The National Carbon Capture Center at the Power Systems Development Facility

> Topical Report Budget Period Two

Reporting Period: June 1, 2015 – July 31, 2016 Project Period: June 6, 2014 – May 31, 2019



DE-FE0022596

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> DOE Cooperative Agreement DE-FE0022596

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Abstract

The Power Systems Development Facility (PSDF) is a state-of-the-art test center sponsored by the U.S. Department of Energy (DOE) and dedicated to the advancement of clean coal technology. In addition to the development of high efficiency coal gasification processes, the PSDF features the National Carbon Capture Center (NCCC) to promote new CO₂ capture technologies for application in existing coal combustion power plants and in the next generation of integrated gasification combined cycle power plants.

The NCCC includes multiple slipstream units that allow technology development of CO_2 capture concepts using coal-derived flue gas and syngas in industrial settings. Because of the ability to operate under a wide range of flow rates and process conditions, research at the NCCC can effectively evaluate technologies at various levels of maturity and accelerate their development to commercialization.

During the Budget Period Two reporting period, spanning from June 1, 2015, through July 31, 2016, efforts at the NCCC focused on post-combustion CO_2 capture, gasification, and pre-combustion CO_2 capture technology development. Testing was conducted at the NCCC's Post-Combustion Carbon Capture Center with membrane technologies, advanced solvents and solvent systems, enzymes, and aerosol mitigation equipment. The gasification process was also operated for evaluation of syngas utilization processes, advanced instrumentation, catalysts, and sorbents. Pre-combustion CO_2 capture projects tested included membrane, solvent, and sorbent technologies. Preparations for future testing were on-going and involved facility upgrades and collaboration with numerous technology developers.

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List of Abbreviations

AC-ABC	Ammonia Carbonate-Ammonium	MTR	Membrane Technology & Research
	Bicarbonate	NCCC	National Carbon Capture Center
BDU	Brownian Demister Unit	NETL	National Energy Technology
BP2	Budget Period Two		Laboratory
BPSC	Bechtel Pressure Swing Claus	OSU	Ohio State University
CCS	Carbon Capture Scientific	PC4	Post-Combustion Carbon Capture
CCSL	Carbon Clean Solutions		Center
CMS	Carbon Molecular Sieve	PCMS	Post-Combustion Membrane Skid
СО	Carbon Monoxide	PDI	Phase Doppler Interferometer
COS	Carbonyl Sulfide	PDMS	Polydimethylsiloxane
DEPG	Dimethyl Ether of Polyethylene	PO-1	Post-Combustion Runs 1 through 5
	Glycol	through 5	
DOE	Department of Energy	PRB	Powder River Basin
ELPI+	Electric Low Pressure Impactor	PSD	Particle Size Distribution
F-T	Fischer-Tropsch	PSDF	Power Systems Development Facility
FTIR	Fourier Transform Infrared	PSTU	Pilot Solvent Test Unit
	Spectrometer	SCL	Syngas Chemical Looping
G-1 through	Gasification Runs 1 through 4	SCU	Syngas Conditioning Unit
G-4		SR	Southern Research Institute
Gen-2	Generation 2	SRI	SRI International
G/L	Gas-to-Liquid Ratio	SSTU	Slipstream Solvent Test Unit
GPS	Gas Pressurized Stripping	TFE-PPZ	Poly(bis-
GPU	Gas Permeation Unit		trifluoroethoxyphosphazene)
H ₂ S	Hydrogen Sulfide	THF	Tetrahydrofuran
IGCC	Integrated Gasification Combined	TPD	Ton per Day
	Cycle	TSA	Thermal Swing Adsorber
L/G	Liquide-to-Gas Ratio	UT-Austin	University of Texas at Austin
MDEA	Methyl Diethanolamine	WGS	Water-Gas Shift
MEA	Monoethanol Amine	WPI	Worcester Polytechnic Institute
MPT	Media & Process Technology		

1.0 EXECUTIVE SUMMARY

The National Carbon Capture Center at the Power Systems Development Facility is a key component of the Department of Energy's (DOE's) strategy in promoting the United States' economic, environmental, and energy security through reliable, clean, and affordable power produced from coal. Located in Wilsonville, Alabama, the NCCC is a cost-effective, flexible test center for evaluating the critical components of advanced CO_2 capture and power generation processes from third-party technology developers, including government entities, industry, and universities. Work at the NCCC supports the development of new power technologies and the continued operation of conventional power plants under CO_2 emission constraints.

Project Partnership with DOE

The DOE Office of Fossil Energy's National Energy Technology Laboratory (NETL), in cooperation with Southern Company Services, established the NCCC in 2008 to become a cornerstone for U.S. leadership in advanced clean coal technology development. After the successful completion of the first contract period, which comprised testing and advancement of numerous CO_2 capture and gasification support technologies, the DOE renewed its support of the project with another cooperative agreement beginning in June 2014.

Reporting Period

This report covers the work performed during Budget Period Two (BP2), from June 1, 2015, through July 31, 2016, of the NCCC's second cooperative agreement with DOE, DE-FE0022596.

Project Mission and Approach

Offering a world-class neutral test facility and a highly specialized staff, the NCCC accelerates the commercialization of advanced technologies to enable fossil fuel-based power plants to achieve near-zero emissions. In undertaking its mission, the NCCC is involved in a range of activities in the areas of post-combustion CO_2 capture, gasification, and pre-combustion CO_2 capture to develop the most promising technologies for future commercial deployment.

The NCCC houses two test sites, shown in Figure 1. To develop CO_2 capture technologies for existing fossil-fueled power plants, the NCCC operates the Post-Combustion Carbon Capture Center (PC4), which utilizes flue gas from a commercially dispatched supercritical coal-fired power plant. The PC4 includes bench-scale and pilot-scale solvent test units and test bays for technology developer skids. At the original Power Systems Development Facility site, the NCCC operates its pilot Transport Gasifier plant to produce syngas for slipstream testing of gasification and pre-combustion CO_2 capture technologies at bench- and pilot-scales.



Figure 1. NCCC Facilities

1.1 Post-Combustion CO₂ Capture Accomplishments

During the reporting period, the PC4 operated in three test runs, supporting more than 10,500 hours of flue gas testing by technology developers, as listed in Table 1. Operation was conducted with bench- and pilot-scale test skids and with the NCCC's Pilot Solvent Test Unit (PSTU) and Slipstream Solvent Test Unit (SSTU). To investigate the issue of solvent emissions, aerosol sampling was conducted with specialized measurement devices, the Electric Low Pressure Impactor (ELPI+) and a Phase Doppler Interferometer (PDI). The post-combustion runs conducted in BP2 included:

- PO-3, beginning in Budget Period 1, from May 1, 2015, through August 10, 2015
- PO-4, occurring from October 10, 2015, through December 21, 2015
- PO-5, beginning on May 18, 2016, and continuing into Budget Period 3 (planned through mid-November 2016)

Table 1. Technologies Tested in Budget Period Two

Run/Venue	Technology Tested	Hours	
PO-3			
Bench-Scale	MTR 1-TPD Membrane Carbon Capture Scientific Ohio State Membrane	1,065 1,004 504	
Pilot-Scale	Linde-BASF Solvent Process MTR 20-TPD Membrane	1,170 900	
PSTU	ION Engineering Solvent	1,116	
РО-4			
Bench-Scale	NETL Membranes	148	
Pilot-Scale	Linde-BASF Solvent Process Air Liquide Cold Membrane	559 1,016	
SSTU	Commissioning with MEA Cansolv Aerosol Mitigation Processes	229 214	
Special Measurements	Amine Emissions w/ ELPI+ Amine Emissions w/ PDI	574 19	
PO-5			
Bench-Scale	Akermin Enzymes NETL Membranes	480 In progress	
Pilot-Scale	Linde-BASF Solvent Process Air Liquide Cold Membrane	1,520 In progress	
PSTU	GE Global Solvent and Desorber	In progress	

Accomplishments in the area of post-combustion CO₂ capture are listed below.

Membrane Technology & Research (MTR) 1-Ton/Day (TPD) CO₂ Membrane

MTR completed final testing on the 1-TPD membrane system in August 2015. The 2015 testing employed a new combination of high-flux Polaris cross-flow modules that yielded CO_2 enrichment from 12 percent in the feed gas to over 60 percent in the permeate, and sweep modules in the second step that produced a treated stream with 2 to 7 percent CO_2 . The modules showed stable performance despite a lengthy outage and excursions in feed temperature and flow rates. After three and half years of testing, the system achieved a total of 11,466 hours of operation with 9,100 hours on flue gas and 2,366 hours on air when flue gas was not available. Out of the 9,100 hours of testing on flue gas, 1,933 hours were conducted with simulated natural gas flue gas. Carbon capture rates of better than 90 percent were achieved with coal-derived flue gas. The test program proved valuable in guiding the design of MTR's 20-TPD membrane system and in serving as a test vehicle for second and third generation membranes following lab testing.

Carbon Capture Scientific (CCS) Gas Pressurized Stripping (GPS) Process

CCS completed testing of the novel GPS process using an amine-based proprietary blended solvent. Long-term testing was conducted in run PO-3 under optimal conditions identified during previous parametric tests. The operating conditions were maintained to achieve 90 percent CO_2 removal and 95 percent CO_2 product purity. The energy consumption of the GPS process was much lower than that of the monoethanol amine (MEA) baseline case, with the sum of reaction heat and stripping heat for the GPS process at 1,562 to 1,600 kJ/kg CO_2 captured.

Ohio State University (OSU) CO₂ Membrane

In the development of a cost-effective design and manufacturing process for CO_2 capture membrane modules, OSU completed testing with a bench-scale membrane unit. The results of the NCCC testing were promising in that they were comparable to those of OSU lab testing with simulated flue gas. The modules showed initial permeance values of about 800 gas permeation units (GPU) and CO_2 /nitrogen selectivity values of about 200, as well as pressure drops of less than 1.5 psi/m. OSU will further develop the membrane module fabrication process for improved performance and stability.

Linde-BASF Pilot Solvent Unit

After operating throughout the last three test runs at the PC4, testing of the Linde-BASF pilot unit was completed. During the overall test period, including start-up, parametric testing, and long-duration testing, the pilot plant operated for a total of 6,764 hours, out of which testing with flue gas was performed for 4,109 hours. The testing demonstrated all of the performance targets including CO₂ capture rate exceeding 90 percent, CO₂ purity exceeding 99.9 mol% (dry), flue gas processing capacity up to 15,500 lb/hr (equivalent of 1.5 MWe), regeneration energy as low as 2.7 GJ/tonne CO₂, and regenerator operating pressure up to 3.4 bar absolute. The emission control feature incorporated in BASF's patented dry bed configuration was validated during the long-duration testing. Testing also proved out the design of several unique equipment features incorporated in the pilot plant. Linde-BASF plan to further develop the process with demonstrations at other facilities.

MTR 20-TPD Membrane System

MTR successfully operated the 20-TPD system during two runs, completing testing in June, 2015. The system first operated in 2015 during run PO-2, and for PO-3 operation, a high efficiency plate-and-frame sweep membrane module was added to replace the conventional spiral-wound design. Operation in PO-3 lasted for 900 hours, exceeding the original goal of 500 hours, and demonstrating the performance of both the 20-TPD system and the plate-and-frame module skid. With the plate-and-frame modules, the system achieved CO_2 capture rates of

87 percent (and over 90 percent under certain conditions). The plate-and-frame sweep modules had roughly four times lower pressure drop than the spiral wound sweep modules, which, at a full scale of 550 MWe, amounts to an energy savings of about 10 MWe. MTR will continue developing the membrane technology at another test site.

Ion Engineering Solvent

ION Engineering's solvent was tested in the PSTU during run PO-3. ION utilized parametric testing to confirm process set points for optimal performance and primary/secondary control mechanisms. During parametric testing, ION maintained 95 percent or greater CO_2 capture throughout a range of liquid-to-gas (L/G) ratios from 2.0 to 3.5. At these conditions, regeneration energy ranged from 1,400 to 1,800 BTU/lb CO_2 . Steady state testing was conducted at an L/G ratio of 3.0 with 95 percent or greater CO_2 capture and a regeneration energy requirement of about 1,600 BTU/lb CO_2 . ION plans for further solvent testing at another facility.

NETL Membranes

NETL performed membrane testing with the Post-Combustion Membrane Skid (PCMS) to identify fabricated membranes with acceptable performance when separating CO₂ from flue gas and maintaining performance in the presence of water vapor and minor contaminants. During run PO-4, NETL operated the PCMS with several types of membrane materials, including polydimethylsiloxane (PDMS), poly(bis-trifluoroethoxyphosphazene) (TFE-PPZ), and hollow-fiber samples made from Torlon[®] and coated with TFE-PPZ based solutions. Each type of membrane was tested for about 20 hours, and results generally agreed with those obtained at NETL prior to the PCMS field trials. Testing will continue through the end of the PO-5 run.

Air Liquide Cold Membrane

Air Liquide began testing of its cold membrane process and evaluation of membrane materials. During run PO-4, the system was commissioned and operated for a total of 1,016 hours. During more than 500 hours of steady state operation, all performance goals were achieved, with a CO_2 capture rate greater than 90 percent, and CO_2 purity between 65 and 70 percent. In the PO-5 run, Air Liquide additionally tested a prototype membrane of next generation polyimide material, PI-2. The PI-2 membrane achieved eight to nine times the CO_2 permeance of the commercial bundle, and demonstrated stable CO_2 recovery and purity over more than 700 hours of operation, which included multiple shutdowns. Operation is planned to continue through the end of the PO-5 run.

Slipstream Solvent Test Unit

Commissioning of the SSTU with MEA solvent began in late November 2015. Following the run, modifications to the system were implemented for operational improvement. MEA baseline testing will resume in late 2016 during the PO-5 run.

Cansolv Technologies Aerosol Mitigation Technologies

Two processes from Cansolv Technologies, a Thermal Swing Adsorber (TSA) and a Brownian Demister Unit (BDU) were installed on the Slipstream Solvent Test Unit. The processes were

designed to mitigate amine losses in a carbon capture process by reducing the formation of amine containing aerosols. Initial testing was conducted in December during run PO-3 while the SSTU operated with MEA. Due to time constraints, limited data was obtained, and further testing is planned for late 2016.

Amine Emissions Measurements

An Electric Low Pressure Impactor was used for aerosol measurements to evaluate means of reducing solvent emissions. The primary objective in 2015 was to establish baseline data that could be compared against results obtained in 2016, when a new activated carbon injection baghouse was brought on-line at Gaston Unit 5, upstream of the PC4. Measurements taken on the Linde-BASF unit showed that the impact of the baghouse operation was significant, causing a drop in particle count of several orders of magnitude. Additional measurements will be made on the PSTU and SSTU locations in late 2016.

In addition to the ELPI+ measurements for aerosol size and count, a Phase Doppler Interferometer, operated by staff from the University of Texas at Austin (UT-Austin), was used on the SSTU treated flue gas stream. The data were generated concurrently with that from the ELPI+ in December 2015 for comparison. The PDI measurements for particle size were larger than the ELPI+ measurements, although the general trends were similar. Further data will be taken during operation of the SSTU with MEA in late 2016, and a detailed comparison of the PDI and ELPI+ generated data will be performed.

Akermin Enzymes

Akermin continued development of an advanced biocatalyst-enabled solvent system for low cost CO_2 capture with a scale-up of a project tested at the NCCC in 2013. Testing began in early June 2016 and continued over a one-month period. However, performance was unstable, and the anticipated performance of 90 percent capture was rarely achieved due to particle accumulation in the absorber. During the most stable operation, the CO_2 capture rate was 93 percent, although the average CO_2 capture rate for the run was 70 percent. After one month of operation, it became clear that the unit in the current configuration was not able to meet the project objectives, and testing was discontinued.

GE Global Aminosilicone Solvent and Desorber

Preparations were completed for testing of the GE solvent in the PSTU during run PO-5. During the first portion of the test, GE will test the aminosilicone solvent using the GE desorber unit in place of the PSTU regenerator. For the second portion, the PSTU regenerator will be used for performance comparisons. Start-up activities were underway at the end of BP2, and the test is expected to continue through the end of PO-5.

PC4 Modifications

Several additions were made to the PC4 to improve data collection and testing capabilities, as listed below:

• Differential pressure measurements of the PSTU column beds for improved data

- Aerosol sampling system for measurements with the ELPI+ and PDI
- Flue gas blower vibration transmitters for remote monitoring
- Differential pressure measurements of the PSTU rich-lean heat exchanger for enhanced data
- Modifications to the SSTU for improved operability
- Process software for data transfer to test partners
- Additional data from Gaston Unit 5 to identify operating conditions

1.2 Gasification Technology Accomplishments

To provide syngas for technology testing, the NCCC's Transport Gasification process was operated over three test runs, which are listed in Table 2. Over 6,000 hours of syngas testing by third-party technology developers were accomplished during the runs, as summarized in Table 3.

Table 2. Summary of Gasification Runs Completed

Run	Run Dates	Run Hours	Fuel
G-2	9/13/15—10/16/15	743	Liberty Fuels Mississippi Lignite
G-3	3/17/16—4/11/16	581	Powder River Basin (PRB) Subbituminous Coal
G-4	4/11/16—6/3/16	877	Red Hills Mississippi Lignite

Table 3. Summary of Gasification Technology Developer Testing

Technology Tested	Hours
Run G-2	
Southern Research Fischer-Tropsch (bottle gas operation)	541
Johnson-Matthey Mercury Sorbent	680
Water-Gas Shift Catalyst	657
Carbonyl Sulfide Hydrolysis Catalyst	656
Run G-3/G-4	
OSU Syngas Chemical Looping	10
Johnson-Matthey Mercury Sorbent	1,167
TDA Research CO ₂ /WGS Sorbent	654
TDA Research Ammonia Sorbent	50
WGS Catalyst	1,081
COS Hydrolysis Catalyst	1,233

Accomplishments achieved in the area of gasification are listed below.

Southern Research Institute (SR) Fischer-Tropsch (F-T) Catalyst

Southern Research continued its development of coal-to-liquids technologies with testing of a Fischer-Tropsch catalyst for production of transportation fuels. The testing demonstrated the target performance values for catalyst activity (more than 0.7 grams of C5+ hydrocarbons per gram of catalyst per hour) and product selectivity (greater than 65 percent jet fuel). SR plans to scale-up the F-T reactor and to operate it with an integrated auto-thermal reformer.

Johnson Matthey Mercury Sorbent

Additional testing of the Johnson Matthey high temperature mercury sorbent was conducted for long-term evaluation, bringing the total accumulated operating time of the sorbent material to about 6,000 hours.

Water-Gas Shift (WGS) and Carbonyl Sulfide (COS) Hydrolysis Catalysts

Operation of WGS and COS hydrolysis catalysts continued with parametric and long-term testing. The WGS catalyst demonstrated shift conversions between 63 and 86 percent, and the COS hydrolysis catalyst showed conversion rates from 44 and 61 percent.

Emerson Rosemount Sapphire Thermowells

Testing was conducted with Emerson's Rosemount sapphire thermowells in gasifier service. The thermowells operated reliably in the highly erosive and corrosive environment, although temperature readings with the sapphire thermowell units were lower than reference thermocouples, with the differences at about three and five percent relative to the reference thermocouples. Further testing is planned.

PCME Particulate Monitor

The VIEW Ex820 particulate monitor from PCME, installed on the outlet of the hot gas particulate filtration system, gave appropriate readings during gasification operation and responded well to calibration testing with ash injection. The new monitor gave clear responses with low particulate concentrations, which validated its potential usefulness as part of a control strategy for protecting gas turbines and other equipment downstream of particulate filters.

OSU Syngas Chemical Looping (SCL)

OSU completed start-up activities for the SCL process, including a short period of operation on syngas, for which OSU reported syngas conversions of greater than 98 percent in the reducer section of the process. OSU will incorporate further modifications prior to continued testing.

TDA Research Ammonia Sorbent

TDA Research operated a new sorbent-based gas clean-up technology for removal of ammonia and hydrogen cyanide, as well as trace metals, at high temperatures in a single process step. TDA demonstrated greater than 99 percent ammonia removal and successful sorbent regeneration. With the successful results of the field tests, TDA plans to further develop the sorbent technology.

TDA Research WGS/CO₂ Sorbent System

As an expansion of previous sorbent testing at the NCCC, TDA Research operated a combined WGS/CO_2 sorbent system with an innovative heat management system. TDA demonstrated that reactor bed temperatures were precisely controlled by direct water injection, and that shift conversions were higher with water injection than with steam addition at comparable H₂O-to-carbon monoxide (CO) ratios. When parameters were adjusted to achieve 90 percent CO conversion in the WGS stage, the overall carbon capture rate was greater than 95 percent. TDA will further refine the technology, with operation of a scaled-up system planned for 2017.

Coal Feeder Instrumentation

Dynatrol and Drexelbrook coal feeder level probes, which have proved useful in automating coal feed cycles, continued to operate reliably. Operation of the Densflow coal flow meter continued to show the need for improved accuracy.

Gasifier Refractory

In evaluating gasifier refractory service time, post-run inspections of hot-face refractory were conducted in erosion-prone areas, and results showed good material integrity and minimal wear.

Hot Gas Filter Elements

Long-term evaluation continued for six types of hot gas filter elements composed of sintered metal fiber and sintered metal powder. Syngas operation of the elements will continue for verification of a two-year or greater service life.

1.3 Pre-Combustion CO₂ Capture Accomplishments

Pre-combustion CO_2 capture operation during the three gasification runs comprised over 3,400 hours of technology developer testing, as summarized in Table 4.

Table 4.	Summarv	of Pre-0	Combustion	CO ₂ (Capture	Technology	Developer	Testing
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Technology Tested	Hours
Run G-2	
Worcester Polytechnic Institute Hydrogen Membranes	630
Membrane Technology & Research Proteus [™] Hydrogen Membranes	480
SRI International Solvent Process	300
Bechtel Pressure Swing Claus Process	90
Run G-3/G-4	
Media & Process Technology Carbon Molecular Sieve	406
Membrane Technology & Research Proteus Hydrogen Membranes	1,000
SRI International Solvent Process	400
Bechtel Pressure Swing Claus Process	131
Carbon Clean Solutions Solvent	

Worcester Polytechnic Institute (WPI) Hydrogen Membranes

Worcester Polytechnic Institute tested palladium-based hydrogen membranes in a seven-fold scale-up of membrane technology previously tested at the NCCC. With only one percent deviation in thickness among the tubes, the consistent fabrication of the membrane tubes demonstrated the replicability of the technology. Syngas operation demonstrated steady permeance values, hydrogen product purity as high as 99.9 percent, and a hydrogen recovery rate of 35 percent. The module was in excellent condition following the testing.

Media & Process Technology (MPT) Carbon Molecular Sieve (CMS)

In continued development of the CMS hydrogen membrane, MPT tested a new water condenser/trap system for membrane permeate and reject lines to more accurately determine the gas phase composition at the membrane. MPT conducted multiple collection sampling runs, and will use the data to validate a membrane permeation model, which will be used in a techno-economic evaluation of the CMS technology. Further membrane testing is planned for future runs.

MTR Proteus[™] Hydrogen Membranes

MTR continued development of the Proteus hydrogen membrane. A four-inch, commercial scale Proteus module enriched the hydrogen concentration in the permeate to roughly six times the feed concentration, which is a significant improvement over previous modules tested at NCCC. The improved performance was due to a combination of advancements in module configuration, new high temperature glues, and continued Proteus membrane development. MTR also conducted parametric tests with two 2.5-inch Proteus modules. Module results were consistent with each other and previous tests, indicating that the modules were of high quality and defect-free. MTR plans to continue to support both types of testing in future runs.

SRI International (SRI) Ammonia Carbonate-Ammonium Bicarbonate (AC-ABC) and Bechtel Pressure Swing Claus (BPSC) Processes

The SRI AC-ABC and Bechtel Pressure Swing Claus processes operated during the G-2 and G-4 runs. Test data demonstrated steady state operation of the pilot plant with greater than 99.5 percent capture of CO_2 and hydrogen sulfide (H₂S), and regeneration of high purity CO_2 and H₂S at pressure. Despite operational issues with the SO₂ delivery system, the BPSC system showed a conversion of more than 99.5 vol% of H₂S gas to elemental sulfur with H₂S in the product gas at ppm levels.

Carbon Clean Solutions Limited (CCSL) Solvent

A CO₂ capture solvent from Carbon Clean Solutions was tested both off-line with bottle gases and on-line during gasification. The CCSL solvent compared favorably to the commercially used solvents methyl diethanolamine (MDEA) and dimethyl ether of polyethylene glycol (DEPG). CCSL estimated that the heat of reaction for the CCSL solvent was 39.2 kJ/mol CO₂, 20 percent lower than that of MDEA (48.9 kJ/mol CO₂).

2.0 POST-COMBUSTION CO₂ CAPTURE

The PC4 utilizes flue gas from Plant Gaston Unit 5, a base-loaded, 880-MW supercritical pulverized coal boiler fired with Alabama medium-sulfur bituminous coal. The unit meets all environmental requirements utilizing state-of-the-art controls; thus, the flue gas extracted for testing is fully representative of commercial conditions. As shown in Figure 2, the PC4 provides sites for technology developers' bench-scale and pilot-scale test units. The Pilot Solvent Test Unit and the Slipstream Solvent Test Unit are fully integrated systems for comprehensive solvent characterization at pilot- and bench-scale, respectively. An air dilution system is also available for CO_2 capture testing under simulated natural gas flue gas conditions.



Figure 2. Schematic of PC4 Test Facilities

During BP2, the PC4 supported more than 10,500 hours of testing for the projects described in the following sections. The three runs occurring during the reporting period included:

- PO-3, beginning in Budget Period 1, from May 1, 2015, through August 10, 2015
- PO-4, occurring from October 10, 2015, through December 21, 2015
- PO-5, beginning on May 18, 2016, and continuing into Budget Period 3 (planned through mid-November 2016)

Table 5 lists the average composition and conditions of the flue gas used for testing at the PC4.

Flue Gas Component	Value
CO ₂ , vol%	12.1
Oxygen, vol%	7.1
H ₂ O, vol%	7.6
Nitrogen Oxide (NO), ppm	41.0
Nitrogen Dioxide (NO ₂), ppm	6.5
Temperature, °F	155
Pressure, inH₂O	20

Table 5. Average Values of Flue Gas Components and Conditions

2.1 MTR 1-Ton/Day CO₂ Membrane System

Beginning in 2011, MTR tested polymeric PolarisTM membranes for separating CO₂ from coalderived flue gas at the PC4. Final testing was completed in August 2015. As shown by the process diagram in Figure 3, the 1-TPD system removes CO₂ from flue gas in two steps. The first step uses cross-flow modules with a vacuum on the permeate for CO₂ enrichment, and the second step uses counter-current sweep air to remove additional CO₂ in the feed gas to meet the overall capture target of 90 percent. Before entering membrane modules, the gas is compressed to 20 to 30 psig to generate the necessary pressure ratio for parametric studies.



Figure 3. Schematic of MTR Flue Gas Membrane Skid

Operations of the 1-TPD unit during the reporting period took place from June through August 2015 in run PO-3. The testing employed high-flux Polaris cross-flow modules in the first step, and sweep modules with high selectivity Polaris membranes in the second step. This combination of modules was used for the first time in the PO-2 run from January to March 2015. The objectives were to determine module performance with coal generated flue gas in the field, and to test module stability over time and with the shutdowns and restarts that are inherent in plant operations.

Figure 4 demonstrates the performance of the system from January to July 2015. For the operating periods with flue gas, the feed gas contained about 12 percent CO_2 . The step-one permeate ranged from 50 to 70 percent CO_2 , representing an enrichment factor of four to six. The system generated a treated flue gas between two and five percent CO_2 as the second step residue stream. The restart of operations in June 2015 after an extended shutdown showed that stable operations continued.



Figure 4. CO₂ Content of Feed, Permeate, and Residue Streams of MTR 1-TPD System from January through July 2015

The period of operations in early 2015 was defined by the external winter weather, with feed streams cooling from around 27°C (80°F) at the start to 13°C (55°F). Lower feed temperature resulted in lower permeate flux in both stages, lower stage cut in step one, and higher CO₂ concentration in the first step permeate, first step residue, and second step residue (the treated flue gas). The fairly steady trend to cooler temperature meant a steady shift in observed CO₂ content as the modules responded over time. These results were consistent with those from previous extended trials in respect to the impacts of operating temperature.

For a brief period from 833 to 855 hours the feed switched from pulverized coal flue gas to simulated natural gas flue gas at 4 percent CO_2 content. The permeate from step one fell to about 40 percent CO_2 , representing an enrichment factor of about 10. With the lower CO_2 content in the feed compared to coal flue gas, the second step residue was reduced to less than 2 percent CO_2 . Upon returning to 12 percent CO_2 feed, the performance recovered, with CO_2 in the first step permeate returning to about 60 percent CO_2 .

With the restart for run PO-3 in June 2015, the downtime was over 1,700 hours. Figure 5 and Figure 6 detail the operations in June and July, 2015. The key parameters governing system performance are the feed flow rate, the feed gas temperature, and the sweep flow rate. Upon restart, the feed rate to the system approached 200 kscfd, which increased the second step residue to just over 5 percent CO_2 . Lowering the feed rate to 150 kscfd returned the second step residue

to under 4 percent CO_2 . In mid-June, the feed temperature to the membrane system increased to about 38°C (100°F). This increased the permeate rate, which increased stage cut, with the net result of lower CO_2 content in the first step permeate and in the second step residue. As seen previously, the first step increased the CO_2 concentration from 12 percent in the feed to over 60 percent in the permeate. The second step residue ranged from 2 to 7 percent CO_2 . The sweep rate was intentionally varied between 20 to 70 kscfd, affecting the step two residue CO_2 concentration and the composition of the sweep out gas.



Figure 5. CO₂ Content of Feed, Permeate, and Residue Streams of MTR 1-TPD System during June and July 2015



Figure 6. Operating Conditions for MTR 1-TPD System during June and July 2015

At 4,020 run hours, the feed rate was lowered to about 100 kscfd, which increased stage cut and generated immediate changes in the first step permeate and the second step residue, both again to lower CO_2 content. At the end of June, the sweep rate in step two was both lowered and raised

by 15 kscfd. This changed the both the pressure drop across the sweep side of the module and the dilution rate of the permeate CO_2 for the second step. Increasing the sweep rate slightly improved the amount of CO_2 captured by the sweep modules. Overall, the sweep flow rate had much less impact on system performance compared to the feed flow rate or temperature.

Readings for CO_2 concentration were not available on July 16 starting at the run clock of 4,592 hours, and the flow and pressure data collection were ceased on July 17 at 4,622 hours. The system achieved over six months of operations with this combination of cross-flow and sweep modules. The modules continued to show stable operations even with the excursions in feed temperature and flow rates.

After three and half years of testing, the system achieved a total of 11,466 hours of operation with 9,100 hours on flue gas and 2,366 hours on air when flue gas was not available. Out of the 9,100 hours of testing on flue gas, 1,933 hours were conducted with simulated natural gas flue gas. Carbon capture rates of better than 90 percent were achieved with coal-derived flue gas. The test program proved valuable in guiding the design of MTR's 20-TPD membrane system and in serving as a test vehicle for second and third generation membranes following lab testing.

2.2 Carbon Capture Scientific Gas-Pressurized Stripping Solvent Process

Carbon Capture Scientific, LLC, in collaboration with CONSOL Energy Inc., Nexant Inc., and Western Kentucky University has been developing a novel gas pressurized stripping process for post-combustion CO_2 capture. A flow diagram of the bench-scale GPS test unit is shown in Figure 7. The GPS process is an innovative technology in which CO_2 is removed from the flue gas in the absorber and released at elevated pressure with high purity in the stripper. Parametric testing was performed during run PO-2, and final, long-term testing was completed in August 2015 in run PO-3. The total flue gas operating time was 1,145 hours.



Figure 7. Flow Diagram of Carbon Capture Scientific Bench-Scale GPS Unit

An amine-based CCS proprietary blended solvent was used in all the parametric and longterm tests. Parametric tests investigated the influences of total flue gas flow rate, gas/liquid volume ratio, stripper operating pressure, and nitrogen flow rate on the GPS system performance. The performance was characterized by the CO_2 removal rate in the absorber and CO_2 product pressure and purity from the stripper. The CO_2 removal rate was calculated based on the average CO_2 concentration at the absorber inlet and outlet, and the CO_2 purity was based on the average CO_2 concentration at the stripper outlet.

Figure 8 illustrates the influence of the total flue gas flow rate on the GPS unit performance. In these tests, the gas-to-liquid (G/L) volume ratio was kept at 145, and the stripper operating pressure was at 6.1 bar. The nitrogen flow rate into the stripper was adjusted proportionally with the flue gas flow rate. With the increase of total flue gas flow rate, the CO_2 removal rate in the absorber reduced markedly, while the CO_2 purity from the stripper reduced slightly. As the flue gas and solvent flow rates increased, the residence time in the absorber was reduced. Less reaction time resulted in lower reaction conversions, and thus lower CO_2 removal rates. The height of stripper packing was more over-designed than that of absorber. Additionally, the stripping reaction was faster than the absorption reaction due to its higher temperature. Thus, the reduced reaction time had less influence on the conversion in the stripper than that in the absorber, which explained why the reduction of CO_2 purity was less significant.



Figure 8. Influence of Flue Gas Flow Rate on the Performance of GPS Process

Figure 9 shows the effect of the G/L volume ratio on process performance. The stripper operating pressure (6 bar), the solvent flow rate (0.89 gpm), and the nitrogen flow rate into the stripper (2.35 slpm) were kept constant. The G/L volume ratio was changed by changing the flue gas flow rate and keeping the solvent flow rate constant. With an increased G/L volume ratio, the CO₂ removal rate reduced significantly, but CO₂ purity was not affected. As the G/L volume ratio increased, the amount of flue gas processed per mass of solvent increased. In this case, to achieve the same the CO₂ removal rate as the low G/L volume ratio, the height of absorber packing would need to be increased. Because the operating conditions in the stripper were kept constant, as G/L volume ratio increased, there was little variation in CO₂ purity from the stripper.



Figure 9. Influence of G/L Ratio on Performance of the GPS Process

Figure 10 demonstrates the influence of the stripper operating pressure on the GPS process performance. A flue gas flow rate of 455 slpm (16 scfm) and a solvent flow rate of 0.95 gpm were maintained. During the experiments, the nitrogen flow rate was increased accordingly to ensure the lean loading was still low enough to achieve over 90 percent removal rate in the absorber. With the increase of stripper operating pressure, both the CO_2 purity from the stripper and CO_2 removal rate in the absorber declined. Because the CO_2 equilibrium partial pressure was a strong function of temperature and the stripper temperature was kept the same for the four tests, CO_2 purity at the top of the stripper decreased when the total pressure increased. As the stripper operating pressure increased, the lean loading of the solvent at the outlet of the stripper increased to maintain a higher equilibrium partial pressure of CO_2 . Higher lean loading solvent compromised the performance in the absorber, resulting in lower CO_2 removal rates.



Figure 10. Influence of Stripper Operating Pressure on GPS Performance

The effect of nitrogen flow rate on the GPS performance is shown in Figure 11. In these tests, the flue gas flow rate was maintained at 500 slpm (18 scfm), the stripper operating pressure was kept at 5.9 bar, and the solvent flow rate was maintained at 1.09 gpm. With the increase of nitrogen flow rate, the CO_2 purity reduced, while the CO_2 removal rate increased. As the nitrogen flow rate increased, the lean loading of the solvent at the outlet of stripper decreased due to the lower CO_2 concentration at the bottom of the stripper. The solvent with lower lean loading enhanced the performance in the absorber subsequently. The nitrogen dilution reduced the CO_2 purity from the stripper.



Figure 11. Influence of Nitrogen Flow Rate on GPS Performance

Energy consumption tests were conducted to validate CCS's previous simulation results. Since the sensible heat amount strongly depends on the selection of a heat exchanger, the tests were designed only to measure the reaction heat and the stripping heat. The sensible heat of the solvent can be estimated based on the working capacity and specific heat of the rich and lean solvents. The estimated sensible heat was in the range of 250 to 500 kJ/kg CO₂ captured. To measure the actual reaction and stripping heat, the steam usage data was obtained after the unit reached steady state. The net steam usage representing the sum of reaction and stripping heat was the difference between the steam usage for operation without flue gas flow was actually the sum of sensible heat and heat loss. Table 6 provides the results for the sum of reaction heat and stripping heat, which were very close to the predicted value of 1,570 kJ/kg CO₂ captured.

able of Results of Energy consumption rest for the GFS Process										
	Solvent Flow	Flue Gas Flow	Stripper	N ₂ Flow	Sum of Reaction and					
	Rate, gpm	Rate, scfm	Pressure, bar	Rate, slpm	Stripping Heats, kJ/ kg CO ₂					
	0.89	14.5	6.0	2.59	1,600					
	1.10	17.8	5.8	2.63	1,562					
	0.57	11.6	6.0	1.67	1,597					

Table 6. Results of Energy Consumption Test for the GPS Process

For the long-term test, the unit was set to run at a condition that could achieve 90 percent CO_2 removal and 95 percent CO_2 purity as established in parametric testing. The incoming flue gas and the solvent flow rates were 330 slpm and 0.56 gpm, respectively, producing a G/L ratio of 156. The stripper pressure was maintained at 6 bar. The skid was operated constantly except for interruptions for maintenance or troubleshooting. The long-term test was conducted from late May through early August, 2015. The operation was fairly stable, and CO_2 concentration data from a representative 24-hour period is shown in Figure 12.



Figure 12. CO₂ Concentration in GPS Streams during Representative 24-Hour Period

The tests of the bench-scale GPS skid at NCCC achieved the project goals. The parametric tests validated the influences of operating parameters on GPS process performance, which were simulated before the tests. The long-term test showed the process could run continuously for an extended period of time. The results demonstrated that GPS process is able to achieve 90 percent CO₂ removal from typical coal derived flue gas, with high pressure, high purity CO₂ product. Additionally, the energy consumption of the GPS process is much lower than that of the MEA baseline case (approximately 1,550 BTU/lb CO₂, or 3,600 kJ/kg CO₂).

2.3 Ohio State University Membranes

OSU is working to develop a cost-effective design and manufacturing process for membrane modules for CO₂ capture from coal-derived flue gas. During the reporting period, OSU completed testing to evaluate the performance and stability of spiral-wound membrane modules with actual flue gas in comparison with that obtained using simulated flue gas in the OSU lab. The membrane consists of a thin selective inorganic layer embedded in a polymer structure so that it can be made in a continuous manufacturing process. It is incorporated in membrane modules (e.g., spiral-wound), for bench scale tests at simulated flue gas conditions. OSU's prototype membrane modules were installed in OSU's gas permeation unit, which is shown in Figure 13 as installed in the PC4 analytical lab. Testing began on May 27 and concluded on June 22, 2015.



Figure 13. OSU Membrane Skid Installed in PC4 Gas Analysis Lab

To prevent feed gas bypass, a commonly encountered problem with spiral wound membranes, OSU optimized the glue-line procedure of membrane fabrication. The new procedure aided in adequate sealing of the non-woven fabric in the membrane leaf and sealing between the membrane leaf and the central tube. The quality of fabrication was successfully improved, as the elements demonstrated essentially no leakage during initial testing. Figure 14 provides an image of the fabricated spiral-wound membrane element installed in the housing.



Figure 14. OSU Membrane Module in Housing

During testing, the feed and sweep gases entered the module in a countercurrent configuration. The dry feed gas flow rate used was 1,000 cc/min at 1.5 psig, and the dry sweep gas flow rate used for the permeate side was also 1,000 cc/min at 1 psig. Both the feed gas and the sweep gas were humidified with water vapor by injecting controlled flow rates of water into them to obtain

the controlled concentrations of water vapor. At the typical flue gas temperature of 57° C, the saturated water vapor concentration in each of the feed and sweep gas streams was 17 percent. This temperature was used for the module testing at NCCC.

Table 7 summarizes the results for the two modules tested at the OSU lab and three modules tested at the NCCC. The modules tested at NCCC showed repeatable results that agreed well with the modules tested in the OSU lab. The first module tested at the NCCC, Module C, was tested for 96 hours and showed a stable result at 820 GPU and 150 CO_2/N_2 selectivity. This module showed good stability for 96 hours, but was replaced with modules expected to exhibit higher CO_2/N_2 selectivity.

Module No.	Test Location	Selective layer thickness (nm)	CO₂ Permeance (GPU)	CO ₂ /N ₂ Selectivity	Feed/Sweep Pressure Drop (psi/m)
А	OSU Lab	180	700	210→160	1.48/1.48
В	OSU Lab	195	585	205	1.97/2.30
С	NCCC	165	820	150	0.98/1.31
D	NCCC	145	800	170 →60	0.98/1.48
E	NCCC	145	800 →630	270 →180	1.31/1.48

Table 7. Summary of OSU Membrane Performance

The second module (Module D) was tested for 208 hours, and there was a flue gas shutdown for a period of 60 hours in the middle of the test. The module showed an initial CO_2/N_2 selectivity of 170, and after the restart, the selectivity dropped to 60. Figure 15 shows the stability plot of the Module D and the comparison to Module A that was tested at OSU. Both the membrane modules showed reasonably stable CO_2 permeance throughout the test and a drop of CO_2/N_2 selectivity.



Figure 15. Performance of Membrane Module D Tested at NCCC and Module A Tested at OSU

OSU believes that the insufficient curing of the glue used and the membrane indentations caused by the rough surface of the feed spacer might have introduced leakage and resulted in the CO_2/N_2 selectivity drop. Figure 16 shows the Module D membrane surface before rolling prior to the test and after testing and unrolling. Indentations were present following the testing, but were not present before rolling into the spiral-wound module configuration.



Figure 16. OSU Module D Membrane Surface before and after Testing

Module E was tested with flue gas for 200 hours, during which a shutdown occurred for a period of 48 hours in the middle of the test. This module, which featured a longer glue curing time, showed a selectivity of 180 to 270 for 200 hours. Figure 17 plots the performance of Module E along with that of Module B, which had a similar glue curing time and was tested at OSU. Both the membrane modules showed a reasonably stable CO_2/N_2 selectivity throughout the test, with the exception of the drop in selectivity at the restart of the test following the 48-hour shutdown for Module E. However, the selectivity following the restart stabilized at about 180, which is still very high. This module showed an initial CO₂ permeance of around 800 GPU; however, the CO₂ permeance dropped to about 630 GPU at the restart of the test. This permeance drop was presumably due to feed gas bypass caused by the glue failure, which was indicated by the change of epoxy glue color from gray to green-yellowish after Hour 208 of the test.

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Figure 17. Performance of Membrane Module E Tested at NCCC and Module B Tested at OSU

The results of the NCCC testing were promising in that they were comparable to those of OSU lab testing with simulated flue gas. The modules showed initial permeance values of about 800 GPU and selectivity values of about 200, as well as pressure drops of less than 1.5 psi/m. OSU will further improve the glue curing and minimize membrane indentations for the improvement of membrane module performance and stability.

2.4 Linde-BASF Solvent Pilot Plant

Linde and BASF are developing a solvent-based post-combustion capture technology offering significant benefits compared to other processes as it aims to reduce overall energy consumption and capital costs using solvents that are very stable under coal-fired power plant feed gas conditions. The technology incorporates BASF's novel amine-based process along with Linde's process and engineering innovations, as highlighted in Figure 18. The technology incorporates use of an advanced aqueous amine-based solvent formulation marketed under the trade name OASE® blue, which was developed by BASF. Under a DOE-supported project, Linde and BASF demonstrated the solvent process at a 1.5-MWe scale at the PC4.



Figure 18. Linde-BASF Pilot Solvent Process Diagram

Mechanical completion of the pilot plant was achieved in July 2014 and the final commissioning activities were completed to enable start-up of operations in January 2015. Parametric tests were performed from January to December 2015 to determine optimal test conditions and evaluate process performance over a variety of operation parameters. A long-duration 1,500-hour continuous test campaign was performed from May to July 2016 at a selected process condition to evaluate process performance and solvent stability over an extended period to mimic commercial operating conditions.

During the overall test period including start-up, parametric testing, and long-duration testing, the pilot plant operated for a total of 6,764 hours, out of which testing with flue gas was performed for 4,109 hours. The testing demonstrated all of the performance targets including CO₂ capture rate exceeding 90 percent, CO₂ purity exceeding 99.9 mol% (dry), flue gas processing capacity up to 15,500 lb/hr (equivalent of 1.5 MWe), regeneration energy as low as 2.7 GJ/tonne CO₂, and regenerator operating pressure up to 3.4 bar absolute. Testing validated the emission control feature incorporated in BASF's patented dry bed configuration, as well as several unique equipment features incorporated in the pilot plant, including high-capacity structured packing, gravity-driven absorber inter-stage cooler, blower location downstream of absorber, and the unique reboiler configuration which minimizes solvent inventory and promotes fast response to load changes.

Table 8 summarizes the process condition ranges for the pilot unit. The flue gas CO_2 concentration varied significantly, ranging from 11 to 12 mol% CO_2 during the morning and
peaking to as much as 13.5 mol% CO_2 in the afternoon on almost every day. This variation resulted in substantial process fluctuations that were controlled to achieve as stable and consistent operation as possible while at the same time maintaining low specific regeneration energy relative to industry standard MEA solvent-based CO_2 capture plants.

Process Condition	Range
Inlet Flue Gas	
Flow Rate, lb/hr	7,500 to 15,750 (10,500 base)
Temperature, °F	86 to 104
Pressure, psig	-0.3 to 0.5
CO ₂ Concentration, mol% (dry)	11 to 13.5
CO ₂ -Depleted Gas at Absorber Outlet	
Flow Rate, lb/hr	5,800 to 13,000
Temperature, °F	86 to 115
Pressure, psig	-0.6 to 0.2
CO ₂ Concentration, mol% (dry)	0.5 to 2
CO ₂ Product Gas at Stripper Outlet	
Flow Rate, lb/hr	1,300 to 2,300
Temperature, °F	70 to 100
Pressure, psig	14.7 to 34.6
CO ₂ Concentration, mol% (dry)	99.9
CO ₂ -Lean Solution Cooler	
Temperature to Absorber, ^o F	104 to 140
Absorber Inter-Stage Cooler	
Inter-Stage Cooler Operation	On (104 °F) / Off
Solvent Circulation and CO ₂ Capture	
Solvent Circulation Rate	80% to 120% of Design
CO₂ Capture Rate	85 to 95+ (90% Typical)

Table 8. Ranges of Process Conditions for Linde-BASF Pilot Solvent Uni

During the parametric testing, significant research was performed in conjunction with NCCC and Southern Research Institute in characterizing aerosol particle number concentration and size distribution in the flue gas and their impact on amine carryover with the CO₂-depleted gas leaving the top of absorber using state of the art analytical measurements (see Section 2.11). Pilot plant operating parameters that minimize amine carryover when the flue gas has a significant concentration of aerosol particles were also identified.

Figure 19 demonstrates the consistently low specific energy consumption, averaging 2.84 GJ/tonne CO_2 for the Linde-BASF technology for the duration of the long-duration test in 2016. The solvent was strengthened slightly at the end of July 2016 to test the impact on energy performance, and the specific energy consumption reduced further to 2.75 GJ/tonne CO_2 . The Linde-BASF technology yielded significantly lower energy consumption than a standard MEA-based capture process, which typically operates at 3.61 GJ/tonne CO_2 .



Figure 19. Specific Energy Consumption for Linde-BASF Solvent Process during Long-Term Testing

Solvent stability can be measured in terms of both the energy consumption, used as an indicator of solvent performance, and via analytical measurements of the solvent composition. The results of both parametric and long-duration tests showed consistently low energy consumption. During testing, bulk components of the solvent (amine, water, CO_2) were analyzed daily to correct the plant inventory for the water balance as appropriate. In addition, batch samples of CO_2 -lean and CO_2 -rich solvent liquid along with some of the process water and condensate streams were collected on a regular basis and transported to BASF labs in Michigan for detailed analysis of contaminants and heat stable salts, which are an indicator of solvent degradation. The measured heat stable salt levels were well below the threshold that BASF uses for solvent degradation.

In the Linde-BASF process, essentially all of the nitrogen and nearly all of the oxygen leaves through the top of the absorber in the CO_2 -depleted gas, resulting in an extremely low concentration of oxygen in the CO_2 product gas leaving the stripper column of less than 100 ppm under most conditions. Figure 20 plots the oxygen concentration in the CO_2 product gas for a typical day during the long-duration test campaign, which shows that the oxygen concentration can be maintained within the limits required for applications in CO_2 , utilization such as enhanced oil recovery. The oxygen concentration averaged 13.3 ppm.



Figure 20. Oxygen Concentration in Treated Flue Gas from Linde-BASF Solvent Process

Figure 21 and Figure 22 plot the steam requirements and corresponding CO_2 recovery rate during the long-duration testing. As shown, roughly 90 percent CO_2 recovery was maintained throughout the long-duration test campaign while maintaining consistently low specific energy consumption over the same time period. The CO_2 recovery was maintained at 90 percent during the last week of testing in July 2016 when the solvent strength was slightly increased, indicating that the reduction in specific energy consumption to 2.75 GJ/tonne CO_2 measured at that time could be consistently compared to the rest of the data from the long-duration testing.



Figure 21. Steam Flow Rate into Reboiler of Stripper during the Linde-BASF Long-Duration Test



Figure 22. CO₂ Recovery during the Linde-BASF Long-Duration Test

Following the completion of the successful test campaign at NCCC, the Linde-BASF team are further developing the technology at other locations. For example, the technology was selected by the DOE for Phase I funding of a project to capture approximately 500 tonnes per day of CO_2 with a 90 percent capture rate from existing coal-fired boilers at the Abbott Power Plant on the campus of the University of Illinois.

2.5 MTR 20-Ton/Day CO₂ Membrane System

In 2014, MTR completed installation and commissioning of the scaled-up, 20-ton/day CO_2 membrane system. The system first operated in 2015 during run PO-2, and for PO-3 operation, a high efficiency plate-and-frame membrane module was added to replace the conventional spiral-wound design. Figure 23 provides a photograph of the MTR system at the PC4.



Figure 23. MTR 20-TPD Membrane System with Plate-and-Frame Sweep Module Skid

The system was commissioned on flue gas in January 2015. During PO-2, the system ran intermittently on flue gas due to cold weather issues on the NCCC side, miscellaneous system issues on the MTR side, and the installation of the plate-and-frame sweep module skid. In early March, cold weather cooling water supply issues on the NCCC side tripped the 20-TPD system causing damage to a critical flow switch. Due to the lead time of a replacement part and scheduling considerations, the 20-TPD system did not run for the remainder of PO-2. During PO-2, the 20-TPD system operated on flue gas for approximately 325 hours with CO₂ capture rates ranging from 85 to 95 percent.

The main goal of the PO-3 campaign was to operate the plate-and-frame sweep skid as the second step of the 20-TPD system for a minimum of 500 hours to validate the lab performance

values and demonstrate the stability of the new module design under real coal-fired flue gas conditions. Another goal was to determine the various operating parameters of the 20-TPD system under summer conditions (ambient temperatures of 32°C and higher) compared to the sub-freezing winter conditions of PO-2.

Downtime of the 20-TPD system was minimized during PO-3 due to lessons learned during PO-2. As shown in Figure 24, the 20-TPD system with the plate-and-frame sweep skid consistently captured CO_2 at a rate of around 87 percent, with capture rates over 90 percent under certain operating conditions.



Figure 24. CO₂ Capture Rate for MTR 20-TPD System during PO-3

Figure 25 shows an example of the CO_2 enrichment produced by the membrane system by tracking the CO_2 content of various gas streams over the period of June 10 through 13. As shown in the figure, the typical flue gas feed to the membrane systems was 11 to 12 percent CO_2 . The first step permeate was enriched about four times to 45 percent CO_2 , while the treated gas leaving in the residue stream contained about 2 percent CO_2 . This performance is very similar to that achieved by the 1-TPD system and is in agreement with MTR's design calculations. For an integrated system (as opposed to the slipstream testing at the NCCC), the CO_2 recycled to the boiler would increase the feed CO_2 content to around 20 percent (instead of 11 percent at NCCC). As a result, with an expected permeate enrichment of three to four times, this stream would contain about 70 percent CO_2 , which would then be sent to a liquefaction system for purification and pumping to sequestration pressures.



Figure 25. CO₂ Content of Gas Streams of the MTR 20-TPD System

The plate-and-frame sweep skid was on-line as the second step of the 20-TPD system for the duration of PO-3. This allowed for direct performance comparison to the spiral-wound sweep modules used as the second step during PO-2. Figure 26 compares the sweep-side pressure drop for the two types of modules under the same conditions during flue gas operation. The plate-and-frame sweep module demonstrated roughly four times lower pressure drop compared to the spiral-wound sweep modules tested during PO-2. For a full-scale power plant (550 MWe), this reduction in pressure drop would amount to an energy savings of about 10 MWe.



Figure 26. Comparison of Sweep-Side Pressure Drop with Plate-and-Frame and Spiral-Wound Sweep Modules in MTR 20-TPD System

Overall, the 20 TPD system was successfully installed, commissioned, and operated during two post-combustion campaigns at NCCC. The system ran on flue gas for 900 hours, exceeding the original goal of 500 hours, and demonstrated the performance of both the 20-TPD system and the plate-and-frame sweep skid. Following the run, the system was decommissioned and transported to another test site. Highlights include:

- Stable system operation meeting design specifications under both sub-freezing winter conditions and high temperature, high humidity summer conditions
- 400 hours of operation during PO-2 with CO₂ capture rates ranging from 85 to 95 percent with spirals as the sweep step
- 900 hours of stable operation during PO-3 with CO₂ capture rates over 85 percent with the plate-and-frame module design as the sweep step
- About four times lower sweep side pressure drop for plate-and-frame sweep modules compared to spiral sweep modules operated under the same field test conditions

2.6 Ion Engineering Solvent

ION Engineering is developing a proprietary advanced solvent which has consistently demonstrated significant advantages over traditional MEA in ION's previous lab and pilot testing. The ION solvent was tested in the PSTU from June 24 through August 10, 2015, for 1,116 hours of operation. In order to meet the overall project objectives of DOE's goal for second generation solvents, ION focused on two major project target achievements during pilot scale testing at the PSTU: confirming solvent performance, and determining solvent lifetime.

The temporary installation of a new process water chiller and associated piping was completed prior to testing at NCCC. This enabled additional flue gas cooling at the direct contact cooler unit operation and was required to achieve ION's temperature target for the flue gas entering the absorber column Also installed for the testing was ION's mobile analytical chemistry lab, with capability of Karl Fischer titration, total inorganic carbon analysis, and gas chromatography.

After completing modifications to the PSTU and identifying the optimal test conditions for parametric testing, two control strategies were prioritized to further define a successful test campaign. The first priority was to maintain process and water balances. The water in the wash tower basin is normally recycled into the process to maintain a reasonable water balance. ION maintained a water balance by operating at or around a prescribed temperature difference between the flue gas containing CO_2 entering the absorber and the treated flue gas exiting the absorber. Water balance was achieved shortly after startup and maintained through the end of testing. The water balance was confirmed with Karl Fischer titrations conducted over the entire testing campaign at NCCC.

Using baseline MEA process data provided by NCCC, ION modeled MEA performance conditions in the PSTU using the ProTreat® simulation software. Completing this evaluation prior to the test campaign enabled ION to perform detailed analysis of the PSTU process and equipment. Given the characteristics of ION's solvent, optimal test conditions were identified,

and results from actual testing were subsequently verified against the predicted model results. Some minor changes to the PSTU equipment were requested after completing a thorough review of boundary conditions and existing equipment design, assisted by results from the simulations. As shown in Figure 27, ION was able to capture more than 95 percent CO_2 at a range of L/G testing conditions, satisfying the project objective of 90 percent or greater CO_2 capture.



Figure 27. CO₂ Capture Rate at Various L/G Ratios for Ion Engineering Solvent

Figure 28 plots the specific heat performance of ION's solvent during actual testing in comparison to design values predicted by ProTreat simulations, and the best performance claimed by another developer at NCCC. Two flue gas outages occurred during the run time shown, which resulted in inaccurate sensor readings of the PSTU instrumentation and of the dependent calculations, such as specific energy requirements. The ION solvent's specific energy result obtained at NCCC was 1,600 BTU/lb CO₂ during steady state, while the design case was 1,100 BTU/lb CO₂. Running one bed of packing was likely the biggest energy penalty compounded by over-stripping and obtaining capture rates exceeding 95 percent.



Figure 28. Specific Energy Requirements of ION Engineering Solvent

Amine-based solvents are known to undergo molecular degradation due to the standard process conditions of a carbon capture plant; this process transforms active solvent into less effective or dangerous byproducts normally restored by implementing solvent replacement methodologies (and their associated costs). For coal-fired carbon capture, solvent degradation also includes irreversible reactions with flue gas contaminants. Throughout the testing, the ION solvent maintained performance with respect to specific heat requirements and capture efficiency, indicating high stability.

Heat stable salts were quantified as well, and the highest level of detection was 1,640 ppm, which was for sulfate. Sulfate is not thought to be a degradation byproduct of ION's solvent; rather, it is thought to originate in the flue gas supply and to react with excess oxygen in the flue gas. The next highest level of heat stable salts was for an acetate oxidation product, at 680 ppm, followed by nitrate at 260 ppm. The other heat stable salts measured at even lower quantities were chloride, fluoride, and other oxidation products.

Solvent samples from the PSTU were analyzed for degradation products using gas chromatography mass spectrometry. Of the degradation products identified, the highest level measured was 0.4 wt% accumulated at the completion of the test campaign. ION did not observe large accumulations of heat stable salts or solvent degradation over the 1,116-hour test period, suggesting solvent longevity, although longer testing would be needed to confirm solvent durability.

Stainless steel corrosion coupons were tested in the PSTU during the solvent testing. At all locations tested, the coupons showed no significant corrosion. Scanning-electron microscopy, energy-dispersive spectroscopy, and weight-loss analysis as per ASTM G1-G4 standard methodologies substantiated the chemical and morphological tenacity observed of common stainless steel metal coupons. Metal ions were also quantified and evaluated against MEA tested at NCCC. The evaluation showed that the ION solvent accumulates significantly less metal ions than MEA solvent.

ION is currently working with national and international partners to further demonstrate its carbon capture technology in real process environments and commercial settings. The data gathered from the NCCC test campaign continues to strengthen ION's solvent technology and positive track record in executing off-site test campaigns. ION anticipates that the pilot-scale test at the NCCC along with future projects will directly impact the state of the art of CO_2 solvent technologies and facilitate advancement of CO_2 capture towards commercialization and implementation of ION's technology.

2.7 National Energy Technology Laboratory Membranes

The primary purpose of the NETL Post-Combustion Membrane Skid is to provide a platform for testing small scale, experimental membranes using commercially representative flue gas. Membrane testing performed in the PCMS is geared toward identifying fabricated membranes with acceptable performance when separating CO_2 from the other flue gas components and maintaining performance in the presence of water vapor and minor contaminants. The PCMS is thus designed to condition the flue gas input by dehumidification, deliver it to the membrane

module, and analyze the gas compositions of both the flue gas feed and the membrane permeate. Two types of membranes have been successfully tested with the PCMS: flat, free-standing polymer films and single strand hollow fiber membranes.

The PCMS was first constructed and tested at NETL in Pittsburgh, PA, before being shipped to NCCC. Installation and GC calibration were performed in early December 2015 followed by a week of testing seven membranes for 15 to 22.5 hours each. All membranes were tested using a standard set of process parameters. The membrane was immersed in a recirculating bath filled with water set at 40°C ($104^{\circ}F$). Both the upstream and downstream sides of the membrane were set at 18.7 psia (1.3 bar) total pressure and 10 cm³/min flow rate. The separation driving force, therefore, was purely the partial pressure differences due to the different stream compositions. Table 9 summarizes typical operating parameters.

Table 9. Operating Parameters for NETL Membrane Testing in December 2015

Operating Parameter	Typical Value
Membrane Temperature	40°C (104°F)
Initial Argon Purge Time	45 minutes
Time to First Sample	30 minutes
Sampling Frequency	30 minutes
Sampling Pattern	4 permeate to 1 retentate
Feed Pressure	18.7 psia (1.27 bar)
Feed Flow Rate	10 cm³/min
Sweep Pressure	18.7 psia (1.27 bar)
Sweep Flow Rate	10 cm³/min

NETL's chosen standard membrane is PDMS, obtained commercially as high purity, high temperature silicone rubber sheets with nominal thickness of 127 microns from McMaster-Carr. Gas permeation properties of PDMS are well-characterized and the platinum-cured PDMS sheets obtained from this source exhibited gas permeability in line with values reported in previous studies. In addition to PDMS sheets, NETL prepared several film coupons of TFE-PPZ, supplied in powder form and then solvent-cast from tetrahydrofuran (THF) solutions in NETL's laboratory. This polymer has been previously characterized in multiple studies and has the right gas permeability to achieve permeate concentrations close to the GC detection limit as a freestanding film. Finally, to demonstrate the PCMS's ability to test thin film composite hollow fibers, NETL tested four hollow fiber samples. The support hollow fibers were made from Torlon[®]. These fibers were then coated with TFE-PPZ based solutions in THF. The goal was to ensure a defect-free TFE-PPZ coating on the fibers, not optimizing for coating thickness (recognizing that TFE-PPZ by itself has sufficiently low CO_2/N_2 selectivity to be commercially pertinent), but instead serving as a springboard to further develop this class of materials. Two of the fibers were coated using a TFE-PPZ+THF solution, while the other two were coated with a TFE-PPZ+THF solution that also contained dispersed SIFSIX-Cu-2i, a metal-organic framework that was previously found to be compatible with TFE-PPZ, creating a mixed matrix membrane coating on these Torlon fibers.

The flue gas fed to the PCMS had CO_2 concentrations varying between 9.8 to 11.5 percent (dry basis), with a typical value of 10.5 percent. O_2 concentration varied from 7.9 to 9.7 percent with

a typical concentration of 9.0 percent. N_2 concentration was found to vary from 80 to 82 percent. The feed gas contained 0.5 to 1.5 percent H₂O, which translated to 15 to 25 percent relative humidity when fed to a membrane held at 40°C. Typical SO₂ concentration was 1.2 ppm and NO₂ concentration was 10 ppm, with spikes no higher than 2.5 ppm and 20 ppm, respectively.

The PCMS operation in December 2015 was the first attempt to quantify the water vapor permeability of a membrane using a constant pressure mixed gas membrane testing system. Water vapor is the most permeable component in flue gas and it is present at low concentrations; consequently, water vapor transport is often mass transfer limited due to concentration polarization. To avoid concentration polarization, previous studies advocated using sufficient feed flow rate in a generic cell to ensure thorough mixing, and in the case of a flat sheet cell, enhanced mixing particularly on the feed side by using stainless steel wool packing. The low velocity of the chosen 10 cm³/min feed flow and lack of enhanced mixing on the feed side of the flat sheet cell suggest that water vapor transport in the membranes was severely mass transfer limited. Consequently, the apparent water vapor permeance calculated from the hygrometer data was considered to underestimate the true water vapor permeance of the membrane.

Following the initial PCMS installation and calibration, the PDMS flat sheet membrane was tested for 20 hours, and the results are shown in Figure 29. After the first hour, a fairly steady gas permeability was measured: 3,300 barrer for CO_2 , 400 barrer for N_2 , and 760 barrer for O_2 . These values were nearly identical to the results obtained in lab testing at NETL (3,400 barrer CO_2 and 420 barrer N_2 at 40°C). Previous studies have shown only very slight lowering of CO_2 permeability for a PDMS composite membrane in a wet flue gas compared to dry, and likewise the unit did not show a notable drop in CO_2 permeability in the partially dehydrated flue gas test. Finally, the apparent water vapor permeability seen over the period of 20 hours varied from 16,000 to 20,000 barrer. The large variation, plus the fact that a number as high as 40,000 barrer has been reported previously, further confirmed that the 10 cm³/min feed flow rate selected was not enough to prevent concentration polarization, and thus did not provide accurate values for the water vapor permeability.



Figure 29. CO₂, N₂, and O₂ Permeability of PDMS Membrane

The gas permeability of the second flat sheet membrane tested, a coupon of TFE-PPZ, is shown in Figure 30. The membrane area and thickness were chosen so that the permeate composition was close to the GC lower detection limit to test the measurement capability of the PCMS. Despite the resulting higher measurement uncertainty, the gas permeability values were stable over the 22-hour test. The average CO₂ permeability, 780 barrer, was only slightly higher than the condition tested at NETL (680 barrer), but was much higher than the numbers reported elsewhere: 470 barrer and 580 barrer, both taken at 35°C. The tested membrane film's pure and mixed gas CO_2/N_2 selectivity was around 8.5, lower than previously reported values of 13.4 and 11.2, so it is possible oxidation over time (as the film was three years old) led to increased CO_2 permeability and reduced CO_2/N_2 selectivity.



Figure 30. CO₂, N₂ and O₂ Permeability of TFE-PPZ Membrane

Following these flat sheet coupon tests, experiments were performed on the four hollow fiber modules. The results from two of the thin film composite hollow fibers are given in Figure 31. Three of the four fibers, consisting of one TFE-PPZ and two TFE-PPZ/SIFSIX coated fibers, displayed CO_2/N_2 selectivity around 10.7 and exhibited stable CO_2 , N_2 , and O_2 permeance. The permeance values were very close to the results obtained at NETL prior to the PCMS field trials, further confirming the reliability of the instrument and the short-term stability of these fibers in flue gas. The fourth fiber, a TFE-PPZ coated fiber (left of the figure), was loaded into the PCMS during system down time and was exposed to the moist, stagnant environment inside the unit for a few hours.



Figure 31. CO₂, N₂ and O₂ Permeability of Two Porous Torlon[®] Hollow Fibers

In a typical experiment, due to the dry argon sweep, the dewpoint on the permeate side is lower than the feed side. However, at the beginning of this experiment, the permeate side dewpoint was almost equal to the feed side dewpoint and continued to drop over time such that the calculated apparent water vapor permeance did not stabilize until about 15 hours into the experiment. This strongly implied that the down time allowed the stagnant water vapor to condense on the membrane, and it dried out as the drier gases flowed through the module. Interestingly, while N₂ and O₂ permeance remained stable throughout the experiment even when the membrane was presumably wet, CO₂ permeance started much lower in the first half hour (33 GPU) before rising and plateauing at around 50 GPU starting on the sixth hour until the end of the experiment. The final CO_2/N_2 selectivity, 10.5, was identical with the other fibers and within expectations. However, the unexpected lowering of the CO_2 permeance in the presence of water suggests that CO₂ transport is strongly hindered by water in the TFE-PPZ hollow fiber. Tests conducted by others have previously reported a modest lowering of both CO_2 and N_2 permeability of PDMS with increasing water content in a CO_2/N_2 mixed gas feed stream. In contrast, the permeance decrease in this case was much more dramatic and exclusively applied to CO_2 . The team predicts that the CO_2 permeance of the TFE-PPZ is strongly affected by relative humidity, but the confirmation requires further study beyond the scope of this narrative.

The final membrane tested by the PCMS during the December 2015 testing period was a mixed matrix flat sheet film consisting of two microporous polymers: PIM-1 as matrix and BILP-101 as filler. The testing results for this novel system have been previously reported.

Additional testing began in July 2016. A standard, PDMS membrane was tested for 18 hours, and results are shown in Figure 32. Testing of different membrane materials will continue through the post-combustion run.



Figure 32. CO₂, N₂ and O₂ Permeability of PDMS Membrane

2.8 Air Liquide Cold Membrane

Air Liquide is developing a CO_2 capture process using hollow fiber membranes operating at subambient temperatures. Air Liquide's lab testing has shown that these membranes, when operated at temperatures below $-20^{\circ}C$, yield two to four times increase in CO_2 /nitrogen selectivity with minimal CO_2 permeance loss compared to ambient temperature values. Performance data were used to design a 0.3-MW small pilot-scale process, depicted in Figure 33, to demonstrate commercial size membrane performances using actual flue gas. Two materials are being evaluated, a commercially available membrane from AL, PI-1 material, and a next generation polyimide membrane material (PI-2) for application in the cold membrane hybrid process.



Figure 33. Process Flow Diagram of Air Liquide Cold Membrane Process

The compressor, pre-treatment and membrane skids, shown in Figure 34, were installed at the PC4 in August 2015. The test unit incorporated two 12-inch PI-1 commercial membrane bundles. During run PO-4, the system was commissioned with flue gas, and testing was completed without major operating issues. The system operated for a total of 1,016 hours, including a continuous run of 16 days. During more than 500 hours of steady state operation, all performance goals were achieved. As shown in Figure 35, the CO₂ capture rate was greater than 90 percent, and the CO₂ purity was between 65 and 70 percent.



Figure 34. Air Liquide Skids Installed at the PC4



Figure 35. Air Liquide Cold CO₂ Membrane Performance during PO-4

Prior to further operation in run PO-5, Air Liquide prepared a new one-inch PI-2 prototype membrane module. The new PI-2 membrane fiber was spun at lab scale and showed significant performance improvements—up to 10 times the CO_2 permeance and similar CO_2 /nitrogen selectivity over the PI-1 commercial fiber.

Testing in run PO-5 began in May, 2016. The prototype PI-2 membrane was operated in parallel with the commercial PI-1 bundle. With flue gas operation, the PI-2 membrane achieved eight to nine times the CO_2 permeance of the PI-1 commercial bundle. Figure 36 shows the stable CO_2 recovery and purity over more than 700 hours of operation, which included multiple shutdowns. Near the end of the operating period shown in the figure, the permeance decreased by about 30 percent following a warm shutdown. Air Liquide will adjust operating procedures to prevent recurrence of the loss in permeance in future operation. Operation is planned to continue through the end of the PO-5 run. Air Liquide will continue development of the PI-2 polyimide membranes.



Figure 36. Performance of Air Liquide Advanced Polyimide Membrane Module

2.9 Slipstream Solvent Test Unit

Commissioning of the SSTU with MEA solvent began in late November 2015. Operations remained at the first baseline test condition for several days as different control parameters and flow indications were reviewed. Because of low solvent performance, the system was drained and flushed with water to remove contaminants that may have reacted with the MEA. The system was restarted in mid-December. Initial testing of the Cansolv aerosol mitigation processes was completed, and aerosol measurements were taken with the ELPI+ and PDI on the SSTU wash tower outlet.

Operation of the SSTU was problematic and did not produce useful MEA baseline data. Following the run, modifications to the system were implemented for improvement. Changes included installation of a new blower, flow meters, transmitters, and area gas detectors, relocation of valves and instruments, addition of a larger CO_2 product line, and upgrades to the control system. MEA baseline testing will resume in late 2016 during the PO-5 run.

2.10 Cansolv Aerosol Mitigation Processes

The Cansolv project includes the evaluation of technologies able to mitigate amine losses in a carbon capture process by reducing the formation of amine containing aerosols. These particles are extremely difficult to capture due to their small size, and they typically leave the absorption process and then are emitted to the atmosphere via the stack. Technologies selected by Cansolv for evaluation include a Thermal Swing Adsorber and a Brownian Demister Unit, shown in Figure 37, installed on the Slipstream Solvent Test Unit. The TSA was installed on the flue gas supply line to remove aerosol-producing constituents, such as SO_2 and SO_3 . The BDU vessel was installed on the treated flue gas stream exiting the wash tower to remove aerosols that may form in the CO_2 removal process. The equipment was tested during run PO-4.



Figure 37. Cansolv Aerosol Reduction Equipment

The preliminary test objectives were accomplished using MEA, although sufficient time was not available to test the equipment using Cansolv's proprietary solvents. Completed tests included TSA operation with SO₃ measurements performed by Montrose Air Quality Services and aerosol mitigation tests with ELPI+ measurements taken by Southern Research. Cansolv agreed to resume testing in a later run following the completion of the MEA baseline tests in the SSTU. Measurements taken during the MEA operation are shown below. Figure 38 compares results from ELPI+ measurements taken on the treated flue gas stream (wash tower outlet) without the TSA in operation and two measurements at the same sampling point with the TSA in operation.



Figure 38. First Set of Measurements of Treated Flue Gas Aerosols with and without TSA Operation

Very little difference was observed in the distribution and number count of aerosols at the operating condition. Another test was conducted the following day at a different operating condition, and the results are plotted in Figure 39. A noticeable increase of aerosols in the <0.03 micron range was observed for both cases (with and without TSA operation), which indicates a more significant impact of changing operating conditions over the effects of the TSA unit. Additional tests will be required to determine the net effect of the process changes that resulted in the smaller particle size distribution that was observed, although the TSA impact appeared to be minimal.



Figure 39. Second Set of Measurements of Treated Flue Gas Aerosols with and without TSA Operation

On the last day of testing, data was gathered at the BDU exit to ascertain its collection efficiency. Figure 40 shows the raw data generated by the ELPI, with the particle number concentration for each stage shown.



Figure 40. Particle Concentration Measurements Taken at BDU Outlet

The BDU outlet data showed some unexpected fluctuations that were especially large for stages 2 and 4 and can be seen increasing over time. These results are suspect since current was observed across multiple impactor stages. Collection of liquid droplets in several stages on the ELPI+ impactor was observed when different stages were disassembled after this test. The droplets may have contained solvent that was lost from the absorber. Further detailed aerosol characterizations at the BDU outlet are necessary in future test campaigns to determine if the BDU is inadvertently creating a concentrated solvent aerosol or if an upset condition created this phenomenon. Therefore, Figure 40 may not provide meaningful performance data. There was no additional operating time available after the BDU outlet test to continue the evaluation, so remaining objectives would have to wait until the next operating window.

2.11 Amine Emissions Measurements with the ELPI+

Amine emissions from carbon capture systems in the form of aerosols leaving the absorber are a common problem with commercial solvent processes where SO_3 is present in the flue gas. The formation of aerosols has been found to correlate with the concentration of SO_3 present in the flue gas. The amine leaving the system is difficult to capture due to the small particle size (the vast majority are less than one micron in diameter), and traditional systems do not have an efficient way to remove them from the exiting treated flue gas. Solvent losses from this effect are significant and must be addressed if a commercial system is to be deployed. An understanding of upstream equipment effects and internal process changes are critical to determine all of the mechanisms at work which create aerosols, hopefully leading to a design or

operational philosophy describing how to best mitigate them without expensive downstream equipment. Therefore, a project was initiated to design and construct a sample extraction system for analytical equipment including the ELPI+ device to measure the particle size distribution (PSD) and particle number count in real time. The selected sampling locations included the PSTU inlet (untreated flue gas), the SSTU inlet (following SO₂ removal and cooling within the PSTU process units), and the SSTU wash tower outlet.

The primary objective in 2015 was to establish baseline data that could be compared against results obtained in 2016, when a new activated carbon injection baghouse was brought on-line at Gaston Unit 5, upstream of the PC4. This baghouse is located between the Unit 5 flue gas desulfurizer and the selective catalytic reduction process. It was installed to reduce heavy metals emissions, but has demonstrated the additional effect of removing most of the SO₃ present. Based on the current understanding of the aerosol formation mechanism, this should cause a dramatic decrease in amine emissions. The NCCC and project partners want to quantify this effect in addition to the effects of changes in process conditions.

The ELPI+ was procured and the sampling system was constructed in preparation for sampling in December 2015. Due to time constraints, a focus was placed on gathering stable baseline data versus real-time observations of PSD and count changes caused by process step changes. The three previously listed sample locations were evaluated as well as the treated flue gas stream leaving the Linde-BASF 1-MW solvent unit. Figure 41 provides a view of the equipment setup.



Figure 41. ELPI+ Equipment Setup

Baseline data was gathered to be compared with results after operation post-baghouse installation commenced beginning in April 2016. Figure 42 provides an example of the data gathered by the ELPI+ device. In this instance, three sets of data were collected from the SSTU treated flue gas

stream (wash tower exit) on December 11, 2015. The data are plotted as normalized particles count versus particle diameter.



Figure 42. Particle Size Distribution and Count of Amine Aerosols in SSTU Treated Flue Gas Stream

Additional data will be collected throughout operations in 2016 at the same sample locations previously tested. By the end of the reporting period, the only ELPI+ tests conducted in 2016 were those taken on the treated flue gas stream of the Linde-BASF unit. Therefore, this data was used to compare the net effect of the baghouse on the Linde-BASF unit emissions and to extrapolate to similarly designed amine-based systems. Figure 43 and Figure 44 depict this difference at low load and high load conditions for the generating plant (Plant Gaston Unit 5).



Figure 43. Aerosol PSD and Count of Flue Gas Stream of the Linde-BASF Unit at Gaston Unit 5 Low Load Conditions



Figure 44. Aerosol PSD and Count for Treated Flue Gas Stream of the Linde-BASF Unit at Gaston Unit 5 High Load Conditions

As demonstrated by the figures, the impact of the baghouse operation was significant, causing a drop in particle count of several orders of magnitude. Additionally, more than 97 percent of the cumulative aerosol number was below 0.1 microns after the baghouse installation. Further analysis will be required to determine the effects on net amine emissions rate and the effects of changes in internal process conditions. Regardless, initial indications are that amine emissions may be significantly reduced by the inclusion of an activated carbon injection baghouse on coalderived flue gas streams where SO_3 is present.

2.12 Amine Emissions Measurements with the Phase Doppler Interferometer

In addition to the ELPI+ measurements for aerosol size and count, a PDI, operated by staff from UT-Austin, was used on the SSTU treated flue gas stream. The data were generated concurrently with that from the ELPI+ in December 2015 for comparison. Differences with the sampling methods were noted that could have significant effects on the measured values. In particular, the PDI samples were not extracted from the process isokinetically, and ambient effects on uninsulated sample lines could be substantial. A Fourier Transform Infrared Spectrometer (FTIR) was also installed adjacent to the PDI to measure the composition of the stream. Figure 45 shows the equipment as installed in the field, and Figure 46 provides a process flow diagram of the SSTU and sampling system.



Figure 45. PDI and FTIR Field Sampling Arrangement



Figure 46. Process Flow Diagram for PDI Measurements at the SSTU

Objectives for the test were to obtain comparable data for the adjacent ELPI+ measurements, observe the effects of process changes, and provide data for the analysis of the baghouse effect. Figure 47 gives results from the PDI for two different operating conditions: operation of the SSTU with the SSTU blower in service and with only the PSTU blower in service.



Figure 47. PSD and Count for Aerosols at the SSTU Wash Tower Outlet for Two Modes of Operation

The PDI measurements for particle size were larger than the ELPI+ measurements. The cause for the difference may be due to ambient heat losses in the sample lines resulting in further condensation of the aerosol particles. However, the general trend and peaks were similar to those of the ELPI+ data. An important result was the difference apparent between the operating modes and the significant effect on the particle size distribution. Repetition of the tests in 2016 will yield additional clarity on the effects of process changes and the difference in sample extraction techniques between the two measurement devices. Further measurements with the PDI and FTIR are planned for during operation of the SSTU with MEA in late 2016. A final comparison of the PDI and ELPI+ generated data will be performed once all of the test objectives are completed.

2.13 Akermin Enzymes

Akermin continued development of an advanced biocatalyst enabled solvent system for low cost CO_2 capture with a scale-up of a project tested at the NCCC in 2013. The novel system, depicted in Figure 48, combines the next-generation biocatalyst delivery system and a non-volatile salt solution, the AKM24 solvent. The biocatalyst delivery system entails carbonic anhydrase enzymes, immobilized within proprietary polymeric micro-particles, which accelerate hydration of CO_2 to bicarbonate to enhance the performance of the solvent for CO_2 capture. The micro-particles have high surface area to enable higher mass transfer rates and provide a protective environment for the enzymes against inactivation by temperature, solvent, and shear forces.



Figure 48. Process Flow Diagram of Akermin Enzyme Process

In modifying the previously tested system, a biocatalyst recovery system and a new absorber column were installed, as shown in Figure 49. System commissioning with water and testing with blank solvent (without biocatalyst) were completed in December 2015.



Figure 49. Akermin Enzyme Test Equipment

Parametric testing began in early June, 2016, with the addition of 0.7 kg of biocatalyst. The capture immediately increased, from about 48 percent without catalyst to as much as 93 percent with catalyst. However, unlike Akermin's experience in the laboratory, the particle concentration in the recirculating solution began to decline precipitously, and the CO_2 capture rate declined correspondingly. In an attempt to improve capture, another 0.7 kg of biocatalyst was added into the system. The addition of the biocatalyst resulted in the immediate improvement of system performance. However, as the biocatalyst concentration in the suspension declined, the CO_2 capture declined as well. Controlling spillover rate was found to be problematic. After two days of operation, the system was brought to partially stable performance and data were gathered for the peak performance at the design lean-to-rich spread with 30 wt% AKM24. Table 10 lists the peak performance values.

Table 10. Peak Performance	Values of Akermin E	inzyme System
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Parameter	Value
Gas Flow Rate, Sm ² /hr	30
Liquid Flow Rate, L/hr	200
CO_2 Loading Range, mol CO_2 /mol K+	0.35 – 0.65
CO₂ Capture Rate	93.3
KGa, mmol/m²/s/kPa	0.10
Lean Multiplier, X	11
Regeneration Energy, $GJ/ton CO_2$	3.1

The measured regeneration energy of the bench unit at $3.1 \text{ GJ/ton } \text{CO}_2$ was higher than predicted by the developed Aspen model. The reasons for this discrepancy appeared to be the following:

- Due to issues balancing water make up rates, the AKM-24 solvent concentration was diluted to 30 wt%, lower than the model value of 35 wt%. This increased the sensible duty compared to that predicted.
- The NCCC rich loading target of 0.7 mol/mol was achieved, but commercially the rich loading target is 0.8 mol/mol CO₂. This higher rich loading is expected to have a significant impact on the observed energy.
- High heat losses occurred in lines to and from the stripper due to scale.

The system operated over a one-month period; however the run was affected by a number of engineering issues making the performance unstable. The primary issues were uncontrolled rich solvent spillover resulting in significant fluctuations of the particle hold up in the biocatalyst recovery system and in solvent loading and a general loss of recirculating particles in the system resulting from their accumulation in the absorber. It was hypothesized that the significant and unexpected particle retention in the absorber resulted from low area efficiency of the absorber column (about 15 percent) that was primarily due to the low liquid load in the system. Indeed, when the recirculation rate was increased for a brief time, a significant amount of particles was eluted from the absorber. When the flow was brought back to the design condition, the particles again concentrated in the absorber. Due to these issues and a temporary plant shutdown

(resulting in flue gas and steam supply interruptions) the system operated for about 20 days. The anticipated performance of 90 percent capture was rarely achieved due to particle accumulation in the absorber. The CO_2 capture rate for the run is plotted in Figure 50. The average capture was around 70 percent.



Figure 50. CO₂ Capture with Akermin Enzymes in 30 wt% AKM24 at 40°C

It remains unclear why such a significant accumulation of particles occurred in the pilot unit while only little accumulation occurred in the lab-scale reactor. It was hypothesized that low area efficiency of the bench unit absorber resulted in the particles accumulating in dry areas of the column. Higher temperature of the bench unit absorber (sometimes reaching 58°C or 136°F) could have contributed to the particle drying and increased adherence to the internals of the column. Another hypothesis was that some unintended misalignment of the column contributed to the decreased area efficiency consequently to the particle retention in the column. After one month of operation it became clear that the unit in the current configuration was not able to meet the project objectives, and it was shut down. The following steps to improve the performance might be considered:

- Check the column alignment and re-align if necessary
- Redesign the absorber to improve area efficiency
- Modify configuration in the biocatalyst recovery system to achieve a more stable spillover and improve separation efficiency to minimize particle accumulation in multimedia filters

2.14 GE Global Aminosilicone Solvent and Desorber Unit

GE Global has been developing a CO_2 capture process using aminosilicone solvents. Compared to alkanolamines such as MEA, aminosilicones possess properties that substantially decrease the

cost of solvent-based CO_2 capture, including lower vapor pressures, higher boiling points, greater thermal stability, and lower heat capacity. In addition, the replacement of water with a nonvolatile co-solvent results in a substantial energy savings. GE's process uses a continuous stirred tank reactor desorber unit instead of a traditional column solvent regenerator. The desorber features simple operation and small footprint, and compared to the column regenerator, requires lower capital cost.

During the reporting period, preparations were completed for testing of the GE solvent in the PSTU during run PO-5. During the first portion of the test, GE will test the aminosilicone solvent using the GE desorber unit in place of the PSTU regenerator. For the second portion, the PSTU regenerator will be used for performance comparisons. The GE desorber was installed on a newly added floor of the PSTU structure, as shown in Figure 51. Equipment checkouts were performed in late 2015, and start-up activities were underway at the end of BP2. The test is expected to continue through the end of PO-5.



Figure 51. GE Global Desorber Unit Installed in PSTU Structure

2.15 PC4 Modifications

Modifications were ongoing to increase the PC4 testing capabilities. The most significant of these projects are listed below.

PSTU Column Bed Differential Pressure Measurements

To improve the accuracy of differential pressure readings across the packed beds of the absorber and regenerator columns in the PSTU columns, new Rosemount ERS transmitters were installed. The previously used transmitter readings varied based on the ambient temperature and sunlight received on the sensing lines. The ERS transmitter includes two remote sensors, one at the high end and one at the low end, that connect to the transmitter via wiring, thus eliminating errors caused by temperature variations. During testing, the instruments exhibited data consistency and improved resistance to ambient effects compared with previously used instruments.

Aerosol Sampling Systems

A project was completed to design and construct sample extraction systems for analytical equipment including the ELPI+ and the PDI for aerosol measurements. Sampling locations included the PSTU inlet (untreated flue gas), the SSTU inlet (following SO_2 removal and cooling within the PSTU process units), and the SSTU wash tower outlet.

Flue Gas Blower Vibration Transmitters

Transmitters were installed on the flue gas blowers to allow operators to monitor vibration from the distributed control system.

PSTU Rich-Lean Heat Exchanger Differential Pressure Measurement

In support of test partner requests for additional data points, new differential pressure transmitters were installed on each side of the rich/lean heat exchanger.

Slipstream Solvent Test Unit

Modifications to the SSTU were completed in preparation for the PO-5 run. Changes included installation of a new blower, transmitters, and area gas detectors, relocation of valves and instruments, addition of a larger CO_2 product line, and upgrades to the control system. A new programmable logic controller was installed, and interlocks and other control changes were made to provide greater operability and safety. In addition, an air circulation system was installed for the Green Technology project.

Data Automation for Test Partners

Implementation was underway of new software to improve and automate data transfer to technology developers from the PC4 plant historian. The software identified to serve this purpose was E-Notification. The software will provide an automated service and will periodically send to developers process data in an Excel spreadsheet with pre-selected frequencies and formats. It will also provide electronic communication alerts to process deviations of interest. The system was tested and proved to function in a manner consistent with site specifications.

PC4 Unit 5 Operational Information

The project scope included the addition of new process tags to the NCCC data historian to actively monitor and analyze process changes to the upstream Gaston Unit 5 equipment. The data will provide a method for determining the feed composition of the boiler. Rates for coal only feed or co-firing with natural gas can be measured and historically tracked. Additionally, data from the environmental control systems and continuous emissions monitoring systems will be captured to help quantify their effects on downstream capture processes.

3.0 GASIFICATION

The NCCC gasification process, represented in Figure 52, features several key components of an Integrated Gasification Combined Cycle (IGCC) plant. These include high pressure solids feed systems; a Transport Gasifier; syngas coolers; a hot gas filter vessel, the Particulate Control Device; and continuous ash depressurization systems for ash cooling and removal. Gasification operation, which began in 1999, provides syngas for testing of gasification-related technologies in addition to testing of pre-combustion CO_2 capture technologies.



Figure 52. NCCC Gasification Process

During the reporting period, 2,201 hours of gasification operation were achieved over three runs: G-2, occurring from September 13, 2015, through October 16, 2015; G-3, beginning on March 17, 2016, and ending on April 11, 2016; and G-4, immediately following G-3 on April 11, 2016, and lasting through June 3, 2016. The runs supported multiple technology developer projects, as described in the following sections. Table 11 provides the average syngas composition and carbon conversion for the three runs.

Table II. Average Syngas composition and carbon conversion for Steady State Ferrow.

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Syngas Component	Run G-2, Operation with Liberty Fuels Lignite	Run G-3, Operation with PRB Coal	Run G-4, Operation with Red Hills Lignite		
Carbon Monoxide, vol%	6.5	9.2	6.2		
Hydrogen, vol%	5.6	6.3	5.1		
Carbon Dioxide, vol %	8.8	7.6	8.4		
Methane, vol%	0.6	1.0	0.7		
Nitrogen, vol%	67.3	68.1	68.9		
Water, vol%	10.9	7.4	10.2		
Carbon Conversion, %	99.8	97.9	99.2		

3.1 Southern Research Institute Fischer-Tropsch Catalyst

The SR Fischer-Tropsch catalyst project incorporates a novel approach of F-T synthesis that eliminates the conventional product upgrading and refining steps and enhances the ability of coal-to-liquids and coal/biomass-to-liquids processes to compete with petroleum-based processes. SR's 5-lb/hr bench-scale test skid consists of a F-T synthesis reactor system to produce liquid transportation fuels using a selective, wax-free, cobalt F-T catalyst from Chevron.

The G-2 testing of the F-T catalyst was conducted to verify the performance of a specially formulated hybrid catalyst to achieve the catalyst activity of greater than 0.7 grams of C5+ hydrocarbons per gram of catalyst per hour (gC5+/gcat/hr) and product selectivity of greater than 65 percent jet fuel. The selected catalyst was tested in SR's coal-biomass-to-liquid two-inch F-T reactor skid utilizing a micro-fiber entrapment catalyst technology to aid in heat transfer for the highly active catalyst.

The test campaign was a continuation of parametric experiments conducted in the lab to screen catalysts for productivity and selectivity performance. The selected catalyst was tested at a variety of pressures, temperatures, and gas compositions. The tests successfully achieved the catalyst performance targets. However, due to difficulties in precisely controlling the operating conditions, the results were not quite as high as those observed in the lab. Nonetheless, the catalyst was able to achieve the necessary hydrocarbon productivity and product selectivity at conditions that were less than optimal. Figure 53 plots the CO conversion, methane selectivity, and light hydrocarbon selectivity with varying operating conditions.



Figure 53. CO Conversion and Product Selectivities of SR Fischer-Tropsch Catalyst

Table 12 summarizes the yields and carbon distributions for the experiments. The target productivity and jet fuel (C8-C16) selectivity values were reached or exceeded for several experiments.

	C4-C7	C8-C16	C17-C21	C22+	Liquid Productivity (gC5+/gcat/hr)
Group 1	26.2%	69.4%	4.1%	0.5%	0.83
Group 2	21.0%	65.2%	11.9%	2.5%	0.76
Group 3	24.0%	64.9%	10.0%	1.9%	0.84
Group 4	21.2%	64.7%	12.5%	2.6%	0.70
Group 5	14.4%	58.3%	19.5%	5.1%	0.61
Group 6	15.8%	59.3%	17.9%	4.6%	0.62
Group 7	16.2%	58.6%	17.8%	4.7%	0.66
Group 8	18.1%	58.4%	16.9%	4.3%	0.60
Group 9	18.2%	60.8%	15.6%	3.8%	0.52

Table 12. Jet Fuel Selectivity for Liquid Products of the SR Fischer-Tropsch Catalyst

Future testing at the NCCC will include demonstration of the selective F-T catalyst and microfiber entrapment catalyst in a four-inch reactor. Current reactors are limited by the heat removal rate and by the surface area-to-volume ratio of the reactor tubes. The demonstration of a fourinch reactor tube will expand the range of successful operation of tubular F-T reactors by a factor of four beyond that demonstrated in the two-inch reactor. This will dramatically simplify the design of tubular F-T reactors, and with the selective F-T catalyst, reduce the overall reactor size and associated capital costs. SR is also to add an auto-thermal reformer.

3.2 Johnson-Matthey Mercury Sorbent

Testing continued with the Johnson Matthey palladium-based sorbent for removal of mercury and other trace contaminants at high temperature. The sorbent, which had been regenerated prior to testing in 2014, was operated throughout the G-2, G-3, and G-4 runs with desulfurized, shifted syngas for 1,847 hours at a flow rate of 50 lb/hr, an operating pressure of 12.4 to 13.1 bar (180 to 190 psig), and a temperature of 260°C (500°F). NCCC gas analysis technicians took periodic inlet and outlet samples, with breakthrough of mercury and selenium detected in the outlet samples during the G-4 run. The total testing of this material is approximately 6,000 hours distributed over ten gasification runs, with the last 2,943 hours tested on the regenerated sorbent.

3.3 Water-Gas Shift and COS Hydrolysis Catalysts

Operation continued with a previously tested WGS catalyst during the runs. During G-2, testing was conducted for 657 hours, and the main test objective was evaluation of long-term stability at a flow rate of 50 lb/hr and a temperature of 250° C (482° F). The G-3/G-4 testing included parametric and long-term testing at the operating conditions given in Table 13. During the long-term testing, the catalyst was overheated for a short time due to the failure of a heater controller. Once the problem was corrected and testing resumed, the shift conversion decreased. The

G-3/G-4 testing lasted for 1,081 hours with fresh catalyst, bringing the total operational time of this catalyst type to about 6,500 hours.

Table 13.	Operating	Conditions for	WGS	Catalyst	Testing	during th	e G-3/G-4	Runs

Operating Conditions	Range
Syngas Flow Rate, lb/hr	25 to 50
Steam-to-CO Molar Ratio	0.7 to 1.4
Operating Temperature, °C (°F)	203 to 251 (397 to 484)
Operating Pressure, psig	180
Bed Temperature, °C (°F)	286 to 321 (546 to 610)
Shift Conversion, %	63 to 86

A COS hydrolysis catalyst from the same developer was evaluated with parametric and longterm tests using sour syngas at the operating conditions given in Table 14. The catalyst operated for 656 hours during G-2 and for 1,233 hours during G-3 and G-4, bringing the total test time for this catalyst to 2,621 hours over three runs. Further operation of this catalyst is planned for future runs.

Table 14. Operating Conditions for COS Hydrolysis Catalyst Testing

Operating Conditions	Range
Syngas Flow Rate, Ib/hr	25 to 50
Operating Temperature, [°] C ([°] F)	251 to 350 (484 to 662)
Operating Pressure, psig	112 to 180
Bed Temperature, °C (°F)	212 to 317 (415 to 603)
COS Conversion, %	44 to 61

3.4 Emerson Sapphire Thermowells

Testing was performed with Emerson Process Management's Rosemount sapphire thermowells as an expansion of previous operation using a single thermowell installed in the gasifier riser above the coal feed nozzles. For run G-2, the thermowells, which are designed to withstand erosive environments and thermal stress, were placed in three different sections of the gasifier with varying degrees of solids flow rates and temperature fluctuations. Figure 54 provides a schematic of the gasifier denoting the thermowell locations. The thermowells in the riser and lower standpipe were operable throughout G-2, and were subsequently tested during G-3 and G-4. However, the thermowell installed in the riser crossover failed shortly after the G-2 run began, and therefore no data was available from this location.



Figure 54. Sapphire Thermowell Test Locations in the Gasifier

Data from the two operable units were compared to nearby HR-160 thermowell units, which are the standard design used in the gasifier. As shown in Figure 55, the difference in the temperature readings for the riser location was $65F^{\circ}$ ($36C^{\circ}$) on average during G-2. Although the sapphire thermowell unit gave lower measurements than the reference thermocouple, it showed good responsiveness and agreement with temperature changes.



Figure 55. Comparison of Thermocouple Measurements Using Sapphire and HR-160 Thermowells in Gasifier Riser

Figure 56 plots the temperature readings from the sapphire unit and from the reference thermocouple for the lower standpipe location during G-2. The sapphire unit was on average $35F^{\circ}$ ($19C^{\circ}$) lower than the reference thermocouple, and it also demonstrated good responsiveness to temperature changes.



Figure 56. Comparison of Thermocouple Measurements Using Sapphire and HR-160 Thermowells in Gasifier Lower Standpipe

For both locations, the G-3/G-4 test results were comparable to the G-2 results. Both sapphire units will be tested further in future runs.

3.5 PCME Particulate Monitor

Because the original instrument from PCME, Ltd. (a UK-based supplier of particulate emission monitoring systems) used for detecting particulate leaks downstream of the particulate filter had become obsolete, a new, commercially available replacement instrument was installed before the G-2 run. The replacement instrument, purchased from the same supplier, was a PCME View Ex820 system. The system has a grounded sensing rod which protrudes into the syngas flow. It can sense the frequency of particle collisions on the rod and provide an output signal (from 0 to 100 percent) which may be correlated with particulate concentration based on in-situ sampling results.

As expected, the PCME monitor readings during normal operation were near zero with responses to the periodic particulate filter back-pulse (0.1-second reverse flow filter cleaning). Calibration testing was completed using injected gasification ash at known flow rates. The results of calibration testing during G-2 and G-4 were compared with the results from the TC06 (2001) and TC07 (2002) runs. Figure 57 plots the normalized particle concentrations as a function of the PCME monitor output. The data were normalized to the same syngas flow rate, since the PCME

does not determine the particle concentrations directly, but instead measures the number of particles passing the probe per unit time and provides a percent output.



Figure 57. Ash Injection Responses of Old and New PCME Particulate Monitors

The G-2 and G-4 results with the newly installed monitor show data points at relatively lower concentrations obtained by ash injection. The results indicate that the tests are reasonably repeatable and comparable with the data of TC06 and TC07 test campaigns with the older PCME monitor. The new monitor gave a clear response with ash concentrations as low as 0.6 to 1.0 ppmw, which indicates its potential usefulness as part of a control strategy for protecting gas turbines and other equipment downstream of particulate filters. Additional calibration testing will be conducted at higher ash concentrations.

3.6 Ohio State University Syngas Chemical Looping

OSU's SCL process uses countercurrent moving beds and iron-based composite oxygen carriers under reduction-oxidation conditions, converting coal-derived syngas into carbon-free energy carriers for electricity or hydrogen/chemical production. The project is funded by DOE's Advanced Research Projects Agency-Energy. The SCL process installed at the NCCC is a pilotscale, 250-kW system using up to 900 lb/hr syngas.

Following the identification of needed design changes for the process burner during attempted operation in 2014, OSU completed fabrication of a new burner. Off-line testing of the new burner was conducted at the NCCC in August 2015, which showed high shell temperatures on the refractory lined burner vessel. To address the high shell temperatures, OSU incorporated a system modification involving the injection of propane into the burner leg vessel. After test-firing the burner with the propane injection system, OSU identified additional needed modifications to prevent condensation, and these were completed prior to the start of G-3.
During gasifier operation in G-3, OSU conducted start-up activities of the SCL process over a 120-hour test run. The SCL pilot test unit was heated to an operating temperature of 870°C (1,600°F) at a pressure of 75 psi. Initial syngas testing commenced for 10 hours with greater than 98 percent conversion of syngas components (carbon monoxide, methane, and hydrogen) in the reducer reactor observed throughout syngas operations. Control of the pressure seal and solids flow was maintained throughout the start-up and testing. Issues with fluidization prevented further syngas operation, and OSU began preparations for modifications to be incorporated prior to further operation.

3.7 TDA Research Ammonia Sorbent

TDA Research completed the first NCCC testing of a sorbent-based gas clean-up technology to remove ammonia and hydrogen cyanide as well as mercury and other trace metals from syngas at high temperatures in a single process step. The sorbent is operated in a regenerable manner to remove ammonia and mercury, while irreversibly absorbing hydrogen cyanide and other contaminants. TDA's clean-up system operates at 260°C (500°F) downstream of a warm gas desulfurization system.

TDA operated the system for approximately 50 hours. Figure 58 shows the first three cycles of the field test during which the sorbent achieved greater than 99 percent ammonia removal efficiency. The capacity in Cycles 2 and 3 was lower due to the regeneration step being carried out under pressure swing conditions instead of a combination of pressure and mild temperature swing conditions. With the successful results of the field tests, TDA plans to further develop the sorbent technology.



Figure 58. TDA Research Ammonia Sorbent Results over Three Cycles

Figure 59 shows the ammonia concentration, temperature, and flow rate profiles during a typical pressure swing cycle illustrating the ammonia removal and subsequent release. Ammonia measurements were taken with a mass spectrometer and with Gastec detector tubes.



Figure 59. Absorption and Regeneration Profiles for TDA Research Ammonia Sorbent

3.8 TDA Research CO₂/WGS Sorbent

In a project funded by DOE, TDA is demonstrating the technical viability of an integrated low temperature water-gas shift catalyst/ CO_2 removal/thermal management system for an IGCC power plant. The project involves designing and testing reactors that are tailor-made to house a proven high temperature CO_2 sorbent with commercially available low temperature WGS catalyst while providing all the thermal management equipment needed to ensure the optimum operating conditions.

To demonstrate the concept, TDA developed a fully automated test unit capable of removing CO_2 from raw unshifted syngas with a gas treatment capacity of 1 to 2 SCFM. After optimizing the bed cycle sequence at TDA facilities, the unit was installed at the NCCC to evaluate the prototype unit using actual coal-derived syngas. During the G-2 run, a four-bed unit containing the combined WGS/CO₂ removal and thermal management system in a test apparatus was tested. The goal of the testing was to demonstrate the key aspects of the combined shift and CO_2 separation system, such as CO conversion, overall carbon capture, temperature rise in the beds, and the functionality of the thermal management system while using coal-derived syngas. The testing apparatus was operated for over 90 hours on syngas during which several parameters were explored such as altering the inlet CO concentration and varying the water injection rate while observing their effects on the bed temperature, carbon removal, and CO conversion.

TDA successfully demonstrated the integrated WGS catalyst/CO₂ removal sorbent operation, as well as the thermal management system in controlling the reactor temperatures during adsorption and WGS. Shown in Figure 60, the amount of CO entering the adsorption/WGS beds was increased from 1.5 mol% to 4.0 mol%; during this time, the amount of water injected into the reactors was increased from 1.0 to 5.0 mL/min. The energy used to convert the injected water into steam was significant enough to maintain the reactor bed temperatures despite the increase in WGS activity. During the entire testing period, the system averaged greater than 97 percent carbon capture. The average CO conversion in the reactor beds was greater than 76 percent.



Figure 60. Effects of Increasing CO Inlet Concentration on Bed Temperature

For the G-3 and G-4 runs, TDA conducted additional parametric tests, altering the reactor inlet CO concentration and varying the injected water rates while observing their effects on bed temperature, carbon removal, and CO conversion. Test results will be used in the design of a scaled-up system to be tested in the next run.

TDA demonstrated that reactor bed temperatures can be precisely controlled by direct water injection, achieving a temperature decrease of 20 C° (54 F°) throughout the bed when steam addition was stopped and direct water injection began. To investigate the effect of water injection on CO conversion and sorbent capacity, water was injected to achieve an H₂O-to-CO ratio of three. During this period, average CO conversion was 90 percent and the average sorbent capacity was 5.5 g of CO₂ adsorbed per liter of sorbent. For a direct comparison, a similar amount of steam was added in the inlet syngas stream to achieve an H₂O-to-CO ratio of 3 or higher. The results showed that the CO conversion was always lower when steam was added to the inlet stream compared to direct water injection into the reactors.

To assess the effect of inlet CO concentration on CO conversion and ultimately overall carbon capture, inlet CO concentrations were altered by adjusting how much of the syngas feed was pretreated in an upstream water gas shift reactor. As shown in Figure 61, the inlet CO was varied between 3 and 9 percent. During the periods where the CO inlet was below 5.5 percent, the system was able to achieve 90 percent CO conversion, resulting in a carbon capture rate of greater than 95 percent. At CO concentrations above 5.5 percent, the system had difficulty achieving high CO conversions, resulting in a lower carbon capture rate of 85 to 90 percent.



Figure 61. Operational Data from TDA Research WGS/CO₂ Sorbent Unit

3.9 Coal Feeder Instrumentation

Long-term evaluation continued on solids level probes installed in the PDAC feeder as shown in Figure 62. The Dynatrol vibration level probes installed in the dispense vessel and lock vessel in 2009 have provided reliable indications of solids level in both vessels for lignite and subbituminous coals. The level probes in the dispense vessel performed consistently throughout the gasification runs. The level probe in the lock vessel, however, was replaced following the G-2 run after it was found to be broken. This probe had been replaced in 2014 due to mechanical damage after more than 7,500 hours of consistent operation.



Figure 62. Schematic of PDAC Feeder

The Drexelbrook point sensitive level probe was vertically installed in the top of the PDAC feeder dispense vessel in 2010 to permit higher level control of the coal inventory in the vessel. Since installation, the probe continually provided steady solids level control, mitigating the impact of solids level variation on coal feed rate. The original probe was replaced in 2013 due to electrical failure after more than 6,500 hours of reliable operation. The new probe had been repaired and recalibrated prior to G-2, and performed consistently during the following runs.

As seen in previous runs, measurements from the Densflow coal flow meter on the PDAC feeder differed from the calculated mass flow rates based on the weigh cell data. Work is ongoing to address the inconsistency.

3.10 Gasifier Refractory

Following gasification runs, inspections of the gasifier hot-face refractory were conducted on areas most prone to wear or damage. Figure 63 provides a comparison of boroscope images before and after the G-3/G-4 runs, which indicates minimal wear in these areas. The areas of special interest include the seal leg return from the solids separation unit to the standpipe (shown in green in the figure), the J-leg/lower mixing zone interface (shown in red in the figure), and the J-leg/standpipe interface (shown in purple in the figure). The J-leg/lower mixing zone interface uses Resco Sureflow 88 refractory, which was installed in 2006. The other two locations use Resco Sureflow 17E refractory that was installed in 2011 when the standpipe was replaced.



Figure 63. Schematic of NCCC Transport Gasifier with Refractory Inspection Images

3.11 Hot Gas Filter Elements

The hot gas filters operated with stable pressure drop and collection efficiency above 99.9999 percent. Table 15 lists the six types of filter elements tested and the maximum hours of exposure for individual elements of each type. For commercial operation, the elements are expected to operate for a least two years, or about 16,000 hours. The filter element testing thus far has shown that the Iron Aluminide elements have maintained excellent collection efficiency for more than 16,000 hours, and testing with the other element types will continue to assess their commercial suitability as well.

Table 15.	Exposure Hours for Hot Gas Filter Elements Tested
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Filter Media Type	Material	Supplier/ Brand	Maximum Hours of Exposure
Sintered Metal Powder	Iron Aluminide	Pall/PSS	19,162
Fine Sintered Metal Fiber	HR-160	Pall/Dynalloy	12,005
Coarse Sintered Metal Fiber	HR-160	Pall/Dynalloy	14,030
Sintered Metal Powder	High alloy (SR-75)	Mott	10,508
Sintered Metal Fiber	Coated high alloy	Porvair/Sinterflo	10,985
Sintered Metal Fiber	Fecralloy	Bekaert	5,967

4.0 PRE-COMBUSTION CO₂ CAPTURE

The NCCC's pre-combustion CO_2 capture program allows evaluation of solvents, sorbents, catalysts, membranes, and other emerging technologies at an appropriate scale with coal-derived syngas produced during gasification runs. Figure 64 is a schematic of the pre-combustion facilities, which include the Syngas Conditioning Unit and a separate unit for pilot-scale testing. The SCU uses up to 1,500 lb/hr and accommodates simultaneous testing of multiple technologies at different syngas conditions and flow rates. The pilot unit operates at syngas flow rates up to 1,000 lb/hr. A variety of syngas treatment steps can be implemented to meet developer requirements such as sulfur removal, trace metal removal, WGS, and hydrocarbon treatment.



Figure 64. Schematic of Pre-Combustion CO₂ Capture Facilities

4.1 Worcester Polytechnic Institute Hydrogen Membranes

In continued development of its palladium-based hydrogen membranes, WPI tested a multi-tube membrane module during G-2. The module, a seven-fold scale-up from previous testing, was composed of seven palladium-gold composite membranes, with a total permeable area of $1,050 \text{ cm}^2$. Each tube was fabricated with a dense inner layer of palladium about 5.4 microns thick, a second layer of 0.4 microns of gold for improved stability and recoverability, and a final layer of palladium of about 1.6 microns. With only one percent deviation in thickness among the tubes, the consistent fabrication of the membrane tubes demonstrated the replicability of this

technology. Lab testing performed prior to the gasification run showed a cumulative helium leak rate of less than $0.01 \text{ cm}^3/\text{min/bar}$.

The performance of the membrane module was evaluated based on its hydrogen permeance, hydrogen product purity, and hydrogen recovery. Hydrogen permeance is defined as follows:

$$H_2$$
 Permeance= $\frac{\text{Permeate H}_2 \text{ Flow Rate}}{\text{Surface Area }(\sqrt{\text{pH}_{2,\text{avg}}} - \sqrt{\text{pH}_{2,\text{permeate}}})}$

The values of pH_2 , avg and pH_2 , permeate are the partial pressures of hydrogen in the module and in the permeate, respectively. Hydrogen purity is calculated as the flow rate of the permeate hydrogen divided by the flow rate of the retentate. Hydrogen recovery is defined as the difference between the hydrogen feed flow rate and the hydrogen permeate flow rate divided by the hydrogen feed flow rate.

During G-2, the module operated at a temperature of 450°C (842°F) and a pressure of 12.6 bar (183 psig) with 10 lb/hr of syngas enriched with bottle hydrogen to achieve an inlet hydrogen concentration of 34 percent. Testing was conducted continuously for 837 hours, with 207 hours under hydrogen/nitrogen mixtures and 630 hours under syngas conditions. Figure 65 plots the hydrogen permeance and purity of the module as a function of time.



Figure 65. Hydrogen Permeance and Purity Profiles of the WPI Membrane Module

Initially, the membrane module showed a permeance in the range of 7 to $10 \text{ Nm}^3/\text{m}^2/\text{h/bar}^{0.5}$ (6 to 8.6 scfh/ft²/psi^{0.5}) when tested under a hydrogen/nitrogen mixture as depicted in the figure with solid black circles. When syngas feed to the module began, a slight increase in permeance was observed, followed by steady performance. The maximum flux achieved by the seven membranes was 6 lb hydrogen/day. For comparison, an eighth membrane of the same fabrication tested with pure hydrogen in WPI labs showed hydrogen permeance of

80 Nm³/m²/h/bar^{0.5} (69 scfh/ft²/psi^{0.5}), equivalent to 1.03 lb hydrogen/day at a pressure difference of 0.35 bar. The hydrogen purity produced by these membranes began at 99.5 percent with hydrogen/nitrogen feed. When syngas feed began, the purity increased to 99.6 percent, and was as high as 99.9 percent after 67 hours of operation. The product purity then decreased steadily, reaching a minimum purity of 98.8 percent after 670 hours. At the end of the test, the hydrogen purity was of 98.1 percent with hydrogen/nitrogen feed.

Figure 66 shows the hydrogen recovery achieved. When using hydrogen/nitrogen feed at the beginning of the test, the recovery reached 52 percent. Under syngas conditions, the hydrogen recovery decreased to 35 percent and remained fairly constant throughout the test. The maximum theoretical hydrogen recovery achievable by the module is greater than 90 percent which can be further improved by the presence of sweep gas in the permeate side and/or by increasing the retentate pressure. The module was in excellent condition after the G-2 testing.



Figure 66. Hydrogen Recovery Profile of the WPI Membrane Module

4.2 Media & Process Technology Hydrogen Membranes

Media and Process Technology's main test objective for the G-3/G-4 runs was to evaluate a new water condenser/trap system for the CMS membrane permeate and reject streams. The equipment was installed to more accurately determine the gas phase composition at the membrane and validate a membrane permeation model to be used in a techno-economic evaluation. Approximately 50 water collection sampling runs were conducted during gasification operation. The syngas water content was determined from sour shifted syngas in the range of 15 to 30 lb/hr at 170 to 180 psig. MPT also performed a membrane separation test for about 12 hours with hydrogen enriched, shifted syngas. After optimizing the new water collection systems, MPT obtained multiple sets of gas composition including the water content. MPT will conduct a comprehensive simulation study on membrane gas separation based upon the data obtained from this test. MPT plans to further test the membrane system in future runs.

4.3 Membrane Technology & Research Membrane

MTR continued development of Proteus hydrogen membranes with full-length 4-inch modules using a 50-lb/hr system and with small-scale 2.5-inch modules using a 1-lb/hr system. Operation of the 50-lb/hr membrane skid allowed MTR to test the performance of commercial-size Proteus modules in parallel with parametric testing of small Proteus modules in an industrial setting for an extended time. MTR plans to continue to support both types of testing in future runs.

G-2 Test Results

The two 4-inch membrane modules tested were made with an improved glue and different spacer configuration on both the feed and permeate sides to determine their effect on performance. For the duration of testing, the feed temperature was maintained at 120°C (248°F) and feed pressure was kept at 170 to 180 psig. The first 4-inch module was evaluated during the first week of testing and was replaced with the second module for the duration of the campaign (about 480 hours). The results for the second module during the long-term evaluation are summarized below.

Figure 67 provides the feed and permeate composition over the course of the long-term test. The 4-inch Proteus module enriched hydrogen concentration in the permeate to roughly six times the feed concentration, which is a significant improvement over modules tested during G-1, during which the permeate enrichment was approximately three to four times the feed concentration. The increase in the permeate hydrogen concentration indicates a higher quality membrane module, which could be due to fewer module bypass and glue line leak issues. Higher quality, virtually defect-free Proteus membranes with minimal non-selective pinholes on the membrane surface also contributes to the improved module performance.



Figure 67. Composition of Syngas Feed and Permeate Streams for MTR 4-inch Proteus Membrane Module during G-2

Parametric testing was performed on two, 2.5-inch modules. Similar to the 4-inch Proteus modules, both 2.5-inch Proteus modules were made with an improved glue, and different spacer configurations were used on both the feed and permeate sides to determine their effects on performance. With this small test system, MTR engineers were able to vary several key process conditions, such as temperature, pressure, and feed flow rate. The parametric test trends and results were similar for each small module, so the results of only one of the modules are shown in this report.

For stage cut (changing syngas feed flow rate to the module) experiments, the feed pressure (170 psig), system temperature (120°C), and permeate pressure (5 psig) were held constant. The feed flow rate was varied to meet the desired module stage cut, which is defined as the total amount of gas permeating the module relative to the feed gas flow rate. Figure 68 shows the permeate concentration of the small module over a stage cut range of 5 to 50 percent. Consistent with membrane module process design fundamentals, the bulk removal of hydrogen increased while the hydrogen purity in the permeate stream decreased with increasing stage cut.



Figure 68. Permeate Stream Composition vs. Stage Cut for MTR 2.5-inch Proteus Module

The influence of the pressure ratio (relative ratio between feed and permeate pressures) was studied by using a back pressure regulator to set various permeate pressures. The feed pressure (170 psig), temperature (120°C), and stage cut (4 percent) were held constant for all data points. Figure 69 shows the permeate stream composition for different pressure ratios. As the pressure ratio increases, the driving force for hydrogen permeation increases, and because the Proteus membrane is selective to hydrogen over the other present gas species, the hydrogen permeate concentration also increases.



Figure 69. Permeate Stream Composition vs. Pressure Ratio for MTR 2.5-inch Proteus Module

Temperature experiments were conducted by varying the module temperature from 100 to 135°C (212 to 275°F) while keeping the stage cut (4 percent) and permeate pressure (5 psig) constant. Figure 70 provides the permeate stream composition at different temperatures. Consistent with previous Proteus membrane stamp and module temperature experiments, the small 2.5-inch module exhibited a peak in the hydrogen permeate concentration (and therefore, hydrogen selectivity) at approximately 120°C.



Figure 70. Permeate Stream Composition vs. Temperature for MTR 2.5-inch Proteus Module

G-3/G-4 Test Results

Two 4-inch diameter membrane modules were tested during the G-3/G-4 gasification campaign. Both modules were made with an improved glue and different spacer configurations on the feed side to determine the effect on performance. For the duration of testing on the 50 lb/hr unit, the feed temperature was maintained at 110°C (230°F) and feed pressure was kept constant at 170 psig. The first 4-inch module was evaluated during the first 300 hours of testing and was replaced with the second module for the duration of the campaign (about 900 cumulative hours on-line). Over the course of this syngas campaign, the MTR Proteus modules were exposed to syngas from both PRB and lignite coals and hydrogen feed gas concentrations ranging from 7 vol% to 37 vol%, depending on the coal and hydrogen enrichment conditions.

Figure 71 gives the feed and permeate compositions for the first 4-inch module, which was only exposed to syngas from PRB coal and four H_2 enrichment conditions while on-line. As shown in the figure, the high selectivity of the Proteus module enriched the permeate to over 90 vol% H_2 under certain hydrogen enrichment conditions.



Figure 71. Composition of Syngas Feed and Permeate Streams for MTR 4-inch Proteus Membrane Module during G-3/G-4

Figure 72 shows the feed and permeate hydrogen concentrations for both 4-inch Proteus modules during G-3/G-4. The 4-inch modules enriched the hydrogen concentration in the permeate to roughly six times the feed concentration, which is consistent with the improved Proteus module performance shown during the G-2 run. The high hydrogen enrichment values and sensitivity of the permeate hydrogen concentration to the feed composition indicate high quality, leak-free modules. The lower average hydrogen concentration in the permeate stream of the second module was due to the lower hydrogen content of syngas from lignite coal compared to PRB coal.



Figure 72. Hydrogen Content of Syngas Feed and Permeate Streams for MTR 4-inch Proteus Membrane Module during G-3/G-4

Parametric testing was performed on two, 2.5-inch diameter modules, which were made with the same feed and permeate spacer configuration as the second 4-inch module but were fabricated with a new experimental glue. During G-3/G-4, MTR only varied the inlet hydrogen concentration and the system temperature. The test results were similar for each small module, so the results of only one module are given. Figure 73 shows the feed and permeate hydrogen concentrations for one 2.5-inch module for different hydrogen enrichment conditions at 120°C. The small module enriched the hydrogen concentration in the permeate to roughly five times the feed concentration, signifying a high quality module. Over the course of testing, no degradation in performance was observed, which indicated the new experimental glue used for the module did not degrade under syngas process conditions.



Figure 73. Hydrogen Content of Syngas Feed and Permeate Streams for MTR 2.5-inch Proteus Membrane Module during G-3/G-4

4.4 SRI International AC-ABC and Bechtel Pressure Swing Claus Processes

The AC-ABC process relies on the ability of the aqueous ammoniated solution to absorb CO_2 and H_2S at near ambient temperatures and to release it as a high pressure gas at a moderately elevated temperature. SRI International, in collaboration with EIG Inc., and Bechtel Hydrocarbon Technology Solutions Inc., is performing a multi-year effort to develop the AC-ABC solvent process, as well as to develop the Bechtel Pressure Swing Claus process for converting H_2S to elemental sulfur.

The 500-lb/hr pilot-scale AC-ABC reactor system was installed at the NCCC with absorber and regenerator columns and associated pumps and instrumentation for simultaneous capture of CO_2 and H_2S and for regeneration of CO_2 and H_2S at high pressure. The BPSC process was installed downstream of SRI's with a liquid SO₂ supply, catalytic reactors, and heat exchangers to convert H_2S to elemental sulfur. The AC-ABC process was operated with syngas produced from gasification of lignite, which contained about 2,000 ppmv H_2S , and which was pre-treated with WGS and hydrocarbon removal. The syngas feed was composed of 14 to 15 percent CO_2 , 1 percent CO_2 , 12 percent hydrogen, 0.5 percent methane, and the balance of nitrogen.

During G-2, more than 300 hours of data was collected from the integrated operation of the AC-ABC system, including a continuous run of 100 hours. The operation demonstrated simultaneous capture of CO_2 and H_2S , with capture efficiencies of each greater than 99 percent, simultaneous stripping of CO_2 and H_2S at high pressure up to 350 psig, and low ammonia losses from the system. The BPSC system operated for 90 hours and converted the H_2S in the AC-ABC outlet CO_2 stream to sulfur, producing an H_2S -free CO_2 stream. Based on the G-2 operation, several modifications were made, as summarized below.

- A particle filter was installed upstream of the syngas compressor to remove any solids entrained in the raw syngas and prevent damage to the compressor.
- Heat tracing and insulation on the system process piping and vessels was improved to prevent precipitation from the rich solution during the process upset conditions. The gas-sampling lines were heat traced to prevent precipitation from the gas phase.
- The absorber top stage initially contained bubble cap trays to control ammonia emissions, although flooding and solvent carryover occurred during G-2, so the bubble cap trays were replaced by structural packing. However, due to low liquid loads, the structural packing was not effective. The third stage of the absorber was bypassed, and the absorber was operated with two working stages. Test results showed that capture efficiency was still very high with only two operating stages. Ammonia emission from the absorber was measured at 500 to 1,000 ppm under steady operating conditions. In a commercial system, ammonia would be recovered in a sour-water stripper.
- Steam-cleaning valves were added to the piping in which clogging was experienced due to process upset conditions during the first test campaign. This enabled faster turnaround between test runs and resulted in greater than 80 percent availability for the pilot plant during the second test campaign.

- Viton diaphragms on the solvent circulation pump were replaced with ethylene propylene diene monomer material, which is more chemically compatible with sulfides in the solvent.
- Thermal mass flow meters in the exit gas lines were replaced by a Coriolis meter for better gas flow data.
- The particles entrained in raw syngas during the first test campaign damaged the FTIR mirrors. Hence, ammonia emissions could not be monitored during the first test campaign. The FTIR spectrometer was repaired and installed to monitor ammonia in the gas outlet from the absorber column.
- A gas heater was added to provide heated nitrogen for regeneration of sulfur from the catalytic bed.
- The SO₂ delivery system was modified, and a pulsation dampener was added to the SO₂ line to reduce flow fluctuations due to the diaphragm pump. A new SO₂ vaporizer was installed to convert liquid SO₂ to vapor. Under the modified arrangement for SO₂ delivery, a recirculation loop was added to the pump and a Coriolis-based flow control was designed to withdraw the desired amount of liquid from the loop. The performance of SO₂ delivery system improved, but further improvements were needed.

The modifications resulted in significantly improved operation during the second test campaign in G-4, with longer continuous operation (175 hours of 400-hour total testing time) and higher CO_2 loading in the solution (120 g CO_2/L solution compared to 100 g CO_2/L solution in G-2). Figure 74 plots data from the period of continuous operation. With two stages operating, the absorber achieved greater than 99.5 percent CO_2 capture and H_2S capture in a single vessel. During a period from 30 to 84 hours, the capture efficiencies for both CO_2 and H_2S were marginally lower due to low ammonia concentration in the solvent. Fresh ammonia solution was added to the system, which resulted in higher capture efficiencies.



Figure 74. Capture Efficiency and CO₂ Loading in Solvent for SRI AC-ABC Process

The BPSC process operated for 131 hours during G-4. The regenerated gas stream, CO₂, and H_2S from the AC-ABC system, was fed to the BPSC skid at 350 psig, and bottle SO₂ was injected into the feed stream in a stoichiometric ratio. The operation showed that the BPSC technology is capable of converting the gas stream of 99.5 vol% H_2S to elemental sulfur with H_2S in the product gas at ppm levels. Sulfur formed on the catalyst at sub-dewpoint conditions according to the thermodynamic concept during the absorption step. Although no long-term data was collected, the unit recovered the sulfur as a high-purity liquid, validating the underlying design concepts.

4.5 Carbon Clean Solutions Solvent

The CCSL solvent was tested in the bench-scale solvent batch reactor with bottle gas and with syngas. Initial bottle gas testing was conducted at temperatures ranging from 45 to 120° C (113 to 248° F) and CO₂ concentrations ranging 20 to 80 mol% to obtain vapor-liquid equilibrium data. After the completion of bottle gas testing, tests were performed with syngas during the G-3/G-4 runs. Total gas flow to the batch reactor was maintained at 6 lb/hr with various amounts of CO₂ enrichment added to elevate the CO₂ concentration for certain tests. Each test was run until the inlet and outlet CO₂ concentrations reached equilibrium. Syngas testing could only occur at lower partial pressures due to the limit of the syngas supply pressure and operable range of the syngas flow control valve. Figure 75 plots the results for the bottle gas and syngas testing.



Figure 75. Results of CCSL Solvent Testing with Bottle Gas at Various Temperatures and with Syngas

Data was then used to compare the CCSL solvent with two solvents widely used in high pressure commercial applications—activated MDEA and Selexol. Figure 76 gives the vapor-liquid equilibrium curves for the CCSL solvent, activated MDEA (aMDEA), and DEPG (used to represent Selexol). The CCSL solvent compared favorably to the commercial solvents, achieving significantly higher CO_2 loading values. Using the vapor-liquid equilibrium data,

CCSL estimated that the heat of reaction for the CCSL solvent was 39.2 kJ/mol CO_2 , 20 percent lower than that of MDEA (48.9 kJ/mol CO_2).



Figure 76. Comparison of CCSL Solvent Bottle Gas Results with MDEA, and DEPG Solvents

5.0 CONCLUSIONS AND LESSONS LEARNED

5.1 Post-Combustion

During the reporting period, the PC4 operated in three test runs, supporting more than 10,500 hours of the technology developer testing. Projects tested included membrane technologies, advanced solvents and solvent systems, enzymes, and aerosol mitigation equipment.

MTR 1-TPD CO₂ Membrane

MTR completed final testing on the 1-TPD membrane system in August 2015. The 2015 testing employed a new combination of high-flux Polaris cross-flow modules that yielded CO_2 enrichment from 12 percent in the feed gas to over 60 percent in the permeate, and sweep modules in the second step that produced a treated stream with 2 to 7 percent CO_2 . The modules showed stable performance despite a lengthy outage and excursions in feed temperature and flow rates. Operations showed that:

- Lower feed temperature resulted in lower permeate flux in both stages, lower stage cut in step one, and higher CO₂ concentration in the first step permeate, first step residue, and second step residue (the treated flue gas). These results were consistent with those from previous extended trials in respect to the impacts of operating temperature.
- Increasing the sweep rate slightly improved the amount of CO₂ captured by the sweep modules. Overall, the sweep flow rate had much less impact on system performance compared to the feed flow rate or temperature.

After three and half years of testing, the system achieved a total of 11,466 hours of operation with 9,100 hours on flue gas and 2,366 hours on air when flue gas was not available. Out of the 9,100 hours of testing on flue gas, 1,933 hours were conducted with simulated natural gas flue gas. Carbon capture rates of better than 90 percent were achieved with coal-derived flue gas. The test program proved valuable in guiding the design of MTR's 20-TPD membrane system and in serving as a test vehicle for second and third generation membranes following lab testing.

Carbon Capture Scientific Gas Pressurized Stripping Process

CCS completed testing of the novel GPS process using an amine-based proprietary blended solvent. Long-term testing was conducted in run PO-3 under optimal conditions identified during previous parametric tests. The results of the parametric tests showed that:

- With an increase of total flue gas flow rate, the CO₂ removal rate in the absorber reduced markedly, while the CO₂ purity from the stripper reduced slightly.
- With an increased G/L volume ratio, the CO₂ removal rate reduced significantly, but CO₂ purity was not affected.
- With an increase of stripper operating pressure, both the CO₂ purity from the stripper and CO₂ removal rate in the absorber declined.

• With an increase of nitrogen flow rate, the CO₂ purity reduced, while the CO₂ removal rate increased.

The long-term test conditions were maintained to achieve 90 percent CO_2 removal rate and 95 percent CO_2 product purity. The energy consumption of the GPS process was much lower than that of the monoethanol amine (MEA) baseline case, with the sum of reaction heat and stripping heat for the GPS process at 1,562 to 1,600 kJ/kg CO_2 captured. The estimated sensible heat was in the range of 250 to 500 kJ/kg CO_2 captured.

OSU CO₂ Membrane

In the development of a cost-effective design and manufacturing process for CO_2 capture membrane modules, OSU completed testing with a bench-scale membrane unit. OSU optimized the glue-line procedure of membrane fabrication. The new procedure aided in adequate sealing of the non-woven fabric in the membrane leaf and sealing between the membrane leaf and the central tube. However, insufficient curing of the glue used and the membrane indentations caused by the rough surface of the feed spacer might have introduced leakage and resulted in the CO_2/N_2 selectivity drop seen in the second module tested.

The results of the NCCC testing were promising in that they were comparable to those of OSU lab testing with simulated flue gas. The modules showed initial permeance values of about 800 GPU and selectivity values of about 200, as well as pressure drops of less than 1.5 psi/m. OSU will further improve the glue curing and minimize membrane indentations for the improvement of membrane module performance and stability.

Linde-BASF Pilot Solvent Unit

After operating throughout the last three test runs at the PC4, testing of the Linde-BASF pilot unit was completed. During the overall test period, including start-up, parametric testing, and long-duration testing, the pilot plant operated for a total of 6,764 hours, out of which testing with flue gas was performed for 4,109 hours. The testing demonstrated all of the performance targets including CO_2 capture rate exceeding 90 percent, CO_2 purity exceeding 99.9 mol% (dry), flue gas processing capacity up to 15,500 lb/hr (equivalent of 1.5 MWe), regeneration energy as low as 2.7 GJ/tonne CO_2 , and regenerator operating pressure up to 3.4 bar absolute. Findings included:

- The flue gas CO₂ concentration varied significantly, ranging from 11 to 12 mol% CO₂ during the morning and peaking to as much as 13.5 mol% CO₂ in the afternoon. This variation resulted in substantial process fluctuations that were controlled to achieve as stable and consistent operation as possible while at the same time maintaining low specific regeneration energy.
- The stable solvent performance as indicated by the energy consumption suggested high solvent durability. The measured heat stable salt levels were well below the threshold that BASF uses for solvent degradation.
- The oxygen concentration can be maintained within the limits required for applications in CO₂, utilization such as enhanced oil recovery.

MTR 20-TPD Membrane System

MTR successfully operated the 20-TPD system during two runs, completing testing in June, 2015. The system first operated in 2015 during run PO-2, and for PO-3 operation, a high efficiency plate-and-frame membrane module was added to replace the conventional spiral-wound design. Operation in PO-3 lasted for 900 hours, exceeding the original goal of 500 hours, and demonstrating the performance of both the 20-TPD system and the plate-and-frame sweep membrane module skid. Testing showed that:

- The 20-TPD system with the plate-and-frame sweep skid consistently captured CO₂ at a rate of around 87 percent, with capture rates over 90 percent under certain operating conditions.
- The plate-and-frame sweep modules had roughly four times lower pressure drop than the spiral wound sweep modules, which, at full scale of 550 MWe, amounts to an energy savings of about 10 MWe.
- The first step permeate was enriched about four times to 45 percent CO₂, while the treated gas leaving in the residue stream contained about 2 percent CO₂. This performance is very similar to that achieved by the 1-TPD system and is in agreement with MTR's design calculations.

MTR will continue developing the membrane technology at another test site.

Ion Engineering Solvent

ION Engineering's solvent was tested in the PSTU during run PO-3. ION utilized parametric testing to confirm process set points for optimal performance and primary/secondary control mechanisms. ION plans for further solvent testing at another facility. Observations from the test are listed below.

- Completing process simulations prior to the test campaign enabled ION to perform detailed analysis of the PSTU process and equipment and identify optimal test conditions.
- During parametric testing, ION maintained 95 percent or greater CO₂ capture throughout a range of L/G ratios from 2.0 to 3.5. At these conditions, regeneration energy ranged from 1,400 to 1,800 BTU/lb CO₂.
- Steady state testing was conducted at an L/G ratio of 3.0 with 95 percent or greater CO₂ capture and a regeneration energy requirement of about 1,600 BTU/lb CO₂. The ION solvent's specific energy result obtained at NCCC was 1,600 BTU/lb CO₂ during steady state, while the design case was 1,100 BTU/lb CO₂.
- Running one bed of packing was likely the biggest energy penalty compounded by overstripping and obtaining capture rates exceeding 95 percent.
- No significant accumulation of heat stable salts or solvent degradation occurred. An evaluation of metal ions showed that the ION solvent accumulates significantly less metal ions than MEA solvent.

• ION maintained a water balance by operating at or around a prescribed temperature difference between the flue gas containing CO₂ entering the absorber and the treated flue gas exiting the absorber.

NETL Membranes

NETL performed membrane testing with the Post-Combustion Membrane Skid (PCMS) to identify fabricated membranes with acceptable performance when separating CO_2 from flue gas and maintaining performance in the presence of water vapor and minor contaminants. During run PO-4, NETL operated the PCMS with several types of membrane materials, including PDMS, TFE-PPZ, and hollow-fiber samples made from Torlon and coated with TFE-PPZ based solutions. Testing will continue through the end of the PO-5 run. Observations were:

- The low velocity of the chosen 10 cm³/min feed flow and lack of enhanced mixing on the feed side of the flat sheet cell suggest that water vapor transport in the membranes was severely mass transfer limited. Consequently, the apparent water vapor permeance calculated from the hygrometer data is considered to underestimate the true water vapor permeance of the membrane.
- With the PDMS flat sheet membrane a fairly steady gas permeability was measured: 3,300 barrer for CO₂, 400 barrer for N₂, and 760 barrer for O₂. These values were nearly identical to the results obtained in lab testing at NETL.
- The gas permeability values of the second flat sheet membrane tested, a coupon of TFE-PPZ, were stable over the 22-hour test. The average CO_2 permeability, 780 barrer, was only slightly higher than the condition tested at NETL (680 barrer). The tested membrane film's pure and mixed gas CO_2/N_2 selectivity was around 8.5, lower than previously reported values of 13.4 and 11.2, so it is possible oxidation over time (as the film was three years old) led to increased CO_2 permeability and reduced CO_2/N_2 selectivity.
- Three of the four hollow fiber modules, consisting of one TFE-PPZ and two TFE-PPZ/SIFSIX coated fibers, displayed CO₂/N₂ selectivity around 10.7 and exhibited stable CO₂, N₂, and O₂ permeance. The permeance values were very close to the results obtained at NETL prior to the PCMS field trials.
- The fourth fiber, a TFE-PPZ coated fiber, was loaded into the PCMS during system down time and was exposed to the moist, stagnant environment inside the unit for a few hours. While N₂ and O₂ permeance remained stable throughout the experiment even when the membrane was presumably wet, CO₂ permeance started much lower in the first half hour (33 GPU) before rising and plateauing at around 50 GPU starting on the sixth hour until the end of the experiment. The unexpected lowering of the CO₂ permeance in the presence of water suggests that CO₂ transport is strongly hindered by water in the TFE-PPZ hollow fiber.

Air Liquide Cold Membrane

Air Liquide began testing of the cold membrane process and evaluation of membrane materials. During run PO-4, the system was commissioned and operated for a total of 1,016 hours. During more than 500 hours of steady state operation, all performance goals were achieved, with a CO_2 capture rate greater than 90 percent, and CO_2 purity was between 65 and 70 percent. In the PO-5 run, Air Liquide conducted testing with a prototype membrane of next generation polyimide material, PI-2. The PI-2 membrane achieved eight to nine times the CO_2 permeance of the commercial bundle, and demonstrated stable CO_2 recovery and purity over more than 700 hours of operation, which included multiple shutdowns.

Near the end of the operating period, the permeance decreased by about 30 percent following a warm shutdown. Air Liquide will adjust operating procedures to prevent recurrence of the loss in permeance in future operation. Operation is planned to continue through the end of the PO-5 run. Air Liquide will continue development of the PI-2 polyimide membranes.

Slipstream Solvent Test Unit

Commissioning of the SSTU with MEA solvent began in late November 2015. Operation of the SSTU was problematic and did not produce useful MEA baseline data. Following the run, modifications to the system were implemented for improvement. Changes included installation of a new blower, flow meters, transmitters, and area gas detectors, relocation of valves and instruments, addition of a larger CO_2 product line, and upgrades to the control system. MEA baseline testing will resume in late 2016 during the PO-5 run.

Cansolv Technologies Aerosol Mitigation Technologies

Cansolv Technologies' Thermal Swing Adsorber and Brownian Demister Unit were installed on the Slipstream Solvent Test Unit. Initial testing was conducted in December during run PO-4, while the SSTU operated with MEA. A comparison of aerosol measurements taken with and without TSA operation showed very little difference in the distribution and number count of aerosols at the operating condition. At another operating condition, a noticeable increase of aerosols in the <0.03 micron range was observed for both cases (with and without TSA operation), which indicates a more significant impact of changing operating conditions over the effects of the TSA unit. Additional tests will be required to determine the net effect of the process changes that resulted in the smaller particle size distribution that was observed, although the TSA impact appeared to be minimal. Due to time constraints, limited data was obtained, and further testing is planned.

Results from the BDU testing using the ELPI+ were suspect since current was observed across multiple impactor stages. Collection of liquid droplets in several stages on the ELPI+ impactor was observed when different stages were disassembled after this test. Further detailed aerosol characterizations at the BDU outlet are necessary in future test campaigns to determine if the BDU is inadvertently creating a concentrated solvent aerosol or if an upset condition created this phenomenon.

Amine Emissions Measurements

The ELPI+ was used for aerosol measurements to evaluate means of reducing solvent emissions. The primary objective in 2015 was to establish baseline data that could be compared against results obtained in 2016, when a new activated carbon injection baghouse was brought on-line at Gaston Unit 5, upstream of the PC4. Measurements taken on the Linde-BASF unit showed that

the impact of the baghouse operation was significant, causing a drop in particle count of several orders of magnitude. Initial indications are that amine emissions may be significantly reduced by the inclusion of an activated carbon injection baghouse on coal-derived flue gas streams where SO_3 is present. Additional measurements will be made on the PSTU and SSTU locations in late 2016.

In addition to the ELPI+ measurements for aerosol size and count, a Phase Doppler Interferometer, operated by staff from UT-Austin, was used on the SSTU treated flue gas stream. The PDI measurements for particle size were larger than the ELPI+ measurements. The cause for the difference may be due to ambient heat losses in the sample lines resulting in further condensation of the aerosol particles. However, the general trend and peaks were similar to those of the ELPI+ data. An important result was the difference apparent between the operating modes and the significant effect on the particle size distribution. Repetition of the tests in late 2016 will yield additional clarity on the effects of process changes and the difference in sample extraction techniques between the two measurement devices.

Akermin Enzymes

Akermin continued development of an advanced biocatalyst enabled solvent system for low cost CO_2 capture with a scale-up of a project tested at the NCCC in 2013. Testing began in early June 2016 and continued over a one-month period. However, the run was affected by a number of engineering issues making the performance unstable. The primary issues were uncontrolled rich solvent spillover resulting in significant fluctuations of the particle hold up in the biocatalyst recovery system and in solvent loading and a general loss of recirculating particles in the system resulting from their accumulation in the absorber. It was hypothesized that the significant and unexpected particle retention in the absorber resulted from low area efficiency of the absorber column (about 15 percent) that was primarily due to the low liquid load in the system. The anticipated performance of 90 percent capture was rarely achieved due to particle accumulation in the absorber. After one month of operation, it became clear that the unit in the current configuration was not able to meet the project objectives, and testing was discontinued.

GE Global Aminosilicone Solvent

Preparations were completed for testing of the GE solvent in the PSTU during run PO-5. Startup activities were underway at the end of BP2, and the test is expected to continue through the end of PO-5.

PC4 Modifications

Several additions were made to the PC4 to improve data collection and testing capabilities, as listed below:

- Rosemount ERS differential pressure transmitters on the PSTU column beds showed data consistency and improved resistance to ambient effects compared with previously used instruments.
- Sample extraction systems were installed and successfully used for measurements with the ELPI+ and PDI.

- Vibration transmitters were installed on the flue gas blowers to allow for remote monitoring.
- Differential pressure measurements of the PSTU rich-lean heat exchanger were added for enhanced data collection at the request of test partners.
- Modifications to the SSTU were incorporated for improved operability prior to the PO-5 run.
- E-Notification process software was purchased for data transfer to test partners. The software provides an automated service and periodically sends process data to developers in an Excel spreadsheet with pre-selected frequencies and formats. It also provides electronic communication alerts to process deviations of interest.

5.2 Gasification

The gasification process operated in three runs, G-2, G-3, and G-4, for a total of 2,201 hours. The runs allowed for more than 6,000 hours of gasification technology developer testing. Fuels used included Mississippi lignite and PRB coal. Operation was stable, with high carbon conversions and consistent quality syngas for use in gasification and pre-combustion tests.

Southern Research Fischer-Tropsch Catalyst

Southern Research continued its development of coal-to-liquids technologies with testing of a F-T catalyst with jet fuel selectivity. The testing demonstrated the target performance values for catalyst activity and product selectivity of greater than 65 percent jet fuel. However, due to difficulties in precisely controlling the operating conditions, the results were not quite as high as those observed in the lab. Nonetheless, the catalyst was able to achieve the necessary hydrocarbon productivity and product selectivity at conditions that were less than optimal. SR plans to scale-up the F-T reactor and to operate it with an integrated auto-thermal reformer.

Johnson Matthey Mercury Sorbent

Additional testing of the Johnson Matthey high temperature mercury sorbent was conducted for long-term evaluation, NCCC gas analysis technicians took periodic inlet and outlet samples, with breakthrough of mercury and selenium detected in the outlet samples during the G-4 run. The total testing of this material is approximately 6,000 hours distributed over ten gasification runs, with the last 2,943 hours tested on the regenerated sorbent.

WGS and COS Hydrolysis Catalysts

Operation of WGS and COS hydrolysis catalysts continued with parametric and long-term testing. During the long-term testing, the WGS catalyst was overheated for a short time due to the failure of a heater controller. Once the problem was corrected and testing resumed, the shift conversion decreased. The WGS catalyst demonstrated shift conversions between 63 and 86 percent, and the COS hydrolysis catalyst showed conversion rates from 44 and 61 percent.

Emerson Rosemount Sapphire Thermowells

Testing was conducted with Emerson's Rosemount sapphire thermowells in gasifier service. The thermowells in the riser and lower standpipe were operable throughout G-2, and were subsequently tested during G-3 and G-4. However, the thermowell installed in the riser crossover failed shortly after the G-2 run began, and therefore no data was available from this location. The riser and lower standpipe thermowells operated reliably in the highly erosive and corrosive environment, although temperature readings with the sapphire thermowell units were lower than reference thermocouples, with the differences at about three and five percent relative to the reference thermocouples. Further testing is planned.

PCME Particulate Monitor

The VIEW Ex820 particulate monitor from PCME gave appropriate readings during the run and responded well to calibration testing with ash injection. The new monitor gave clear responses with low particulate concentrations, which validated its potential usefulness as part of a control strategy for protecting gas turbines and other equipment downstream of particulate filters. The G-2 and G-4 results with the newly installed monitor show data points at lower concentrations obtained by ash injection compared to previously performed ash injection tests. Additional calibration testing will be conducted at higher ash concentrations.

OSU Syngas Chemical Looping

Following the identification of needed design changes for the process burner during attempted operation in 2014, OSU completed fabrication of a new burner. Off-line testing of the new burner was conducted at the NCCC in August 2015, which showed high shell temperatures on the refractory lined burner vessel. To address the high shell temperatures, OSU incorporated a system modification involving the injection of propane into the burner leg vessel. After test-firing the burner with the propane injection system, OSU identified additional needed modifications to prevent condensation, and these were completed prior to the start of G-3. OSU completed start-up activities for the SCL process during G-3, including a short period of operation on syngas, for which OSU reported syngas conversions of greater than 98 percent in the reducer section of the process. Issues with fluidization prevented further syngas operation, and OSU began preparations for modifications to be incorporated prior to further operation.

TDA Research Ammonia Sorbent

TDA Research operated a new sorbent-based gas clean-up technology for removal of ammonia and hydrogen cyanide, as well as trace metals at high temperatures in a single process step. TDA demonstrated greater than 99 percent ammonia removal and successful sorbent regeneration. TDA operated the system for approximately 50 hours. The sorbent capacity was lower when the regeneration step was carried out under pressure swing conditions instead of a combination of pressure and mild temperature swing conditions. With the successful results of the field tests, TDA plans to further develop the sorbent technology.

TDA Research WGS/CO₂ Sorbent System

As an expansion of previous sorbent testing at the NCCC, TDA Research operated a combined WGS/CO_2 sorbent system with an innovative heat management system. TDA demonstrated that

reactor bed temperatures were precisely controlled by direct water injection, and that shift conversions were higher with water injection than with steam addition at comparable H_2O -to-CO ratios. When parameters were adjusted to achieve 90 percent CO conversion in the WGS stage, the overall carbon capture rate was greater than 95 percent. TDA will further refine the technology, with operation of a scaled-up system planned for 2017.

Coal Feeder Instrumentation

Dynatrol and Drexelbrook coal feeder level probes, which have proved useful in automating coal feed cycles, continued to operate reliably. As seen in previous runs, measurements from the Densflow coal flow meter on the PDAC feeder differed from the calculated mass flow rates based on the weigh cell data.

Gasifier Refractory

In evaluating gasifier refractory service time, post-run inspections of hot-face refractory were conducted in erosion-prone sections, and results showed good material integrity and minimal wear. The two types of refractory that were inspected include Resco Sureflow 88 refractory, which was installed in 2006 and Resco Sureflow 17E refractory that was installed in 2011.

Hot Gas Filter Elements

Long-term evaluation continued for six types of hot gas filter elements including sintered metal fiber and sintered metal powder. Syngas operation of the elements will continue for verification of a two-year or greater service life.

5.3 Pre-Combustion

Pre-combustion CO_2 capture operation during the three gasification runs comprised over 3,400 hours of technology developer testing, involving membrane, solvent, and sorbent technologies.

WPI Palladium-Based Hydrogen Membranes

Worcester Polytechnic Institute tested a seven-fold scale-up of palladium-based hydrogen membranes. Each of the seven tubes was fabricated with a dense inner layer of palladium about 5.4 microns thick, a second layer of 0.4 microns of gold for improved stability and recoverability, and a final layer of palladium of about 1.6 microns. With only one percent deviation in thickness among the tubes, the consistent fabrication of the membrane tubes demonstrated the replicability of this technology. Syngas operation demonstrated steady permeance values, hydrogen product purity as high as 99.9 percent, and a hydrogen recovery rate of 35 percent. The module was in excellent condition following the testing.

MPT Carbon Molecular Sieve

In continued development of the CMS hydrogen membrane, MPT tested a new water condenser/trap system for membrane permeate and reject lines to more accurately determine the gas phase composition at the membrane. MPT conducted multiple collection sampling runs, and will use the data to validate a membrane permeation model, which will be used in a techno-

economic evaluation of the CMS technology. Further membrane testing is planned for future runs.

MTR Proteus[™] Hydrogen Membranes

MTR continued development of the Proteus hydrogen membrane. A four-inch Proteus module enriched the hydrogen concentration in the permeate to roughly six times the feed concentration, which is a significant improvement over previous modules tested at NCCC. The improved module performance was due to a combination of advancements in module configuration, new high temperature glues, and continued Proteus membrane development. MTR also conducted parametric tests with two 2.5-inch Proteus modules. The parametric studies demonstrated the following:

- Consistent with previous Proteus membrane stamp and module temperature experiments, the small 2.5-inch module exhibited a peak in the hydrogen permeate concentration (and therefore, hydrogen selectivity) at approximately 120°C.
- As the pressure ratio increases, the driving force for hydrogen permeation increases, and because the Proteus membrane is selective to hydrogen over the other present gas species, the hydrogen permeate concentration also increases.
- The bulk removal of hydrogen increased while the hydrogen purity in the permeate stream decreased with increasing stage cut.

Module results were consistent with each other and previous Proteus membrane stamp and module tests, indicating that the modules were of high quality and defect-free. The influence of each experimental parameter on module performance will aid in future process design and scale-up of Proteus membrane module systems.

SRI AC-ABC and BPSC Processes

The SRI AC-ABC and Bechtel Pressure Swing Claus processes operated during the G-2 and G-4 runs. Test data demonstrated steady state operation of the pilot plant with greater than 99.5 percent capture of CO_2 and H_2S , and regeneration of high purity CO_2 and H_2S at pressure. Despite operational issues with the SO₂ delivery system, the BPSC system showed a conversion of more than 99.5 vol% of H_2S gas to elemental sulfur with H_2S in the product gas at ppm levels. Based on the G-2 operation, the following modifications were made prior to G-4:

- A particle filter was installed upstream of the syngas compressor to remove any solids entrained in the raw syngas and prevent damage to the compressor.
- Heat tracing and insulation on the system process piping and vessels was improved to prevent precipitation from the rich solution during the process upset conditions. The gassampling lines were heat traced to prevent precipitation from the gas phase.
- The absorber top stage initially contained bubble cap trays to control ammonia emissions, although flooding and solvent carryover occurred during G-2, so the bubble cap trays were replaced by structural packing. However, due to low liquid loads, the structural packing was not effective. The third stage of the absorber was bypassed, and the

absorber was operated with two working stages. Test results showed that capture efficiency was still very high with only two operating stages. Ammonia emission from the absorber was measured at 500 to 1,000 ppm under steady operating conditions. In a commercial system, ammonia would be recovered in a sour-water stripper.

- Steam-cleaning valves were added to the piping in which clogging was experienced due to process upset conditions during the first test campaign. This enabled faster turnaround between test runs and resulted in greater than 80 percent availability for the pilot plant during the second test campaign.
- Viton diaphragms on the solvent circulation pump were replaced with ethylene propylene diene monomer material, which is more chemically compatible with sulfides in the solvent.
- Thermal mass flow meters in the exit gas lines were replaced by a Coriolis meter for better gas flow data.
- The particles entrained in raw syngas during the first test campaign damaged the FTIR mirrors. Hence, ammonia emissions could not be monitored during the first test campaign. The FTIR spectrometer was repaired and installed to monitor ammonia in the gas outlet from the absorber column.
- A gas heater was added to provide heated nitrogen for regeneration of sulfur from the catalytic bed.
- The SO₂ delivery system was modified, and a pulsation dampener was added to the SO₂ line to reduce flow fluctuations due to the diaphragm pump. A new SO₂ vaporizer was installed to convert liquid SO₂ to vapor. Under the modified arrangement for SO₂ delivery, a recirculation loop was added to the pump and a Coriolis-based flow control was designed to withdraw the desired amount of liquid from the loop. The performance of SO₂ delivery system improved, but further improvements were needed.

Carbon Clean Solutions Solvent

A CO₂ capture solvent from Carbon Clean Solutions was tested both off-line with bottle gases and on-line during gasification. Initial bottle gas testing was conducted at temperatures ranging from 45 to 120°C (113 to 248°F) and CO₂ concentrations ranging 20 to 80 mol% to obtain vaporliquid equilibrium data. After the completion of bottle gas testing, tests were performed with syngas during the G-3/G-4 runs. Total gas flow to the batch reactor was maintained at 6 lb/hr with various amounts of CO₂ enrichment added to elevate the CO₂ concentration for certain tests. Each test was run until the inlet and outlet CO₂ concentrations reached equilibrium. Syngas testing could only occur at lower partial pressures due to the limit of the syngas supply pressure and operable range of the syngas flow control valve. Data was then used to compare the CCSL solvent with two solvents widely used in high pressure commercial applications—activated MDEA and DEPG (used to represent Selexol). The CCSL solvent compared favorably to the commercial solvents, achieving significantly higher CO₂ loading values. Using the vapor-liquid equilibrium data, CCSL estimated that the heat of reaction for the CCSL solvent was 39.2 kJ/mol CO₂, 20 percent lower than that of MDEA (48.9 kJ/mol CO₂).