stream to provide an estimate of the lean  $CO_2$  loading. This will be a key strategy for upset conditions and extended shutdowns to facilitate the shutdown procedure.
- Continual solvent circulation and maintaining appropriate solvent temperatures via low levels of steam or heat tracing are the most critical factors in avoiding precipitation in the system.
- Accommodations should be made to drain the solvent into a practical but minimal number of locations if power is lost. This will allow the plant to better address any possible solids.
- Hot water connection ports should be installed around pumps, and a portable hot water heater should be located onsite to allow for injection of hot water to areas of local solidification.
- Portable gas heaters can be used to maintain local temperatures, if no other method is available.

The testing opportunity at NCCC not only allowed B&W PGG to gain operational experience regarding upset conditions, but also contributed to understanding overall operation from the operator view point. Some of additional findings in this area are:

- Liquid flow meters should be installed at the absorber inlet, absorber outlet, and regenerator outlet to facilitate location of leaks. This will also help to characterize performance across the CHX.
- A quick online indication of  $CO_2$  loading as well as inlet and outlet  $CO_2$  concentrations will be important for safe operation.
- Plate and frame heat exchangers have performed well in RSAT service with the OptiCap solvent.

## **18.0 THERMAL RECLAIMER TEST**

B&W PGG engineers operated the thermal reclaimer at the PSTU for one week from November 14<sup>th</sup> to 20<sup>th</sup> during the OptiCap solvent test program. This test had the following primary objectives:

- To verify that the OptiCap solvent can easily be thermally reclaimed.
- To insure that the rate of additional thermal degradation species formed during reclamation was low.
- To analyze the composition of the solvent heel remaining in the reclaimer after each test run.

Three different sets of test conditions were operated during the week. For each test condition, the independent parameters (intercooler temperature, flow rate, regenerator pressure, etc.) were set to the desired conditions. Then, a slip stream of the liquid solution was diverted from the hot lean stream to the thermal reclaimer. The temperature of the reclaimer was gradually increased to the required set point using steam. This allowed for the volatilization of organic compounds to the regenerator and the concentration of heat stable salts in the reclaimer. In industry applications, sodium hydroxide (NaOH) would be added to break the heat stable bonds between OptiCap solvent and the acid gas, which allows the amine to volatilize and the acid gas to bond with the stronger base (Na+), which would be purged in the heel. B&W PGG engineers decided not to add NaOH, in an effort to concentrate the original heat stable compounds for analysis. Samples of the concentrated heel were collected and sent for analysis at the end of each of the three test runs.

Although some minor equipment limitations existed (for example, a leaking ram valve), B&W PGG engineers were able to confirm that no operational issues existed when using a thermal reclaimer for the OptiCap solvent. However, the equipment limitations did compromise the composition and volume of the heel product by allowing solvent to leak into the catch pot. The composition of the reclaimer heel has not been analyzed to date. However, this analysis will be completed in the future.

# **19.0 ACTIVATED CARBON**

Although the original test plan required operating the activated carbon bed during the thermal reclaimer portion of the test campaign, B&W PGG engineers decided not to run the activated carbon filtration system during the test period. The reasons for this decision included:

- The activated carbon bed was a large tank which required a substantial amount of the solvent inventory in the system to fill the piping and vessel for operation. Due to the limited volumes of extra solvent available, B&W PGG engineers decided that it was more important to insure the ability to run optimization cases following the reclaimer test than to run the carbon bed for one week. This would apply especially if another emergency event occurred and a significant amount of solvent was lost.
- The BWRC pilot has an activated carbon bed which was operated during each of the three-week pilot campaigns conducted there. If further research regarding the capabilities of the carbon bed were required, the research could be completed at BWRC.

# **20.0 RECOMMENDATIONS**

B&W PGG completed a successful three-month test campaign of its OptiCap solvent in the PSTU at NCCC during the fall of 2011. Some important recommendations and observations from the study include:

- Nitrosamines <u>do not</u> appear to be an issue which would preclude the use of the OptiCap solvent for PCC systems. Nitrosamines are primarily a function of inlet NO<sub>2</sub> concentration, and the liquid concentration of nitrosamines was controlled via the regenerator temperature at NCCC. However, this is a subject which requires further research and data collection, as this was not a comprehensive study and the topic requires additional investigation. An online NO<sub>2</sub> measurement should be added for all future studies.
- Amine emissions are an area in which further research is required. Data collected from NCCC suggests that a correlation exists between increased amine emissions and aerosols. This phenomenon is not unique to the OptiCap solvent, as it was also experienced in other recent pilot tests (e.g. Maasvlakte on MEA). This phenomenon can be addressed via engineering design. However, additional research is required to find the optimum solution.
- The OptiCap solvent is a commercially viable solvent, and is ready for a commercial scale "demonstration" project. This would be an appropriate opportunity to further study solvent degradation, as extended run times (6 months or longer) are required in order to gather meaningful and reliable data.
- Due to the OptiCap solvent's resistance to oxidative degradation, it should be a suitable candidate for  $CO_2$  capture from flue gas derived from natural gas. This should be validated at pilot scale.

# **21.0 CONCLUSIONS**

The OptiCap solvent has many benefits including low corrosivity, low regeneration energy, and an expected high resistance to solvent degradation. In addition, it offers the ability to operate the RSAT system at elevated pressures due to its thermal stability, which will have a significant favorable impact on mechanical compression energy. Some additional findings include:

- Solvent emissions were higher than expected due to an expected aerosol phenomenon. Similar findings have been observed on multiple solvents during other recent pilot plant tests. Additional testing is required to evaluate cost effective ways to decrease these emissions.
- Solvent degradation results indicate that the degradation rate will be significantly lower for the OptiCap solvent than for MEA, but this analysis is not yet complete due to the complex solvent degradation mechanisms. In addition, regeneration energy values were observed to decrease over time for replicate test conditions indicating that the degradation products created at NCCC were not negatively impacting regeneration energy during this test.
- The nitrosamine reaction occurs in the liquid phase of a PCC process using the OptiCap solvent. The nitrosamine concentration is dependent on inlet NO<sub>2</sub> concentration, regenerator temperature, and solvent concentration. Nitrosamines were observed in only one gas sample, at a concentration below 0.1 ppbv.
- The performance of the OptiCap solvent compares favorably with other commercially ready solvents in areas of regeneration energy, corrosivity and solvent degradation. The additional ability to operate at elevated regeneration pressures due to the thermal degradation resistance will further help to lower the life cycle cost for this solvent.
- The OptiCap solvent is ready for a commercial-sized demonstration project.

## **22.0 ACKNOWLEDGEMENTS**

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  - o Southern Company Services
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- B&W PGG RSAT Team
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  - Kate E. Cardwell
  - o Laura M. McDermitt
  - o Terry M. Powell

## **23.0 ACRONYMS**

- B&W PGG: Babcock & Wilcox Power Generation Group, Inc.
- NCCC: National Carbon Capture Center
- PSTU: Pilot Solvent Test Unit
- WL: Weight loss
- ER: Electrical resistance
- BWRC: Babcock & Wilcox Research Center
- CO<sub>2</sub>: Carbon dioxide
- MEA: Monoethanolamine
- mpy: Mils per year
- FTIR: Fourier transform infrared
- SRI: Southern Research Institute
- ppb: Parts per billion
- MNOC: Mononitroso-OptiCap
- NO<sub>2</sub>: Nitrogen dioxide
- DOE: Department of Energy
- SCS: Southern Company Services
- PCC: Post-combustion capture
- RSAT<sup>TM</sup>: Regenerable Solvent Absorption Technology
- LCOE: Levelized cost of electricity
- AQCS: Air quality control systems
- SO<sub>2</sub>: Sulfur dioxide
- NO<sub>x</sub>: Nitrogen oxides
- CO<sub>2</sub>: Carbon dioxide
- SBS: Small boiler simulator

- BTU: British thermal unit
- MOC: Management of change
- MW: Megawatt
- PFD: Process flow diagram
- BOP: Balance of plant
- RP: Rich precipitation
- LP: Lean precipitation
- CHX: Cross heat exchanger
- WFGD: Wet flue gas desulfurization
- ICP-OES: Inductively coupled plasma optical emission spectroscopy
- VLE: Vapor-liquid equilibrium
- LPR: Linear polarization resistance
- CS: Carbon steel
- SS: Stainless steel
- CR: Corrosion rate
- ML: Metal loss
- UT: University of Texas
- HPLC: High-performance liquid chromatography
- IC: Ion chromatography
- AEOC: Aminoethyl-OptiCap
- HEOC: Hydroxyethyl-OptiCap
- SCR: Selective catalytic reduction
- ESP: Electrostatic precipitator
- EPA: Environmental Protection Agency
- NIOSH: National Institute for Occupational Safety and Health
- OSHA: Occupational Safety and Health Administration
- UV: Ultra-violet
- OC: OptiCap

### **24.0 REFERENCES**

1. Van der Fijp, S. et al. (2012, January 26). *Emission Reducing Technologies Aerosols*. Presentation at the UTCCS-1.