Evaluation of Concentrated Piperazine for CO_2 Capture from Coal-Fired Flue Gas

NCCC Report

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Executive Summary

URS Group Inc., the University of Texas (UT) at Austin, and Trimeric Corporation are investigating the use of piperazine (PZ) solvent coupled with a novel solvent regeneration system to capture CO_2 from coal-fired flue gas. The investigation is being conducted as part of Department of Energy (DOE) Cooperative Agreement DE-FE0005654, "Evaluation of Concentrated Piperazine for CO_2 Capture from Coal-Fired Flue Gas". This document summarizes one component of the scope funded under the cooperative agreement: a test conducted at 0.5-MW (gross) scale at the National Carbon Capture Center (NCCC) of 30% (5 molal or 5*m*) PZ coupled with the existing NCCC absorber and a regeneration skid with an Advanced Flash Stripper (AFS) designed, built and integrated for this testing, as shown in Figure 1.

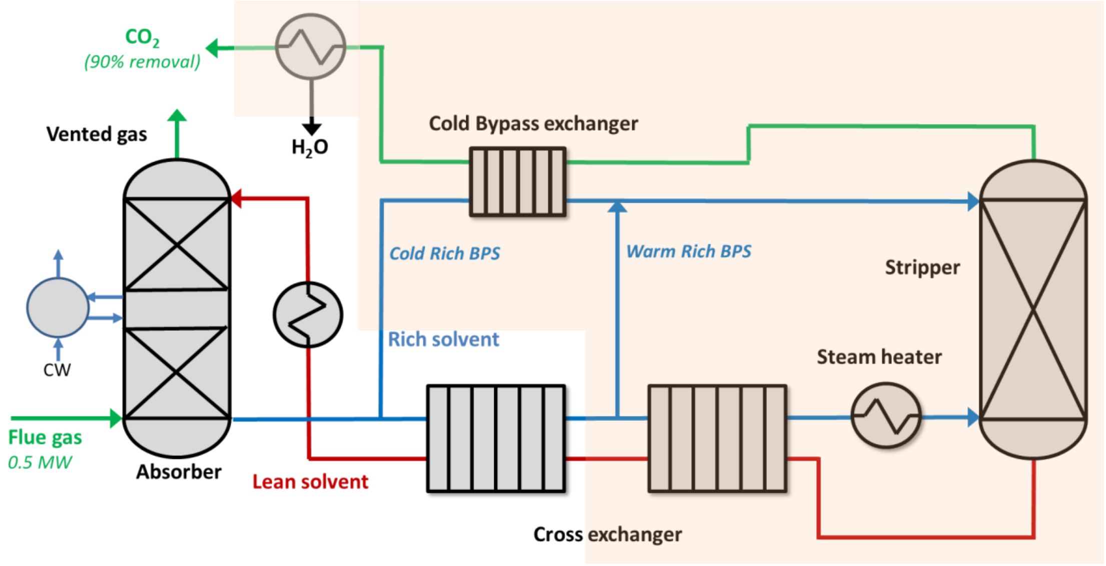

Figure 1. Process Flow Diagram of the AFS Integrated 0.5-MW System at NCCC (Regeneration Equipment Supplied by URS in Peach)

The purpose of the project was to gain operational experience with PZ in coal-fired flue gas, investigate a novel process design for high-temperature flash solvent regeneration (AFS) and compare the AFS performance to a typical simple stripper (SS) regeneration process. Approximately 2000 hours of testing was conducted on the PZ campaign at NCCC, with testing broken into four phases, as shown in Table 1.

Table 1. PZ NCCC Testing Timeline and Goals

Test Phase	Dates Tested	Hours Tested	Goals
Start-up	12/12/17 – 2/22/18	--	Measure heat loss with water operation Load solvent into the pilot system Gather operational experience
Parametric AFS	2/23/18 – 4/12/18	550	Explore factorial matrices for AFS and absorber Optimize energy performance
Parametric SS	4/18/18 – 6/4/18	340	Compare AFS to SS under similar operating conditions
Long-term AFS	6/5/18 – 8/15/18	1250	Quantify performance over long-term Demonstrate system reliability Measure and manage solvent degradation Measure and manage aerosol formation

As shown in Table 2, the PZ/AFS testing achieved the lowest heat duties for 90% CO_2 capture of any reported test campaign at NCCC with an AFS long-term testing heat duty of 1.9 – 2.3 GJ/tonne (an average of 2.1 GJ/tonne CO_2). Reported heat duties have not yet been corrected for heat loss, and are conservative as compared to the actual heat duty. The heat duty for the PZ/AFS testing was also significantly lower than for the PZ/SS testing. PZ/AFS testing also achieved 99% CO_2 removal at 2.3 GJ/tonne CO_2, only a 10% increase in heat duty from 2.1 GJ/tonne CO_2 at 90% removal. The AFS provides a design advantage over the SS because it recovers the latent heat of water vaporization and reduces the energy consumption for solvent regeneration. The AFS also offers a smaller footprint and lower capital cost than a conventional SS. The high pressures possible with the AFS design reduce the stripper diameter and footprint. In commercial applications, the stripper can be designed to match the available steam temperature and pressure, and the increased stripper overhead gas pressure can result in a reduced compressor capital cost.

Table 2. Heat Duty of Campaign at NCCC for 90% CO2 capture

Test Phase	Heat Duty (GJ/tonne CO_2)
URS Group PZ/AFS Long-Term Testing	1.9 – 2.3
URS Group PZ/SS Parametric Testing	3.4 – 4.0
Other Technology Developers (SS)	2.4 – 2.7

The PZ solvent has several advantages over MEA as an amine-based carbon capture solvent, including resistance to oxidative degradation, lower amine volatility, and a lower corrosivity to carbon steel. At a 5*m* concentration, PZ can be readily managed to avoid solids precipitation. Over long-term PZ/AFS testing at NCCC, the project successfully demonstrated all of these solvent characteristics. Solvent degradation was low, with an average of less than 0.2 lbs/tonne CO_2 removed as measured via ammonia emissions from the absorber. PZ solvent atmospheric emissions from the water wash outlet in the presence of up to 2 ppm SO_3 in the flue gas were reduced to < 1 ppm by managing absorber and water wash operating conditions. Stainless steel coupons indicated good corrosion resistance at cold locations but were worse in some instances at hot locations. Carbon steel corrosion coupons showed low corrosion rates at most locations, with higher corrosion at the hot lean location. There is a potential for equipment cost savings by using carbon steel materials of construction at these locations and reducing the surface area of equipment and piping that requires stainless steel materials of construction, though more testing is needed to confirm corrosion rates over prolonged operation beyond this three month campaign.

To manage the risk of solids formation in the PZ solvent, 5*m* PZ (instead of more concentrated 8*m* PZ) was used, and the solvent was stored in the CO_2 rich-phase (where PZ has a much wider solubility envelope). Two PZ solids precipitation events were experienced during operations; however, neither occurred during operation of the AFS within the designed operating window. The project also achieved high reliability despite six unit shutdowns external to the PZ/AFS system, with no shutdowns due to solids precipitation or any other aspect of the PZ/AFS design during normal operating conditions.

NCCC pilot plant testing has demonstrated that the AFS process configuration provides significant improvements in energy performance over the conventional simple stripping configuration for PZ and other solvents, and approaches the DOE's economic targets for second generation carbon capture technologies. In addition, extended testing allowed the project team to demonstrate reliable long-term operation of this novel regeneration technology and solvent combination.

Introduction

URS Group Inc., the University of Texas (UT) at Austin, and Trimeric Corporation are investigating the use of piperazine (PZ) solvent coupled with a novel solvent regeneration system to capture CO_2 from coal-fired flue gas. The investigation is being conducted as part of Department of Energy (DOE) Cooperative Agreement DE-FE0005654, "Evaluation of Concentrated Piperazine for CO_2 Capture from Coal-Fired Flue Gas". This document summarizes one component of the scope funded under the cooperative agreement: a test conducted at 0.5-MW (gross) scale at the National Carbon Capture Center (NCCC) of 30% (5 molal, or 5*m*) PZ coupled with the existing NCCC absorber and a regeneration skid with an Advanced Flash Stripper (AFS) designed, built and integrated for this testing, as shown in Figure 1 below.

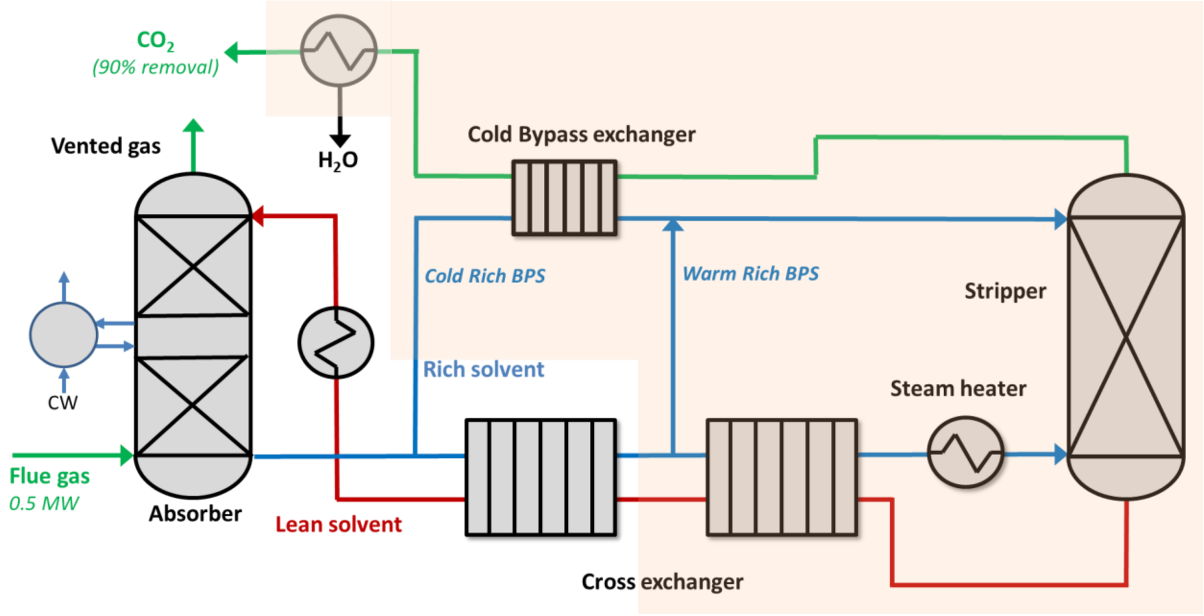

Figure 2. Process Flow Diagram of the AFS Integrated 0.5-MW System at NCCC (Regeneration Equipment Supplied by URS in Peach)

Due to the fast reaction rate of PZ, low volatility and viscosity, good energy performance and resistance to thermal degradation and oxidation, concentrated (30-40 wt%) PZ aqueous solution has been previously tested for amine scrubbing at The University of Texas Separation Research Program (UT-SRP) pilot plant and the Tarong CO_2 capture pilot plant in Australia over a wide range of operating conditions and flue gas compositions. The Advanced Flash Stripper (AFS) with cold and warm rich solvent bypass has been studied and proven at the UT-SRP with PZ.

The purpose of the NCCC testing was to gain operational experience with PZ in coal-fired flue gas and investigate a novel process design for high-temperature flash solvent regeneration (AFS) and compare the AFS performance to a typical regeneration process using a simple stripper (SS). The first objective was to quantify and demonstrate the robustness of concentrated PZ with coal-fired flue gas in an integrated absorption/stripping system with solvent regeneration at 150°C. The second objective was to validate equipment design and determine the energy performance of the AFS alternative regeneration configuration. Testing at NCCC provided operational experience and energy balance data for the AFS configuration and was compared to the NCCC standard SS configuration. The third objective was to identify and resolve other operational and design issues including aerosol formation, oxidation, process control, corrosion, and solids precipitation. As detailed below, the test objectives were addressed through parametric and long-term testing of the PZ solvent at NCCC with the AFS equipment. Testing was also conducted on the SS equipment to compare to parametric testing conditions with the AFS equipment.

Testing at the NCCC facility will be used to develop the protocols to operate this process in an industrial environment. The results will also be used to evaluate the technical and economic feasibility of a full-scale implementation of the process.

NCCC Test Matrix

For PZ/AFS testing at NCCC, the project team integrated the AFS equipment into the existing NCCC pilot solvent test unit (PSTU). The AFS skid equipment included the AFS, a lean-rich solvent heat exchanger, a steam heater, a cold bypass exchanger and the AFS overhead condenser. Some existing equipment from the PSTU was used during AFS testing, including the absorber and absorber intercooler, wash tower, mist separator, solvent storage tank, solvent pump, a lean-rich solvent heat exchanger and lean solvent trim cooler. The existing NCCC PTSU system was modified to change the existing lean solvent storage tank to a rich solvent storage tank. The absorber was also modified to allow the 2nd bed intercooler to serve as a water wash. The NCCC PSTU with AFS configuration is shown in Figure 3 below. During SS testing, the existing SS from the PSTU was used instead of the AFS.

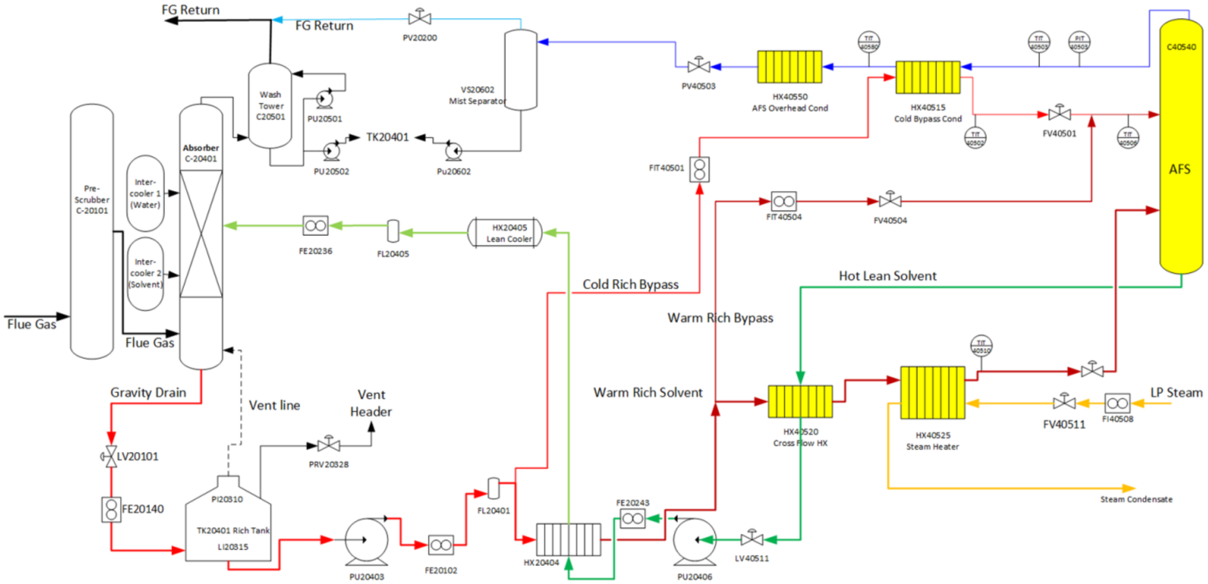

Figure 3. NCCC Test System with Existing Equipment and Project Added Equipment (Yellow)

The test program began with commissioning, and operational development, followed by parametric testing on the AFS and SS systems and long-term testing of the AFS system and solvent, as shown in Table 3 below. The actual calendar length of testing was determined by availability of the host site and was subject to outages. Adjustments to the AFS were also made after initial commissioning and heat loss test based on the results of this testing, and included removal of a steam pressure valve to increase the available steam pressure, removal of the steam strainer due to particulate collection and addition of a gravity drain to the absorber in case of emergency.

Table 3. Outline of Test Program

Item	Purpose	Approximate Duration
Commissioning	**Water Leak and Heat Test** Troubleshoot any equipment issues Learn to operate basic controls with water Heat loss test and energy balance measurements **Load PZ into system** Achieve target composition of solvent (PZ, CO_2) **Operational Development** Operate basic controls with solvent Optimize controls for stable operation Minimize solvent inventory	1 week
AFS Parametric Testing	Test full range of AFS and absorber operating conditions Optimize and validate AFS and absorber process and equipment performance	2 weeks
SS Parametric Testing	Test full range of SS operating conditions Validate and optimize SS process and equipment performance	2 weeks
Long-term AFS Operation	Demonstrate reliable operation at an optimum condition Determine effects of SO_3 aerosol on baseline emissions Test performance optimizations including N_2 sparging, AFS level optimization and pre-scrubber optimization	6 weeks

Commissioning

Commissioning included the start-up of the system, followed by PZ loading and dilution, and operational development to ensure that the system could accommodate the range of parametric testing conditions.

During start-up, the integrated AFS and PSTU system were checked for leaks with water circulation and pressurization testing up to 54 psig. Then a heat loss test was conducted to quantify the heat losses to the ambient at controlled conditions so that PZ energy performance could be accurately quantified. During commissioning, the solvent was prepared to the desired 5*m* concentration from solid 68 wt.% PZ that had been delivered in a tank. The solid 68 wt.% PZ was heated above its melting point, offloaded into the main solvent circulation loop, diluted to a 30 wt.% concentration, and loaded with CO_2 from flue gas. Operational development tasks included establishing and tuning control parameters, confirmation of the design conditions, and exploration of the operating boundaries.

Advanced Flash Stripper Parametric Testing

The objectives of the PZ/AFS parametric testing were to (1) determine operating conditions for long-term testing and future scale-up, and (2) evaluate the full operating window of the system. A range of AFS operating conditions, as summarized in Table 4, were evaluated for their energy performance and operational viability. The following variables were adjusted to achieve these operating conditions: AFS sump temperature, AFS overhead pressure, rich solvent flow rate, cold and warm rich bypass flow rates, and gas and absorber temperatures. The AFS sump level was kept at 80% during this portion of testing to increase solvent residence time at elevated temperatures and intentionally accelerate degradation of the solvent.

Table 4. AFS Parametric Operating Ranges

Variable	Value Varied	Unit
% CO_2 Removal	90-99	%
Rich Solvent Loading	0.38-0.41	[mol CO_2/mol N] *
Lean Solvent Loading	0.21-0.27	[mol CO_2/mol N]*
Gas Rate	4000-5100	lb/hr
AFS Sump Level	80	%

* 2 mol of CO_2 reacts with 1 mol of PZ

Simple Stripper Testing

The primary objective of SS parametric testing was to compare the energy performance of the SS at operating conditions that were directly comparable to the AFS. Both regeneration systems were tested with 5m PZ over the parametric test ranges shown in Table 5.

The parametric test matrix for the SS was designed to test over a range of CO_2 removal rates, rich and lean solvent loadings, and flue gas flow rates. The energy performance and operability of the system was documented for each test matrix condition. To achieve the desired test conditions, the SS sump temperature, SS overhead pressure, rich solvent flow rate, and gas and absorber temperatures were varied.

Table 5. SS Parametric Testing Ranges

Variable	Value Varied	Unit
% CO_2 Removal	90-95	%
Rich Solvent Loading	0.38	[mol CO_2/mol N]*
Lean Solvent Loading	0.21-0.24	[mol CO_2/mol N]*
Gas Rate	4000-5100	lb/hr

*2 mol of CO2 reacts with 1 mol of PZ

Advanced Flash Stripper Long-Term Testing

The test condition for long-term testing is shown in Table 6; it was chosen by identifying the conditions that achieved an optimum for energy performance and operability during AFS parametric testing. The solvent was analyzed for degradation throughout long-term testing; degradation was reduced by decreasing level in the AFS and sparging nitrogen into the rich solvent storage tank to reduce dissolved oxygen concentration in the solvent.

Table 6. AFS Long-Term Testing Conditions

Variable	Value Varied	Unit
% CO_2 Removal	90	%
Rich Solvent Loading	0.38	[mol CO_2/mol N]*
Lean Solvent Loading	0.24	[mol CO_2/mol N]*
Gas Rate	4000-5000	lbs/hr
AFS Sump Level	15	%

*2 mol of CO2 reacts with 1 mol of PZ

SO_3 Injection Testing

The Plant Gaston flue gas that was the source gas for the pilot unit at NCCC had low concentrations of SO_3 in the flue gas. A recent upgrade at Plant Gaston implemented an improved bag filter with $Ca(OH)_2$ alkaline sorbent and activated carbon injection, which has been effective in reducing SO_3 concentrations in the flue gas. Because other coal-fired power plants may have significantly higher SO_3 concentrations than Plant Gaston, an SO_3 injection parametric test was conducted during brief periods of the long-term test to determine the effect of SO_3-induced aerosols on PZ emissions from the absorber. Absorber intercooler temperature, lean solvent temperature and absorber 3rd bed water wash flow, were varied to evaluate their effectiveness in reducing PZ emissions.

Measurements

A variety of measurements were made to monitor the performance of the PZ-AFS technology, as shown in Table 7. These measurements allowed the team to monitor corrosion, solvent degradation and oxidation, aerosol emissions, energy performance and, solvent concentration and solvent loading.

Emissions measurements were recorded throughout the test program using two Fourier Transform Infrared (FTIR) analyzers to monitor gas-phase amine and ammonia emissions. The FTIR measurements also validated the CO_2, SO_2, and H_2O data reported by the NCCC online analytical instruments. During SO_3 aerosol testing, the FTIR and an Electrical Low Pressure Impactor (ELPI) aerosol measurement device measured the gas phase aerosols generated during the test; sorbent tubes measured PZ gas-phase byproducts.

CO_2 and PZ concentrations in the solvent were inferred from a correlation based on continuous on-line measurement of temperature, viscosity and density. These concentrations were cross-checked using on-line, semi-continuous, acid-based titration. Intermittent liquid samples were collected and analyzed offline via gas chromatography (PZ) and a total inorganic carbon analyzer (CO_2). Periodic liquid samples were collected and analyzed offline for PZ and degradation product concentrations by ion chromatography (IC), Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES), and High-Performance Liquid Chromatography (HPLC) at the UT laboratories.

Electrical resistance corrosion probes and corrosion coupons were inserted at several locations in the system to measure corrosion and provide data to guide future equipment materials specification.

Table 7. Sampling and Measurements Locations, Methods and Frequency

Measurement	Locations	Measurement Method	Measurement Frequency	Purpose
Gas-Phase NH_3, Amines, CO_2, SO_2, H_2O	Water wash outlet, absorber gas outlet, mid-bed absorber, absorber gas inlet	FTIR	Continuous (required daily calibration)	Measure solvent emissions, compare to PLC flue gas data
Weight Loss (WL) Corrosion Coupons (C1010, 316L, 304)	Absorber sump, absorber mid-bed (2), absorber top, cold lean solvent, hot lean solvent, water wash, mist eliminator, rich solvent, warm rich bypass, cold rich bypass, absorber sump	SEM/XRD, weight	Installed and removed during plant outage	Monitor corrosion, determine appropriate materials of construction (MOC) for larger-scale installations
Electrical Resistance (ER) Corrosion Probes (C1010)	Absorber sump, absorber mid-bed, cold rich bypass, warm rich bypass, rich solvent, hot lean solvent	Resistance/PLC	Continuous	Monitor corrosion, determine appropriate MOC for larger-scale installations (duplicate measurement to coupons)
Gas-Phase Aerosols	Water wash outlet	ELPI	Daily during SO_3 testing	Measure PZ aerosol density as created by SO_3 in flue gas
Gas-Phase Aldehyde, Ammonia, Ketones, Amine, Nitrosamine	Water wash outlet	SKC Tubes	2 times during SO_3 testing	Measure vapor-phase products, generated from PZ aerosols as created by SO_3, in flue gas and baseline
Amine Concentration	Absorber intercooler, absorber outlet, wash tower	GC, Auto-Titrator	Daily/condition change	Monitor PZ concentration in system
CO_2 Concentration	Absorber intercooler, absorber outlet, wash tower	TIC, Auto-Titrator	Daily/condition change	Monitor CO_2 loading in system
Sulfite, thiosulfate	Pre-scrubber	Titration	Weekly as needed	Monitor pre-scrubber performance for removal of NO_2
Density/Viscosity	Lean solvent, rich solvent	Viscometer	Continuous	Monitor PZ concentration and CO_2 loading in system

Results

Operational Performance

The PZ/AFS test campaign exhibited process stability over a wide variety of operating conditions. The campaign also demonstrated high reliability of the PZ/AFS process through six unit shutdowns that were the result of causes external to the PZ/AFS testing system. No shutdowns occurred due to the PZ/AFS design during normal operating conditions.

To manage the risk of solids formation in the PZ solvent, 5*m* PZ (instead of more concentrated 8*m* PZ) was used, and the solvent inventory was stored in the rich phase where PZ has a much wider solubility envelope. The risk of solids formation was also reduced by maintaining lean loading equal to or greater than 0.24 mol CO_2/equiv PZ. At this lean conditions solids precipitation will not occur at temperatures greater than 20°C. Two PZ solids precipitation events were experienced during operations; however, neither occurred during operation of the AFS within the designed operating window. The conditions that caused PZ solids precipitation were not ones that would be seen in commercial operation, including during start-up, shutdown or other non-standard operation conditions. No solids precipitation occurred during unit shutdowns, with successful gravity drain of the inventory to the rich storage tank in the solvent circulation loop in all instances. CO_2-loaded solvent inventory was successfully prepared on-site from solid 68 wt % PZ.

Solvent Degradation

The test program began with a period in which solvent degradation was accelerated by operating with a high AFS sump level. Once the AFS sump level was decreased for long-term testing, thermal and oxidative degradation were successfully reduced. Unlike MEA, PZ does not directly oxidize at absorber conditions. However, PZ will react with NO_2 to make nitrosamine, which thermally degrades in the AFS and contributes to oxidation of the PZ. For most of the campaign, the inlet NO_2 concentration was low (i.e., not measurable) at the inlet to the PSTU due to recent upgrades at Plant Gaston, which implemented an improved bag filter with $Ca(OH)_2$ alkaline sorbent and activated carbon injection. However, there were some intermittent issues with high NO_x and SO_3 emissions due to load changes or process upsets at Plant Gaston. The effects of the increased emissions were not noticed directly, though they may have contributed to slightly higher solvent degradation rates. For the second half of the test campaign, thiosulfate was added to the pre-scrubber; the thiosulfate was added to attempt to mitigate the increased NO_x concentrations in the flue gas from Plant Gaston. However in the second half of testing, no high NO_x events were observed, so it is not clear whether the thiosulfate addition would have impacted NO_x concentrations in the flue gas to the PSTU.

PZ also reacts with dissolved oxygen at elevated temperatures, and it reacts with Fe^{+3} in degraded solution in the AFS sump. The majority of the dissolved oxygen was stripped out of the rich solvent due to flashing in the hot exchanger before it reached the hot sump of the AFS, which limited PZ oxidation by dissolved oxygen. In the second half of the campaign, the testing team attempted to reduce the potential for further limit oxidation by reducing the level in the AFS sump to 15%, sparging the bottom of the absorber sump with nitrogen to remove dissolved oxygen, and adding thiosulfate to the SO_2 pre-scrubber to promote NO_2 removal; with all three methods of oxidation reduction, the data indicate that there was a decrease of degradation products in the solvent corresponding in time to introduction of these methods.

As the oxidation of one mole of PZ produces one mole of ammonia, ammonia concentration was used as a direct indicator of oxidation in the solvent. As shown in Figure 4, the ammonia concentration in the outlet gas from the absorber water wash averaged 6 ppmv, or 0.17 lb/tonne CO_2 removed. Around 2000 hours of testing, the oxidative degradation began to increase, which may be caused by the increase of degradation products in the solvent as testing goes on; however this potential cause is still being investigated. Further testing would be needed to determine if the degradation rate continued to increase with degraded PZ solvent.

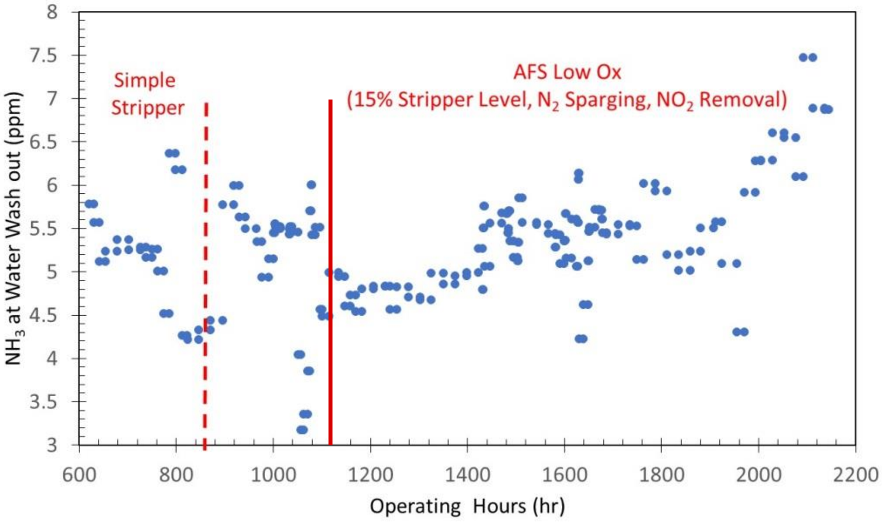

Figure 4. Ammonia Emissions (Measured by FTIR; Indicator of Oxidation)

The total formate concentration, a primary thermal degradation product for PZ solvent, was used as an indicator of the relative concentration of degradation products in the solvent. As shown in Figure 5, the accumulation of formate, and thus degradation of the PZ, was significantly lower at NCCC compared to previous pilot campaigns using PZ solvent with coal-fired flue gas at Pilot Plant 2 (PP2) and Tarong. This decreased oxidation is a result of reduced concentrations of NO_2 in the NCCC host plant flue gas; in contrast, PP2 and Tarong flue gases contained up to 1–5 ppmv NO_2. Degradation product concentrations in the PZ solvent during NCCC testing were much more comparable to the UT-SRP testing, which contained no NO_2 in the flue gas. The stabilization of formate concentration in the second half of the NCCC testing seems to have been caused by the oxidation mitigation techniques implemented in the second half of the campaign, as described above.

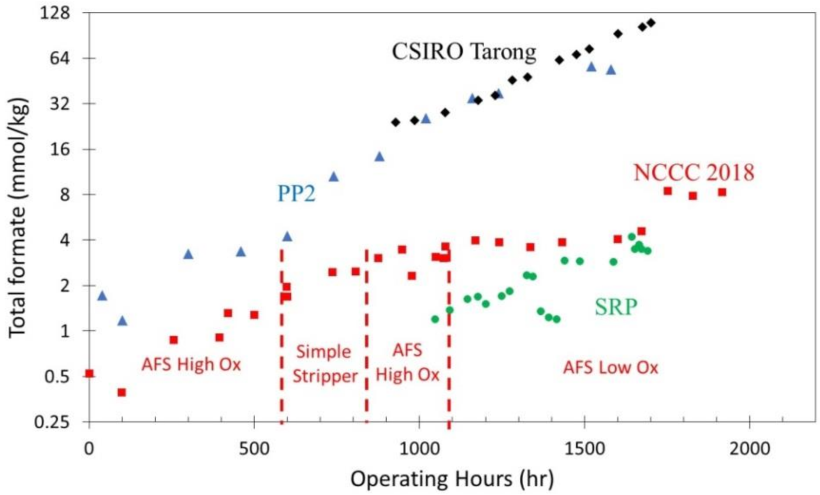

Figure 5. Accumulation of Total Formate (Indicator of Thermal Degradation Products) in the PZ Solvent at NCCC and Other Campaigns

Solvent Emissions

Although the boiling point of PZ is lower than MEA solvent, it interacts strongly with water at the lean loading conditions within the absorber to produce a lower volatility compound, which reduces the potential for aerosols. However, significant concentrations of SO_3 aerosol in the host plant flue gas can encourage the growth of PZ aerosols in the absorber, which can then increase PZ emissions in the outlet gas. Throughout much of the campaign, aerosol emissions were low because the host power plant was using a newly installed bag filter to collect SO_3 aerosols.

During AFS long-term testing, 1 to 10 ppm SO_3 was injected into the flue gas before the direct contact cooler to measure the effect on solvent emissions. Figure 6 illustrates that the outlet PZ emissions were reduced by increasing the lean solvent temperature, which increased the temperature at the top of the absorber. A third section of existing packing in the absorber was commissioned as an additional stage of water wash with a pump-around loop, which also decreased the overall PZ emissions. The elevated temperature in the top of the absorber and the greater residence time in the water wash resulted in a greater growth of aerosol, and larger aerosols were removed more effectively in the water wash section of the column. By manipulating absorber and water wash operating conditions, solvent emissions in the outlet gas were successfully managed within a range of 0.5 – 5 ppm PZ, at corresponding inlet flue gas concentration of 0 – 4 ppm SO_3, respectively.

For future PZ/AFS installations, 10 ft of water wash (as at the NCCC) would be sufficient if there is not a source of SO_3 or other aerosols. If moderate aerosol concentrations are expected (1-2 ppm SO_3), aerosols would be managed by feeding warmer lean solvent to the top of the column with adjustments in the water wash temperature to maintain water balance. With greater amount of aerosol nuclei (SO3 > 2 ppm), a two stage water wash analogous to the third bed pump-around loop could be used.

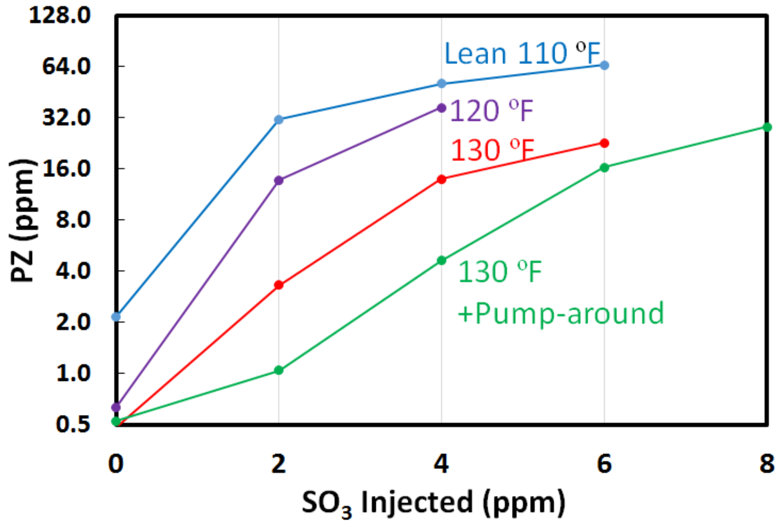

Figure 6. PZ Emissions Decreased with Increasing Lean Solvent Temp and with Pump-Around Water Wash Absorber Bed Operation

Corrosion

In previous testing with PZ, carbon steel was shown to form a protective layer of $FeCO_3$, which inhibited further corrosion in cases where it formed a complete protective layer. There is a potential for equipment cost savings for a full-scale system by using carbon steel materials of construction at some locations and reducing the surface area of equipment and piping that requires stainless steel materials of construction. To gather more corrosion data for the PZ/AFS system, carbon and stainless steel corrosion coupons (C1010, 316L, 304) and electrical resistance probes were installed throughout the PSTU and AFS skid, as shown in Figure 7 and Figure 8 below.

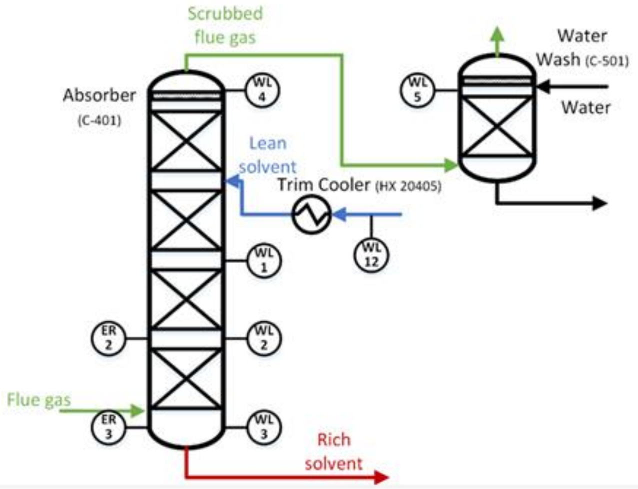

Figure 7. PFD of Absorber Corrosion Coupon (WL) and Electrical Resistance Corrosion Probe (ER) Locations

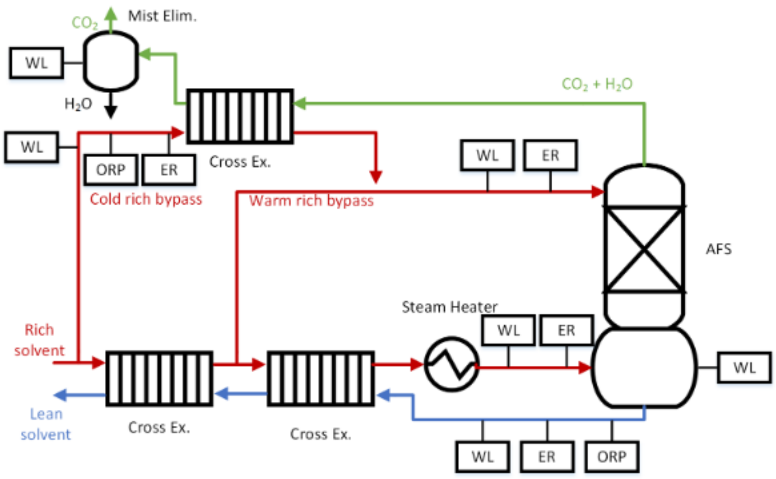

Figure 8. PFD of AFS Corrosion Coupon Locations

Analysis of the stainless and carbon steel samples throughout the system indicated mixed results depending on the location of the samples, as shown in Table 8. Carbon steel coupons showed acceptable corrosion rates (<100 µm/yr) at all locations except for the hot lean line, located in a high velocity, flashing environment. Stainless steel samples showed unacceptable corrosion rates at all hot locations (the hot rich, AFS sump and hot lean locations), probably due to the chromium oxide protective layer was reduced in the hot amine solvent. Analysis of resistance probes has shown inconsistent data with the corrosion coupons, and has been shown to be unreliable.

Table 8 gives corrosion results with coupons for 318 hours of exposure, early in the campaign.
Analysis of the stainless and carbon steel samples throughout the system indicated mixed results depending on the location of the samples, as shown in Table 8. Carbon steel coupons showed acceptable corrosion rates (<100 µm/yr) at all locations except for the hot lean line, located in a high velocity, flashing environment. Stainless steel samples showed unacceptable corrosion rates at all hot locations (the hot rich, AFS sump and hot lean locations), probably due to the chromium oxide protective layer was reduced in the hot amine solvent. Analysis of resistance probes has shown inconsistent data with the corrosion coupons, and has been shown to be unreliable.

Table 8. Corrosion of Carbon Steel (CS1010) and Stainless Steel (SS316L) Coupons with 318 Hrs of Exposure

	C1010		**SS316L**	
Location	**Rate (µm/yr)**	**Product**	**Rate (µm/yr)**	**Product**
Absorber sump	0.9	none	0.5	none
Cold rich bypass	97	Fe	--	--
Warm rich bypass	55	FeO(OH)	9.0	none
Hot rich	36	$FeCO_3$ & Fe_3O_4	630	none
AFS sump	7	$FeCO_3$	490	$FeCO_3$ or $MnCO_3$
Hot Lean	710	$FeCO_3$	1095	

In previous testing with PZ, carbon steel was shown to form a protective layer of $FeCO_3$, which inhibited further corrosion in cases where it formed a complete layer. Multiple samples showed $FeCO_3$ layers, but the AFS sump sample was the only location that likely inhibited corrosion. While the protective $FeCO_3$ layers observed on some samples and the overall low corrosion rates on carbon steel samples analyzed to date may indicate that some equipment may be able to use carbon steel material of construction, more testing is needed to provide a materials of construction recommendation.

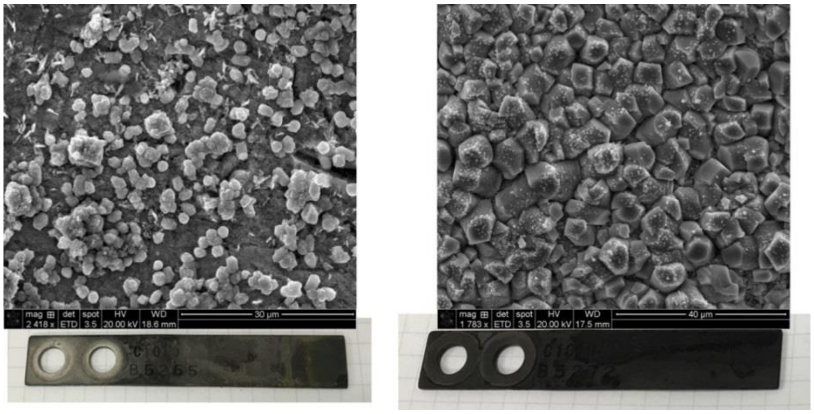

Figure 9. Protective $FeCO_3/Fe_3O_4$ Layer on Carbon Steel at 115 Hrs Exposure
(Left - Cold Rich Bypass - Incomplete Layer; Right - AFS Sump - Protective Layer)

While the partial or protective $FeCO_3$ layers observed on some samples and the overall low corrosion rates on carbon steel samples analyzed to date may indicate that some equipment may be able to use carbon steel material of construction, more testing is needed.

Energy Performance

In Figure 10, the PZ/AFS test campaign was compared to seven other second generation solvents tested at NCCC with a carbon capture rate of 90% (or greater). The other tests (which all used the SS) had estimated energy performances ranging from 2.4 to 2.7 GJ/tonne CO_2, compared to 2.1 GJ/tonne for the PZ/AFS test campaign, with parametric tests done on a 0.5-MW (gross) basis. PZ/SS has a significantly higher heat duty than tests done with other solvents on the SS at NCCC, as PZ is likely not an optimized solvent for the SS design. An explanation for why PZ performs more poorly in the SS than other solvents tested at NCCC has not yet been fully developed. However, one possible explanation is that solvents with a lower heat of absorption, such as PZ, do not perform as well in the SS. The heat duty of the AFS, which is much more independent of the heat of absorption than the SS, would not have the same effect.

UT estimated that heat losses contributed 5 to 15% of the overall energy requirements for the PZ/AFS system. If the heat losses are removed, the energy requirements for the PZ/AFS at 90% removal are reduced to 1.8 to 2.0 GJ/tonne CO_2. The AFS provides a design advantage over the SS because it recovers the latent heat of water vaporization and reduces the energy consumption for solvent regeneration. The primary heat duty with the PZ/AFS system is the heat of CO_2 desorption, which is approximately 1.4 GJ/tonne CO_2.

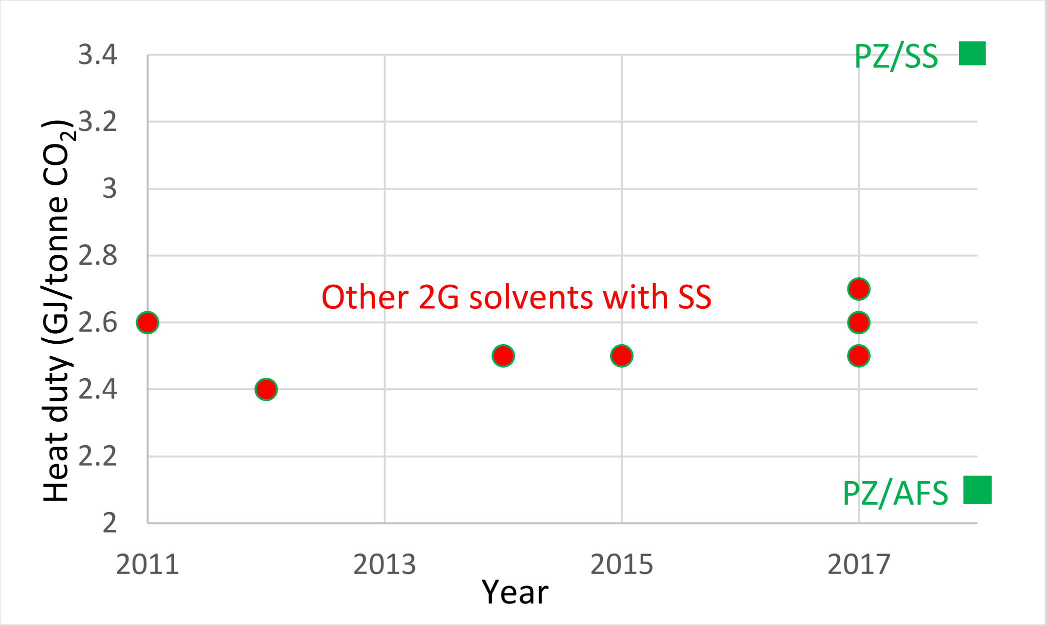

Figure 10. Heat Duty of Second Generation Solvents Tested at NCCC (90% Capture; Not Corrected for Heat Loss)

With two sections of packing (for a total of 16 m packing height) separated by in-and-out intercooling, the NCCC testing achieved 99% CO_2 removal with a steam energy requirement of 2.3 GJ/tonne CO_2, which was only a 10% increase in heat duty from 2.1 GJ/tonne CO_2 at 90% removal on a 0.5-MW (gross) basis. The relatively low energy penalty of additional CO_2 removal was expected, due to PZ solvent's fast CO_2 reaction rate compared to other aqueous solvents that have a larger penalty for additional CO_2 removal.

Conclusions

In this test program, 5*m* PZ with the AFS process configuration was demonstrated with more than 2000 hours of operation at 0.5-MW of coal-fired flue gas at the NCCC, with high reliability and without significant solids precipitation. The energy performance and operability of a variety of NCCC PZ/AFS test conditions were compared, from which a set of optimal long-term process conditions as shown in Figure 11. The PZ/AFS testing achieved the lowest heat duties for 90% CO_2 capture of any reported test campaign at NCCC with an average AFS long-term testing heat duty of 2.1 GJ/tonne CO_2 (not corrected for heat loss).

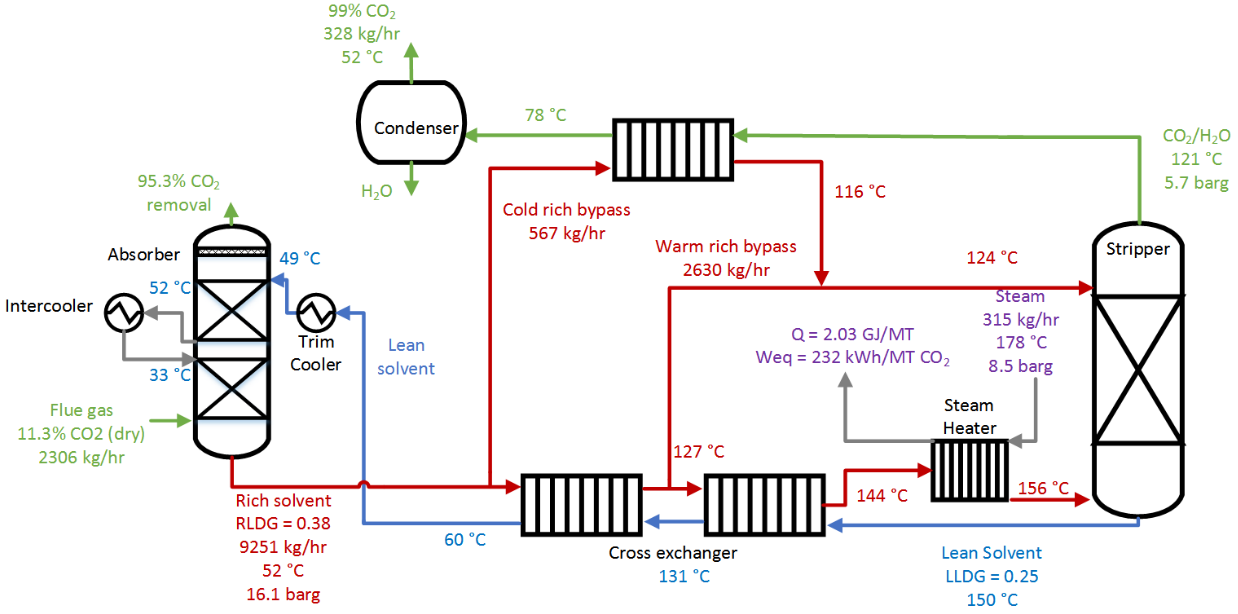

Figure 11. Optimal PZ/AFS Conditions as Determined by NCCC Testing

By manipulating absorber and water wash operating conditions, solvent emissions in the outlet gas were successfully managed within a range of 0.5 – 5 ppm PZ, at corresponding inlet flue gas concentration of 0 – 4 ppm SO_3, respectively. During testing, PZ showed good solvent characteristics, with PZ oxidation limited to less than 0.2 lb PZ/tonne CO_2, and PZ emissions managed to less than 1 ppm. Carbon steel was protected by deposition of $FeCO_3$ at some locations, possibly making it an attractive choice over stainless steel, which was less subject to corrosion in some cases and more in others, and considerably more expensive.

The AFS also offers a smaller footprint and lower capital cost than a conventional SS, as the high pressures possible with the AFS design reduce the stripper diameter and footprint. In commercial applications, the stripper can be designed to match the available steam temperature and pressure, and the increased stripper overhead gas pressure can result in a reduced compressor capital cost.

NCCC pilot plant testing has demonstrated that the PZ/AFS process configuration provides significant improvements in energy performance over the conventional simple stripping configuration for PZ and has the potential to improve the energy performance of other solvents. In addition, extended testing allowed the project team to demonstrate reliable long-term operation of this novel regeneration technology and solvent combination.