Technical Paper
BR-1871

B&W PGG's RSAT™ Process and Field Demonstration of the OptiCap® Advanced Solvent at the U.S.-DOE's National Carbon Capture Center

Authors:
J.W. Gayheart
S.A. Moorman
T.R. Parsons
C.W. Poling

Babcock & Wilcox
Power Generation Group, Inc.
Barberton, Ohio, U.S.A.

X. Guan
J.M. Wheeldon

Southern Company Services,
Wilsonville, Alabama, U.S.A.

Presented to:
Power Plant Air Pollutant
Control "MEGA" Symposium

Date:
August 20-23, 2012

Location:
Baltimore, Maryland, U.S.A.

babcock & wilcox power generation group

B&W PGG's RSAT™ Process and Field Demonstration of the OptiCap® Advanced Solvent at the U.S.-DOE's National Carbon Capture Center

J.W. Gayheart, S.A. Moorman,
T.R. Parsons, C.W. Poling
Babcock & Wilcox Power Generation Group, Inc.
Barberton, Ohio, USA

Xiaofeng Guan,
John M. Wheeldon
Southern Company Services
Wilsonville, Alabama, USA

Presented at:
Power Plant Air Pollutant Control "MEGA" Symposium
Baltimore, Maryland, U.S.A.
August 20-23, 2012

BR-1871

ABSTRACT

Southern Company manages and operates the U.S. Department of Energy's National Carbon Capture Center (NCCC), a focal point of national efforts to develop advanced technologies to reduce greenhouse gas emissions from coal-based power generation. The center, located in Alabama, works with scientists and technology developers from government, industry and universities who are creating the next generation of carbon capture technologies.

In the fall of 2011, Babcock & Wilcox Power Generation Group, Inc. (B&W PGG) conducted a three-month test campaign at the NCCC to develop further commercially viable methods of reducing carbon dioxide (CO_2) emissions from coal-fired power plants. The company tested its regenerable solvent absorption technology (RSAT™) process using its OptiCap® advanced solvent.

This paper will provide general descriptions of results in the areas of regeneration energy, solvent degradation and corrosion, as well as non-quantitative results such as lessons learned and operating experience for a post-combustion carbon capture (PCC) pilot plant in a coal-fired utility power plant.

INTRODUCTION

The United States (U.S.) Department of Energy (DOE) established the NCCC to address the nation's need for cost-effective, commercially viable CO_2 capture options for coal-based power plants (both combustion and gasification). The DOE, Southern Company, and other industrial participants provide the funding for the NCCC, and Southern Company Services manages the project. The NCCC was established at the Power Systems Development Facility, an engineering-scale test center located in Wilsonville, Alabama, that has been in operation since 1996. At this site, the Transport Gasifier provides syngas for pre-combustion CO_2 capture testing. A new test facility, the Post-Combustion Carbon Capture Center (PC4), built at the adjacent power plant (Alabama Power's Plant Gaston), provides flue gas for post-combustion CO_2 capture testing. PC4 was commissioned in early 2011 and includes the 0.5-MW Pilot Solvent Test Unit (PSTU) for testing CO_2 capture solvents on behalf of developers. Space is also available to test developer's bench-scale and pilot-scale equipment.

This facility provided B&W PGG the opportunity to further investigate its OptiCap solvent and aspects of the RSAT technology in commercially representative flue gas conditions (a 0.5 MW slipstream extracted from Alabama Power's Plant Gaston), 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 was 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, which 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, it provided much useful performance data and operational experience for the continued development of the RSAT technology. The primary limitation of operating at the PSTU was the restricted test campaign duration (3 months). This constraint 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.

RSAT PROJECT BACKGROUND

In 2005, B&W PGG began efforts to develop the RSAT process and a team was assembled at B&W PGG's Research Center (BWRC) in Barberton, Ohio. The team initiated an in-depth technology review which included existing and developmental solvent-based, PCC technologies, design methods, solvents, academic research, and other subjects to establish a basis for development of the B&W PGG RSAT product. A dedicated CO_2 control laboratory was built and outfitted with state-of-the-art equipment including a wetted-wall absorption column and fully integrated bench-scale RSAT system to screen candidate solvents and obtain physical and chemical data for the design of the RSAT system. In addition, a seven ton per day CO_2 pilot plant (constructed at the BWRC) was completed in January 2009 for further evaluating the most promising solvents.

B&W PGG's RSAT development process is shown in Figure 1, 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.

SOLVENT DEVELOPMENT

As a result of an extensive research program, the BWRC team selected the most promising solvent candidate tested for more in-depth development and evaluation. The result is B&W PGG's OptiCap solvent.

Extensive lab and pilot testing of the OptiCap solvent at BWRC showed favorable performance characteristics. Under similar test conditions, a lower reboiler heat duty was attained for the OptiCap solvent as compared to a 30% monoethanolamine (MEA) solvent. Additional properties of the OptiCap solvent that were expected to provide savings in capital and operating costs have been identified in laboratory campaigns. More specifically, characteristics of the OptiCap solvent which were further quantified as a result of testing at NCCC include:

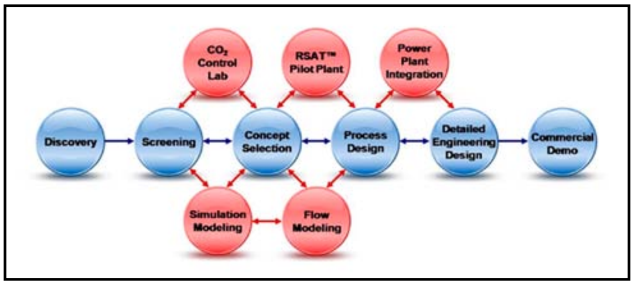


Fig. 1 B&W PGG RSAT development process.[1]

- 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 offered the potential for lower solvent make-up rates as well as lower solid waste generation rates.
- Resistance to thermal degradation. Testing had shown the OptiCap solvent to be stable at operating temperatures up to 300°F. This attribute offered the potential for regeneration at higher operating temperatures and pressures, which could lead to significant CO_2 compression energy savings.
- Ease of reclaiming. Results indicated that thermal reclaiming was likely the primary technology for removing degradation species formed using the OptiCap solvent. Thermal reclaiming is a well-known technology which has been successfully used 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_2 for the OptiCap solvent is approximately twice that of 30 wt% MEA. This kinetic advantage allows absorber towers to be designed with less packing than towers designed for 30 wt% MEA. This characteristic offers capital cost savings through reduced absorber tower height, quantity of packing, structural steel, foundations, and installation cost, as well as auxiliary power consumption savings due to decreased pressure drop through the absorber and decreased pump power required for solvent recirculation. 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 towers can be substantial.
- Increased CO_2 carrying capacity. Because the OptiCap solvent can be loaded with approximately twice the amount of CO_2 per unit of solvent (compared to 30% MEA), the solvent recirculation rate is decreased, saving the energy required to not only pump the solvent within the system, but also to heat and cool the solvent in the various process stages.

Testing under actual power plant flue gas conditions at NCCC was required to confirm the research performed in both the BWRC lab and pilot plant regarding the above 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 during the Fall of 2011was run on flue gas in the PSTU at the NCCC.

PSTU DESCRIPTION

The PSTU was designed to achieve 90% CO_2 capture using a 30% aqueous MEA solution. This was the reference solvent against which the performance of other solvents will be compared. To accommodate a range of solvents and test conditions, the PSTU was designed to be operationally flexible. A schematic of the PSTU is shown in Figure 2.

Up to 12,000 lb/hr of flue gas extracted downstream of the wet flue gas desulfurization (FGD) system from the adjacent power plant (Alabama Power's E.C. Gaston Plant Unit 5) flows to the PSTU. The flue gas flows through a caustic pre-scrubber to remove SO_2 leaving a low concentration of SO_2 in the gas stream. Approximately half of this exit stream is diverted to other units, while nominally 5,000 lb/hr (~0.5 MW) of flue gas flows to the direct contact cooler before entering the absorber.

The PSTU is comprised of five major subsystems:

- The pre-scrubber removes most of the remaining SO_2 in the flue gas using a caustic solution.
- A cooler/condenser unit cools the flue gas to appropriate reaction temperatures and helps to maintain the system water balance.
- An absorber promotes efficient gas-liquid contact for removal of CO_2 from the flue gas. This column was designed to contain up to four packed beds and is equipped with solvent intercoolers.
- A wash tower cools the CO_2-depleted flue gas, removing trace amounts of entrained solvent.
- A regenerator provides heat to release the CO_2 from the solvent. Steam used in the reboiler is extracted from the cold reheat line of Unit 5 and is attemperated as required.

The PSTU was built off-site and delivered in twelve modules for erection. The footprint is approximately 45 ft x 40 ft and the overall height is 165 ft. Table 1 provides dimensions for each of the columns as well as the type of packing currently installed; however, the packing type can be changed as required.

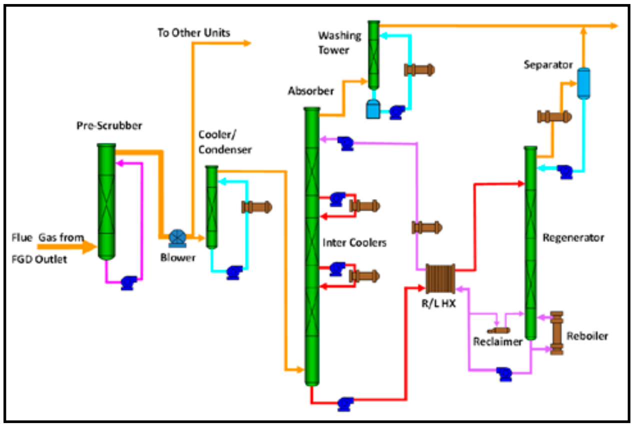


Fig. 2 PSTU schematic.

Table 1
Dimensions and Packing Used in PSTU Columns

Column	Height, m (ft)	Outer Diameter, cm (in.)	No. of Beds	Packing Type
Pre-Scrubber	14 (46)	76 (30)	1	Random
Cooler/ Condenser	9.1 (30)	61 (24)	1	Structured
Absorber	32.9 (108)	66 (26)	3 (*)	Structured
Washing Tower	9.1 (30)	61 (24)	1	Structured
Regenerator	23 (75)	61 (24)	2 (*)	Structured

(*) Space provided for additional bed

The PSTU is well instrumented to enable comprehensive process data collection and thorough characterization of equipment and solvent performance. The available gas analyzers and their locations are listed in Table 2.

An automatic titration system is used to determine the solvent concentration and the CO_2 loading. The water concentration is determined by difference, although it can be determined by the Karl Fischer method (ASTM E203 – 08) if required. Liquid samples were extracted from four locations (note: other extraction locations are possible):

- Hot lean solution leaving the regenerator
- Cool lean solution entering absorber
- Cool rich solution leaving the absorber
- Hot rich solution entering the regenerator

The automatic titrator draws a sample every 30 minutes, so each location is analyzed once every two hours. To determine the CO_2 loading, the samples are titrated with potassium hydroxide and sulfuric acid to determine the solvent concentration. Hot samples are cooled to approximately 100°F to prevent CO_2 flashing from solution, thereby altering the sample composition. The auto-titration measurements

Table 2
Gas Analysis Techniques

Stream	Species	Technique
Absorber Inlet	Oxygen	Zirconia sensor
	CO_2	NDIR
	Moisture	Capacitance
	SO_2	Ultraviolet
Absorber Outlet	Oxygen	Paramagnetic
	CO_2	NDIR/FTIR
	Moisture	FTIR
	NH_3	FTIR
	NO_x	FTIR
	NO	FTIR
	NO_2	FTIR
	Amines	FTIR/condensation
Regenerator Outlet	Moisture	Capacitance
	CO_2	By difference

FTIR: Fourier transform infrared spectroscopy
NDIR: Nondispersive infrared

are cross-checked with laboratory analysis of samples taken manually from the cooled sample streams close to the time that auto-titration samples are extracted. Standard quality control checks (e.g., spiking the solvent concentration) are used to confirm the accuracy of the laboratory procedures.

TEST OBJECTIVES

Along with confirming and quantifying the solvent benefits previously mentioned, several other objectives were identified prior to the start of the test campaign. These objectives are summarized as follows:

- 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.

TEST MATRIX

Using Design for Six Sigma tools, B&W PGG 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 a wide array of operating ranges) to verify the predictions of B&W PGG's simulation model.

The independent test parameters that were varied during the test campaign were as follows:

- L/G ratio
  - » Liquid mass flow rate (L)
  - » Gas mass flow rate (G)
- Regenerator pressure and temperature
- Wash section outlet temperature
- Lean solvent temperature entering the absorber
- Inlet flue gas temperature to the absorber
- Use of the intercooler between 1st and 2nd packed beds
- Intercooler liquid outlet temperature
- CO_2 removal
- Reflux location

All test campaigns varied the steam flow to the reboiler to achieve the specified CO_2 removal efficiency. In most cases, the targeted removal efficiency was 90% removal of CO_2 which was calculated using the following equation.

Equation 1: CO_2 Removal (Volume Basis)

$$\%\ CO_2\ removal = 100 * \left(1 - \frac{A^{out} * \left(1 - \frac{A^{in}}{100}\right)}{A^{in} * \left(1 - \frac{A^{out}}{100}\right)}\right)$$

where:

A^{out} = outlet CO_2 volume percentage as measured by the gas analyzer

A^{in} = inlet CO_2 volume percentage as measured by the gas analyzer

RESULTS

Regeneration Energy

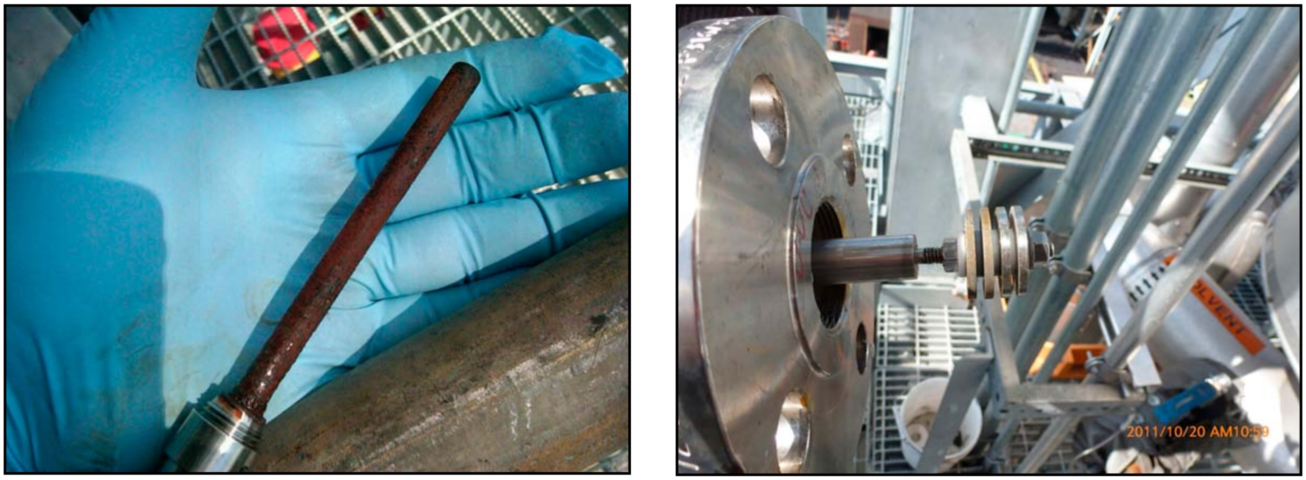
B&W PGG was present at NCCC during the 30 wt% MEA test that was completed during commissioning of the PSTU. This was beneficial in helping the B&W PGG team understand some of the limitations of the PSTU equipment. Table 3 shows a comparison of the regeneration energies gathered from B&W PGG's OptiCap solvent test, the 30 wt% MEA commissioning test, and the 40 wt% MEA test at the PSTU. It is important to note that the MEA tests were conducted differently from the B&W PGG test. The MEA tests did not target 90% CO_2 removal. Instead, test conditions and steam flows were set to specified values allowing the process to stabilize at the equilibrium removal efficiency without adjustment. The process was then allowed to run overnight. No process adjustments were made for changes in load or to maintain a target CO_2 removal for the MEA tests.

Table 3 shows that the lowest MEA regeneration energy (1,245 Btu/lb CO_2) case occurred while running 40% MEA as expected. This case was achieved at a reduced CO_2 removal efficiency. From 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 simulation modeling predicts that this particular case would require approximately 1,300 Btu/lb CO_2 at 90% removal. The lowest OptiCap regeneration energy measured was 1,098 Btu/lb CO_2.

Despite the low measured regeneration energy values at NCCC, these were not the lowest achievable values for the OptiCap solvent. The PSTU was designed for operation using 30% MEA with the flexibility to accommodate other solvents. Since the PSTU's cross heat exchanger was not designed for the higher viscosity of the B&W PGG OptiCap solvent relative to 30% MEA, the measured cross heat ex-

Table 3
PSTU Regeneration Energy Comparison

Solvent	ΔH_{Regen}	CO_2 Removal
30% MEA	1507 Btu/lb CO_2	86%
40% MEA	1245 Btu/lb CO_2	82%
OptiCap	1098 Btu/lb CO_2	90%



Figs. 3a and 3b ER probe (left) and WL coupons (right).

changer approach temperatures during the OptiCap solvent test were slightly higher than the MEA design. By adjusting measured regeneration energy values based on achieving a designed cross heat exchanger approach temperature, regeneration energy values less than 1,050 Btu/lb CO_2 are theoretically achievable.

Corrosion

Preliminary bench top electrochemical tests completed at BWRC as part of the NCCC preparation predicted that the corrosivity of the OptiCap solvent was expected to be less than that of 30% MEA. To better understand OptiCap solvent corrosivity and whether it would change over time with an increase in degradation species, a corrosion program was implemented at NCCC.

The corrosion program utilized a combination of both electrical resistance (ER) probes and weight loss (WL) coupons. The 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 to document how these changed over time. The ER probes and WL coupons are shown in Figures 3a and 3b.

ER probes, installed at seven locations throughout the PSTU, 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 an instantaneous corrosion measurement that could be documented in the control room and compared to each test condition. However, due to the lower than expected OptiCap solvent corrosion rate, the ER probe response time was not sufficient during a three-month test campaign to observe significant differences in corrosion rates using the ER probe technique.

In addition, B&W PGG installed WL coupons at twelve locations throughout the PSTU to characterize the corrosion mechanisms at different areas of the process. At each location where a weight loss coupon holder (Figure 3b) was installed, two carbon steel (CS) 1018 and two stainless steel (SS) 316L coupons were utilized. At six of these locations, a CS ER probe was mounted, while a SS316L probe was installed at the cross heat exchanger outlet. Figure 4 shows one location.

Weight loss analysis is the simplest and most-established method of estimating corrosion losses. A specimen/coupon of the metal or alloy under consideration with known surface area is initially weighed and introduced into the process. After the coupon is exposed to the process for a specified time interval (minimum of 30 days), the specimen is chemically cleaned of all corrosion products and reweighed. The weight loss is then converted to a corrosion rate (CR).

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

The highest measured carbon steel CR, 17 mils per year (mpy), was observed in the regenerator tower as expected. Outside of the regenerator, the measured carbon steel corrosion rates were below 10 mpy. However, some instances of mild CO_2 pitting were observed.

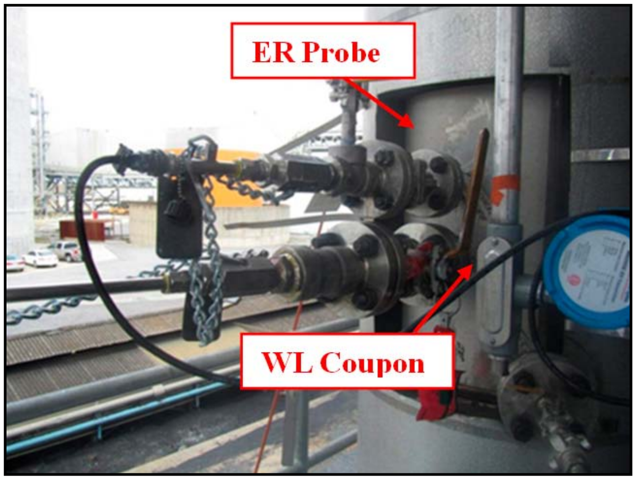


Fig. 4 Typical corrosion measurement location.

After a detailed analysis of the stainless steel WL coupons, results indicated that the highest stainless steel CR was 5 mpy. Again, the highest corrosion rates were observed in the bottom of the regenerator where the highest process temperatures existed.

Electrochemical Corrosion Test

Electrochemical corrosion testing was performed on weekly OptiCap solvent samples extracted from the PSTU to explore the corrosive behavior of the OptiCap solution under different process conditions to aid in future material selection. Variables studied included: process temperatures (similar to regenerator and absorber conditions), fresh OptiCap solutions (after preparation) as well as degraded solutions (subjected to both rich and lean CO_2 loading conditions), and dissolved metals concentration.

Analyses consisted of electrochemical corrosion screening tests using carbon steel (C1010) to evaluate the possibility of utilizing this material in areas of the CO_2 capture plant. In addition, evaluating OptiCap 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 solution samples taken over time intervals of approximately one week, to be compared amongst one another (Figure 5).

Overall, both the degraded and non-degraded OptiCap solvent solutions provided more corrosion resistance to carbon steel than 30wt% MEA, which resulted in a five times higher corrosion rate using the same test method and materials (Figure 5).

SOLVENT DEGRADATION

The degradation of the OptiCap solvent had been studied in a laboratory setting and 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 campaign.

One of the main objectives of the B&W PGG test program was to understand how the solvent changed over time and its subsequent impact on performance. To accomplish this goal, liquid samples were taken on a weekly basis, and before and after test conditions that may have a significant impact on the bulk chemical composition. The samples were refrigerated to minimize any continued chemical reactions until the samples were analyzed using various analytical techniques [anion ion chromatography (IC), cation IC, high-performance liquid chromatography (HPLC), IC-mass spectrometry (MS), liquid chromatography (LC)-MS] and developed methods.

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

The analytical chemistry analysis is still ongoing due to the complex nature of solvent degradation. Figure 6 shows a picture of sample bottles extracted from the process. The color change is one sign of solvent degradation. Early indications are the solvent degradation rate will be low as expected; however, the exact rate is still being assessed.

Despite evidence that some solvent degradation occurred throughout the test program as expected, the lowest regeneration energy values were observed at the end of the test program. This occurred because, despite some solvent degradation, many of the new compounds that were formed will still react with CO_2 showing that solvent degradation is not always negative.

Nitrosamine generation from amine solvent PCC facilities is an important topic for CO_2 capture. Nitrosamines are generated by the reaction of nitrite [anion of nitrogen dioxide (NO_2)] with a secondary amine (such as the OptiCap solvent)

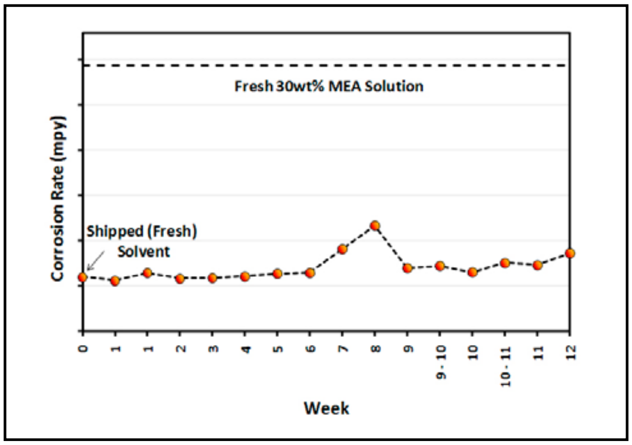


Fig. 5 LPR electrochemical comparison of 30wt% MEA and OptiCap solvent.

Fig. 6 OptiCap solvent samples.

in the absorber vessel. This reaction is expected to achieve one hundred percent conversion in a PCC process.

Equation 2: Generic Nitrosamine Reaction

$$\textit{Secondary Amine} + NO_2 \rightarrow \textit{Nitrosamines}$$

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[2] 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 3.

Equation 3: Proposed OptiCap Solvent Reaction and Degradation

$$OC + NO_2^- \xrightarrow{k_1} Nitrosamine \xrightarrow{k_2} Byproducts$$

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.

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.

Using the data from NCCC, a prediction model was developed by B&W PGG for liquid nitrosamine concentration. The results of the prediction model compared to the actual nitrosamine concentration are shown in Figure 7.

Figure 7 shows that the nitrosamine concentration in the liquid phase was predictable. The above section discussed liquid phase results. Based on results highlighted in the following section, nitrosamines were observed in only one gas phase sample, and the concentration was less than 0.1 ppbv.

GAS EMISSIONS CHARACTERIZATION

A PCC process is used to capture CO_2 in the flue gas that would typically be vented to the atmosphere. Thus, during the process of capturing the CO_2, it is important that additional contaminants are not released to the environment. Therefore, to characterize the chemical composition of the gas stream exiting the PCC 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, and nitrogen dioxide. The levels of NO and NO_2 were expected to be below the detectable limits, but the FTIR was expected to be able to quantify the concentration of the other species.

In addition, B&W PGG worked with Southern Research Institute (SRI) to iso-kinetically collect four gas and entrained condensate samples at the wash tower outlet. The gas samples were passed through a condenser with ice water to knock out entrained droplets (condensables). The collected liquid was gathered, weighed, and analyzed using standard EPA methods. A portion of the remaining vapor sample flowed through 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.

To ensure sample integrity, the sampling train was covered during collection. The sorbent tubes designed to capture nitrosamines were shipped to their respective laboratories in amber vials or wrapped in aluminum foil.

When the gas and condensable samples were analyzed, nitrosamines were observed in only one of the four samples and the concentration was below 0.1 ppbv. Any nitrosamines that may have been present in the other four samples were below detectable limits.

A trend that was observed from both the FTIR and isokinetic data was that the OptiCap solvent emissions were higher than expected. It was also observed that the emissions increased with boiler load, indicating that aerosols were increasing the emissions. In addition, emissions increased with decreased wash tower outlet temperatures due to fogging in the wash tower. This same trend has been observed in other recent pilot studies on various solvents.[3] Engineered solutions can be used to address these issues, but further evaluation is required to identify the best option.

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

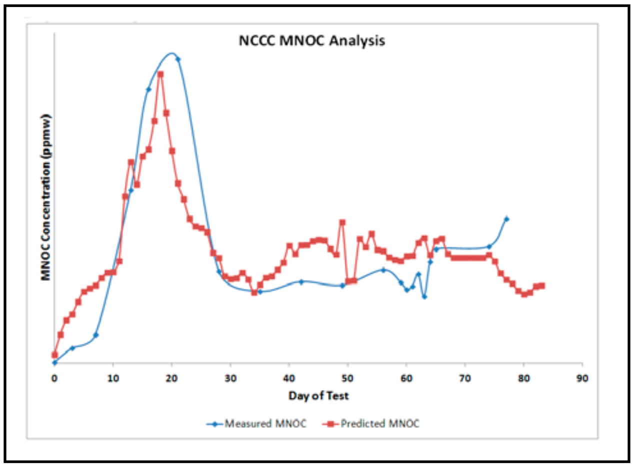


Fig. 7 Liquid nitrosamine prediction model.

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.

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.

Experiencing these departures from normal operation allowed testing of the protocols B&W PGG had previously developed to handle various possible upsets while operating a PCC facility. All the enacted protocols worked effectively and allowed the system to quickly return to normal operation when the upset was resolved.

FUTURE WORK

The NCCC campaign was a very successful and important experience. As expected with an extensive field test campaign, many important questions materialized during the data analysis phase. Further work is suggested in the following areas:

- An extended test run longer than six months is required to better characterize the solvent degradation rate and composition because the OptiCap solvent degradation reactions are relatively slow.
- Another test should be completed to verify gas phase nitrosamine emissions. The PSTU was not originally designed or equipped for a thorough nitrosamine test. Equipment to analyze the NO_2 in the inlet gas is being installed, which will provide further understanding. Also, weekly iso-kinetic samples should be extracted at the wash tower outlet to better characterize the gas phase emissions.
- The concentration of aerosols in the inlet and outlet gas should be measured to verify the correlation between aerosol concentration and amine emissions.
- The OptiCap solvent performance, corrosivity and degradation indicate that this solvent should be tested at a commercial-scale demonstration. This will also provide a long-term test location to further characterize the solvent degradation rate.
- Due to the OptiCap solvent's high resistance to oxidative degradation, it should be a suitable candidate for treating the flue gas from a natural gas combustion process. This should be evaluated at pilot scale.

SUMMARY

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.
- Early 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 the inlet NO_2 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.

ACKNOWLEDGEMENTS

A special thanks to the following organizations for helping make this test program a success:

- U.S. Department of Energy
- Southern Company Services
- Southern Research Institute
- National Energy Testing Laboratory
- Electric Power Research Institute
- National Carbon Capture Center Partners

REFERENCES

1. Gayheart, J.W., Moorman, S.A., Parsons, T.R., and Poling, C.W., "B&W PGG's Demonstration-Ready RSAT™ Technology for Post-Combustion Carbon Capture," Clearwater Clean Coal & Fuel Systems Conference, Clearwater, Florida, June 5-6, 2011.
2. Fine, N., "Formation and Decomposition of N-Nitrosopiperazine in CO_2 Capture," Luminant Carbon Management Program 4th Quarter Report 2011, University of Texas, Austin, Texas, 2011, pp. 307-313.
3. Huizinga, Kester, Kakharia, Tuinman, van Os, Goetheer, and van der Gijp, "Emission Reducing Technologies Aerosols," UTCCS-1, Austin, Texas, January 25-27, 2012.

Copyright© 2012 Babcock & Wilcox Power Generation Group, Inc.
All rights reserved.

No part of this work may be published, translated or reproduced in any form or by any means, or incorporated into any information retrieval system, without the written permission of the copyright holder. Permission requests should be addressed to: Marketing Communications, Babcock & Wilcox Power Generation Group, Inc., P.O. Box 351, Barberton, Ohio, U.S.A. 44203-0351. Or, contact us from our website at www.babcock.com.

Disclaimer

Although the information presented in this work is believed to be reliable, this work is published with the understanding that Babcock & Wilcox Power Generation Group, Inc. ("B&W PGG") and the authors and contributors to this work are supplying general information and are not attempting to render or provide engineering or professional services. Neither B&W PGG nor any of its employees make any warranty, guarantee, or representation, whether expressed or implied, with respect to the accuracy, completeness or usefulness of any information, product, process, method, or apparatus discussed in this work, including warranties of merchantability and fitness for a particular or intended purpose. Neither B&W PGG nor any of its officers, directors, or employees shall be liable for any losses or damages with respect to or resulting from the use of, or the inability to use, any information, product, process, method, or apparatus discussed in this work.