Final Report

Chiyoda's Testing of T-3 Solvent at the National Carbon Capture Center

Chiyoda Corporation
2014

Summary

Chiyoda's test campaign at the National Carbon Capture Center (NCCC) with T-3 solvent commenced mid-December 2012 and ended mid-June 2013 during which time over 1500 hours of testing were achieved and 27 tests were completed supported by good quality mass balances. All the tests were completed on the Pilot Solvent Test Unit (PSTU) using flue gas drawn from the adjacent 900-MW supercritical power plant (Gaston Unit 5), which is supplied with SO_2 and NO_X controls and fired with medium-sulfur bituminous coal.

Foaming occurred in the PSTU wash tower during early testing but this was successfully overcome by injecting an anti-foaming agent, the selection of which was based on laboratory tests completed by NCCC staff.

Tests were completed to identify the optimum operating conditions and a regeneration energy as low as 1050 Btu/lb was achieved at a liquid-to-gas mass ratio of around 2 (2.45 GJ/tonne at a liquid-to-gas ratio of 2.4 L/Nm^3). Tests were completed that lowered solvent circulation rate for a given capture efficiency and thereby lowering the heat of regeneration. These were:

- Recycling solvent leaving the absorber to increase rich solvent CO_2 loading.
- Using intercoolers to reduce the temperature profile of the solvent in the absorber.

The process data collected from the testing will be used by Chiyoda to improve the design approach for its CO_2 capture plant technology. Chiyoda is grateful for the opportunity to test at the NCCC and offers its thanks to the US Department of Energy and the NCCC staff.

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1.0 INTRODUCTION

Chiyoda Corporation is a leading engineering company headquartered in Yokohama, Japan with regional offices around the world. It was founded in 1948 and has completed many projects worldwide in the fields of energy, chemicals, petrochemicals, pharmaceuticals, environmental control technologies including its widely deployed flue gas desulfurizer (FGD) technology, and social and industrial infrastructure.

In response to concerns over global warming, Chiyoda is currently engaged in developing carbon capture and storage technology for use with clean coal technology power plants. Chiyoda has been working on developing designs for commercial post-combustion CO_2 capture plants and has evaluated and screened multiple solvents. Eventually T-3, a high performance blended solvent with performance superior to monoethanolamine (MEA), was selected for comprehensive testing under industrial representative conditions.

Chiyoda has previously tested a solvent equivalent to T-3 on the Commonwealth Scientific and Industrial Research Organisation's (CSIRO) transportable CO_2 capture plant located at Loy Yang power plant in Victoria, Australia. Up to 480 lb/hr of flue gas was processed on a slip stream drawn from Unit 2, a 560-MW pulverized coal sub-critical boiler fired with low-sulfur brown coal.-The-power plant is not supplied with either SO_2 or NO_X controls but there is a pre-scrubber to remove SO_2 ahead of the capture plant. Hence testing at the NCCC extended Chiyoda's data base by testing with flue gas from a 900-MW supercritical unit supplied with SO_2 and NO_X controls, and fired with medium-sulfur bituminous coal. As the CO_2 capture plant (the Pilot Solvent Test Unit [PSTU]) processes up to 6,000 lb/hr of flue gas, testing at the NCCC also allowed a ten-fold increase in operating scale.

Chiyoda's PSTU test campaign with T-3 solvent commenced mid-December 2012 and ended mid-June 2013 during which time over 1500 hours of testing were achieved and 27 tests were completed supported by good quality mass balances. The campaign was extended primarily by a scheduled 10-week outage on Gaston Unit 5, the unit that supplies flue gas to the PSTU.

1.1 Test Objectives and Plan

The main objectives were to

- Collect accurate test data supported by good quality material and heat balances.
- Evaluate performance of the T-3 solvent.
- Collect process data to complete design approach of the CO_2 capture plant.

To accomplish these objectives, the following parametric tests were completed on the PSTU. Following the parametric tests a 500-hour run at optimal conditions was planned to test long-term performance.

- Varying liquid-to-gas (L/G) ratio to determine optimum operating conditions.
- Varying regenerator pressure to determine optimum operating pressure.
- Varying reboiler steam flow rate to determine effect on overall process performance.
- Place intercoolers in service to determine effect on process performance and the absorber temperature profile.

In addition, two process modifications were requested by Chiyoda, carried out by NCCC engineering staff, in support of determining the optimal process design configuration. The benefits of the design changes were established by the parametric tests.

Absorber Modification

New piping was installed to recycle rich solvent back to different levels in the Absorber (see Figure 1). As the CO_2 absorption rate for T-3 solvent is lower than for MEA, in once-through operation the solvent leaving the absorber may not be fully loaded. It was expected that recycling solvent would increase rich solvent CO_2 loading, lowering solvent circulation rate for a given capture efficiency and thereby lowering the heat of regeneration. Using intercoolers to control the absorber temperature profile would also serve to maximize CO_2 capture efficiency.

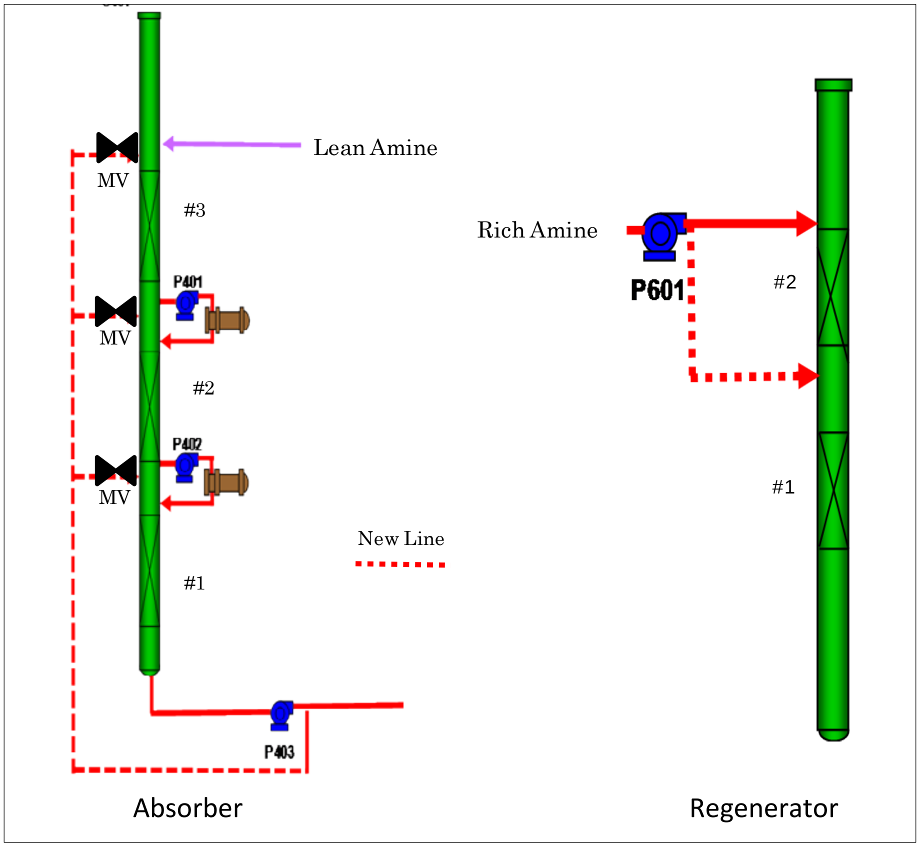


Figure 1. Modifications to Absorber and Regenerator

Regenerator Modification

New piping was installed to allow the hot-rich solvent to be introduced at the middle of the column instead of at the top (see Figure 1). This modification was to address the concern about excess solvent carryover from regenerator. With the new arrangement the top bed is flushed by the condensate return, which is expected to help suppress solvent carryover.

Proposed Test Conditions

Chiyoda proposed a set of test conditions, agreed to by NCCC, to optimize operating conditions and process design for use of T-3 solvent in commercial CO_2 capture plants.

- Table 1 present the parametric tests to investigate process performance.
- Table 2 presents tests to investigate process design features.

Other operating features not included in these Tables are:

- To maintain a water balance, the absorber inlet flue gas, the CO_2-depleted flue gas leaving the wash tower, and the regenerated CO_2 leaving the mist separator were all to be controlled to 104ºF.
- For the intercooler tests the returning solvent was to be cooled to 104ºF.
- All tests were to be completed with three absorber beds.
- The rich solvent was to be pressurized to 50 psig before flashing into the solvent separator upstream of the regenerator.
- To minimize solvent degradation the temperature at the bottom of the regenerator was to be maintained below 270ºF.

Over 1500 hours of operation with T-3 solvent were achieved including a 550-hour extended run at optimum conditions established by the parametric tests.

Table 1. Planned Parametric Tests to Determine Optimum Operating Conditions

Run	Lean solvent flow rate, lb/hr	L/G ratio, lb/lb (1)	Reboiler steam flow, lb/hr	Reboiler solvent flow rate, lb/hr	Mist separator pressure, psig (2) (3)	Comment
1	9040	-	1050	13,500	-	Determine system heat losses
2	7220	1.44	1050	10,800	7.25	Optimize L/G & reboiler solvent flow
3	9030	1.81	1050	13,500	7.25	" "
4	10,800	2.17	1050	16,200	7.25	" "
5	14,400	2.89	1050	21,600	7.25	" "
6	9030	1.81	880	13,500	7.25	Optimize reboiler steam flow and regenerator pressure
7	9030	1.81	1400	13,500	7.25	" "
8	9030	1.81	880	13,500	14.5	" "
9	9030	1.81	1050	13,500	14.5	" "
10	9030	1.81	1400	13,500	14.5	" "
11	9030	1.81	880	13,500	29.0	" "
12	9030	1.81	1050	13,500	29.0	" "
13	9030	1.81	1400	13,500	29.0	" "

(1) Absorber flue gas flow rate 5,000 lb/hr for all conditions except Run 1
(2) Sets regenerator pressure
(3) Rich solvent fed to top of regenerator for all conditions

Table 2. Planned Tests for Process Design Optimization

Run	Lean solvent flow rate, lb/hr	L/G ratio, lb/lb (1)	Reboiler steam flow, lb/hr	Reboiler solvent flow rate, lb/hr (2)	Comment
14	Optimum	Optimum	1050	Optimum	Intercooler operation extracting 50% of solvent flow
15	" "	" "	1050	" "	Intercooler operation extracting 100% of solvent flow
16	" "	" "	1050	" "	Rich solvent fed to middle of regenerator (3)
17	" "	" "	1050	" "	Rich solvent recycled to absorber level 1
18	" "	" "	1050	" "	Rich solvent recycled to absorber level 2
19	" "	" "	1050	" "	Rich solvent recycled to absorber level 3
20	7220	1.44	1050	10,800	Rich solvent recycled to absorber level 1
21	7220	1.44	1050	10,800	Rich solvent recycled to absorber level 2
22	7220	1.44	1050	10,800	Rich solvent recycled to absorber level 3
23	Optimum	Optimum	880	Optimum	Confirm operation at optimum conditions
24	" "	" "	Adjusted to maintain 90% CO_2 capture	" "	Extended run at optimum conditions
25	7220	1.44	880	10,800	Lower steam flow rate compared to Run 2
26	7220	1.44	880	10,800	Intercooler operation extracting 50% of solvent flow
27	9030	1.81	880	13,500	" "

(1) Absorber flue gas flow rate 5,000 lb/hr for all conditions except Run 1
(2) For all conditions mist separator pressure and reboiler steam flow rate set at optimum values
(3) Rich solvent fed to top of regenerator for all other conditions

2.0 DESCRIPTION OF THE PILOT SOLVENT TEST UNIT (PSTU)

2.1 Introduction to the NCCC

The NCCC was founded by the US Department of Energy (DOE) to address the nation's need for cost-effective, commercially viable CO_2 capture options for coal-based power plants, both combustion and gasification. The NCCC was established at the Power Systems Development Facility (PSDF), an engineering-scale test center located in Wilsonville, Alabama, that has been in operation since 1996. The test facilities, shown in Figure 2, include the original PSDF site, which houses the gasification and pre-combustion CO_2 capture processes, and the Post-Combustion Carbon Capture Center (PC4), located at the adjacent Alabama Power E.C. Gaston power plant. The PSTU is located at PC4. The DOE provides 80 percent of the funding for the NCCC, with the remaining 20 percent coming from industrial participants. Southern Company Services manages the project.

Figure 2. NCCC/PSDF Facilities

The flue gas for PC4 testing is supplied by Gaston Unit 5, an 880 MW net supercritical pulverized coal unit. This unit includes selective catalytic reduction (SCR) units for NO_X control, dry electrostatic precipitators for particulate control, and a single Chiyoda wet flue gas FGD for SO_2 control. Hence, the flue gas discharged from the stack meets all emission control limits, and moreover, it is representative of the gas quality that would eventually be subject to

CO_2 emissions control. A view of Plant Gaston showing the location of PC4 is provided in Figure 3.

Figure 3. Alabama Power Gaston Steam Plant with PC4 Location

2.2 Description of the PSTU

Figure 4 provides a computer generated view of the PC4 showing the location of the PSTU. The header for the flue gas from downstream of the FGD enters along the pipe bridge to the left. All processed flue gas is returned to the header and leaves on the pipe bridge to the right to be introduced into the flue gas flow upstream of the FGD. This arrangement eliminates point source emissions so the power plant air permit does not need to be modified. Also shown in Figure 4 is a photograph of the PSTU.

The unit is designed to achieve 90-percent CO_2 capture using a 30-percent aqueous MEA solution, and it can operate with other solvents including hindered amines, amino acid salts, and ionic liquids. To accommodate this range of solvents, and their different physical properties, the PSTU was designed to be operationally flexible. The following major requirements are accommodated by the design.

- The vessels are spaced to allow for modifications and additional equipment to be installed to investigate alternative flow schemes.
- The regenerator is designed to operate at up to 215 psia as some solvents can be regenerated at pressure.

- The absorber and regenerator are designed to allow alternative packing and other gas-liquid contacting arrangements to be readily installed.

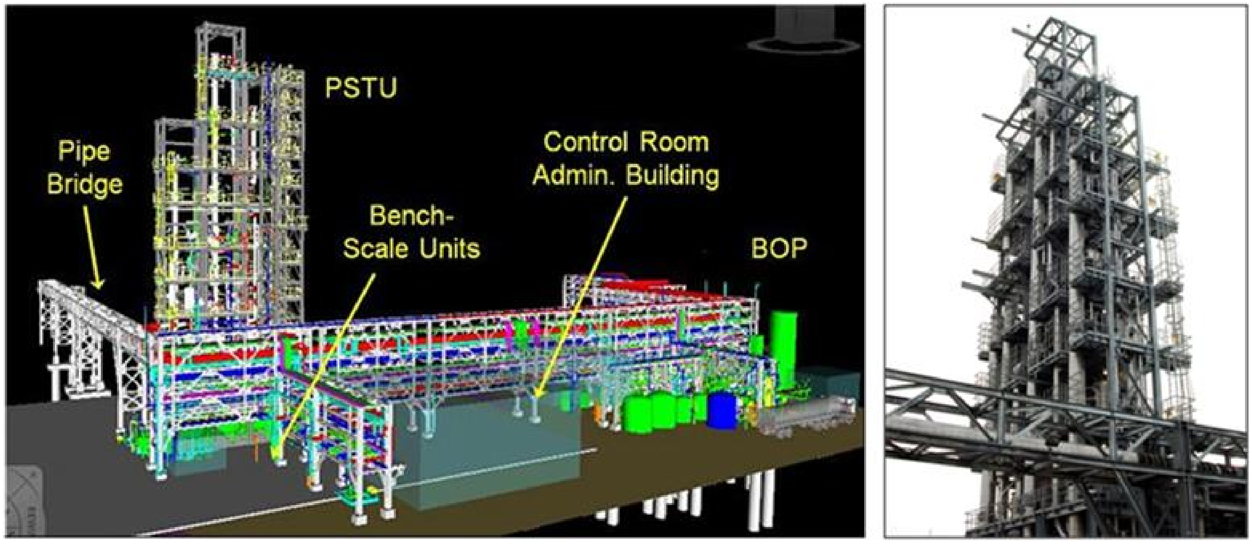


Figure 4. Views of the PSTU

- The absorber and regenerator are designed with numerous process nozzles to allow for different flow schemes and sufficient instrumentation for comprehensive data collection.
- The system is designed to cover a wide range of flue gas and solvent flow turndown to accommodate process variations arising from the use of solvents with different properties. The turndown ratios are 2:1 for gas and 3 to 5:1 for liquid.
- The equipment is easily drained and cleaned for testing different solvents.
- As the corrosivity of the different solvents is not known, for experimental convenience the vessels are made from 316L. Commercially, carbon steel would be a lower-cost option provided that corrosion rates were low or corrosion inhibitors were used.

A schematic of the PSTU is presented in Figure 5. Up to 30,000 lb/hr of flue gas is extracted from downstream of the power plant FGD for PC4 testing. Of this amount, up to 6,000 lb/hr is used in the PSTU. There are five major PSTU sub-systems (shown in green in Figure 5), and their functions will be discussed individually. Table 3 lists the dimensions of each of the columns and the type of packing currently being used.

<u>Pre-Scrubber</u>

This sub-system removes the small amount of SO_2 remaining in the flue gas after the FGD. It is designed to handle up to 12,000 lb/hr, the additional amount being used to provide desulfurized flue gas to other test units. Flue gas in 14-inch fiberglass reinforced piping (FRP) enters at the bottom of the pre-scrubber and flows upwards counter-currently to the 5-wt% caustic soda solution used to remove the SO_2. The caustic soda solution is circulated through a tank operating in batch mode. Periodically, liquid is removed to control the sulfate content, and fresh caustic soda is added. The liquid removed is sent to the PC4 balance-of-plant (BOP) area for treatment. The treated flue gas leaves from the head of the vessel, being drawn through by a blower that also drives the flue gas through the cooler/condenser. The blower generates a head of 2.5 psi.

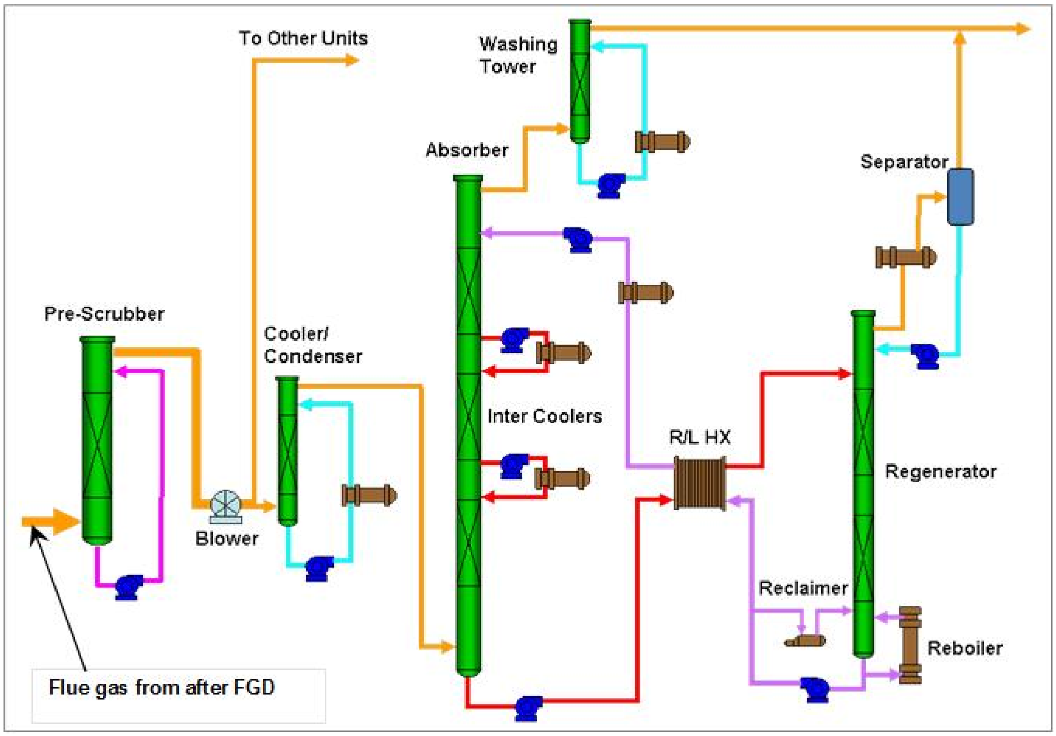


Figure 5. Schematic of PSTU

Table 3. Dimensions and Packing Used in PSTU Columns

Column	Height, ft	Outer Diameter, inches	Number of Beds	Packing Type (1)
Pre-Scrubber	46	30	1	Random
Cooler/Condenser	30	24	1	Structured
Absorber	108	26	3	Structured
Wash Tower	30	24	1	Structured
Regenerator	75	24	2	Structured

(1)All structured packing is Mellapak Plus M252-Y supplied by Sulzer

<u>Cooler/Condenser</u>

This sub-system cools the flue gas to an appropriate temperature for the CO_2 absorption reaction. Cooling also lowers the flue gas water content and limits dilution of the solvent solution in the absorber.

Absorber

This sub-system promotes efficient gas-liquid contacting to remove CO_2 from the flue gas. Flue gas in 10-inch FRP enters at the bottom of the absorber and flows upwards counter-currently to the CO_2-lean solvent returning from the regenerator. The CO_2-rich solvent leaves at the foot of the absorber and passes to the regenerator. The CO_2-depleted flue gas leaves from the head of the vessel and passes to the wash tower.

The absorber contains three sections in which packing is installed. A fourth section can be added if required. The absorption reaction is exothermic and will raise the temperature of the solvent. If it rises too much, it will limit the rate of CO_2 absorption and reduce the capture efficiency. To control solvent temperature, inter-cooling is provided between adjacent sections of packing.

The cool-rich solvent is pumped from the foot of the absorber to a cross-flow heat exchanger that recovers heat from the hot-lean solvent pumped from the foot of the regenerator. The cool-lean solvent passes to the top of the absorber, but can also be introduced at different levels in the absorber as part of the investigation to optimize CO_2 capture efficiency. The hot-rich solvent passes to the top of the regenerator. Before doing so, the hot-rich solvent can be passed to a vessel (not shown) in which some of the CO_2 is flashed off, so lowering the duty of the regenerator reboiler.

The cross-flow heat exchanger is designed for use with MEA, so when using other solvents, the approach temperatures are not optimal and the amount of heat recovered is reduced. Hence, the heat of regeneration is increased correspondingly.

Wash Tower

This sub-system cools the CO_2-depleted flue gas removing trace amounts of entrained solvent and lowering the moisture content of the exiting gas so reducing solvent make-up water requirements. The flue gas leaves the wash tower and passes back to the inlet of the power plant FGD.

Regenerator

This sub-system provides the heat required to release the CO_2 from the solvent. The hot-rich solvent (with or without flashing) flows down the regenerator through the packing or trays, coming into contact with steam rising from the reboiler. The resulting increase in temperature releases the CO_2 from the solvent. Part of the hot-lean solvent leaving the bottom of the regenerator passes to the reboiler to be heated and to raise the regenerating steam. The remaining solvent passes to the cross-flow heat exchanger to transfer its heat to the cool-rich solvent leaving the absorber. The reboiler heat source is low-pressure steam from PC4 BOP.

A small stream (about 4 percent) of the hot-lean solvent can be treated to remove heat stable salts that form through reaction of the solvent with oxygen and SO_2. The stream passes to a reclaimer where caustic soda is added to degrade the salts and release the solvent. The mixture is heated and the solvent and water vapor is returned to the foot of the regenerator leaving the salts in the reclaimer. The reclaimer circuit was not used during the Chiyoda test campaign.

The CO_2 exiting the regenerator (and any from the separator) is cooled to recover solvent and water vapor. The CO_2 is returned to the inlet of the FGD, and the condensate is returned to the regenerator.

Miscellaneous

There are numerous tanks required for collecting and mixing liquids such as the caustic soda and CO_2 solvent. The liquid flow lines include filters to remove particulate matter coming in with the flue gas and filtered water, or generated by the process.

Instrumentation

The PSTU is heavily instrumented to enable comprehensive process data collection and thorough characterization of equipment and solvent performance. The major control instrumentation, in additional to thermocouples and differential pressure measurements over select equipment items, are discussed briefly.

Flow Measurement

V-cone differential pressure flow meters are used to measure the untreated flue gas entering the pre-scrubber, the treated flue gas entering the absorber and the CO_2-depleted flue gas leaving, and the CO_2 stream leaving the regenerator. Coriolis meters are used to measure the flow of cool-lean solvent entering the absorber and cool-rich solvent leaving. These meters can also determine solvent density and how it varies with CO_2 loading and so can serve to monitor solvent composition.

Gas Analysis

The gas analyzers used and their locations are presented in Table 4. All the techniques used are commercially established. The sensor in the zirconia probe used to measure the oxygen in the absorber inlet flue gas operates at 1470°F. As the PSTU may use flammable solvents in the future, this high temperature was considered a potential explosion hazard for the absorber exit, so a parametric sensor was selected for this location. CO_2 content of the gases entering and leaving the absorber are determined by Non-Dispersive Infrared (NDIR) analyzers. The gas stream exiting the regenerator is almost 100 percent CO_2 on a dry basis (some small amount of oxygen and nitrogen is present), so only the moisture content of the wet gas is determined.

Table 4. Gas Analyzers Installed on PSTU

Stream and Species	Technique
Absorber Inlet	
Oxygen	Zirconia sensor
CO_2	NDIR
Moisture	Calculated
SO_2	Ultra violet
NO_X/NO	Ultra violet
Wash Tower Outlet	
Oxygen	Paramagnetic
CO_2	NDIR
Moisture	Calculated
NO_X/NO	Ultra violet
Regenerator Outlet	
Moisture	Calculated
CO_2	By difference

NO_2 reacts with amines forming nitrosamines and the NO_X/NO meters were installed to assist data evaluation: the NO_2 is determined as the difference between NO_X and NO. Capacitance moisture analyzers were installed but did not provide accurate data. As the gas streams at points of interest are saturated, the moisture content can be calculated from pressure and temperature data.

Liquid Analysis

An auto-titration system is used to determine the solvent concentration and the CO_2 loading. The water concentration is determined by difference, although it can be determine by the Karl Fischer method if required. The liquid samples can be extracted from these four locations:

- Hot-lean solution leaving the regenerator, typically 230°F.
- Cool-lean solution entering absorber, typically 110°F with the same composition as the hot-lean solution.
- Cool-rich solution leaving the absorber, typically 130°F.
- Hot-rich solution entering the regenerator, typically 215°F with the same composition as cool-rich solution.

The auto titrator takes a sample automatically every 30 minutes, so each location is sampled once every two hours. The solvent content, on a CO_2-free basis, should be the same at all locations, so the sampling frequency is sufficient for close control of the solvent concentration. To determine the CO_2 loading, the samples are titrated with potassium hydroxide and with sulfuric acid to determine the solvent concentration. The hot samples are cooled to around 100°F to prevent

CO_2 flashing from the solution, which would make its composition measurements unrepresentative.

The auto-titration values are cross-checked with laboratory analysis of samples taken manually from the cooled sample streams close to the time the auto-titration samples are taken. The total carbon analysis procedure developed at the NCCC was used to check the CO_2 content. This technique adds sulfuric acid to the solution and measures the volume of CO_2 released. The solvent content is cross-checked using the laboratory titration procedure. Standard quality control checks, such as spiking the solvent concentration, are used to confirm the accuracy of the laboratory procedures.

Operating experience indicated that the hot samples tended to give lower CO_2 values, some CO_2 possibly being released despite cooling the solvent sample. Therefore, for controlling the plant only cool-lean and cool-rich samples are taken. Sampling each location every hour rather than every two hours, increases the solvent composition data included in mass and heat balance periods.

The auto titrator at the NCCC is best suited to measuring single-component aqueous solvents. For T-3, a blended solvent, the reading for solvent concentration is low and a correction factor had to be applied. The correction factor used was based on the delivered solvent concentration and the initial auto-titrator measurements. Laboratory tests indicated that the CO_2 loading readings were valid and no correction factor was required.

3.0 TEST RESULTS

The T-3 solvent was delivered to the NCCC in 78 drums (about 35,500 lbs) in October, 2012. The NCCC hosted two meetings with Chiyoda engineers to reach agreement on the test plan and its implementation. The equipment modifications requested were essentially complete by December 7, and the solvent was loaded into the PSTU during the week of December 10 with Chiyoda engineers present. The test campaign started on 13 December, 2012 with the test to determine heat losses from the equipment. How the testing progressed is summarized in Table 5.

Table 5. Sequence of Testing

Period	Test Run	Description
13 Dec 2012	1	Hot solvent circulation
14 to 17 Dec 2012	2	Foaming in wash tower
18 Dec 2102 to 15 Jan 2013		Laboratory defoaming tests
18 Jan to 8 Feb 2013	(1 to 13)	Tests completed with valve failed open (1)
9 to 22 Feb 2013	1 to 15, 17, 18, 20 & 21	Parametric tests
23 Feb to 2 May 2013		Extended outage for Gaston Unit 5
7 to 21 May 2013	(16, 23, 25)	Test completed with reboiler in-leakage (2)
25 May to 17 June 2013	24	Extended run
17 and 18 June 2013	26 and 27	Parametric tests

(1) One of the new valves directing the recycled rich solvent to different levels in the absorber failed open. Hence how the recycled solvent was distributed was uncertain.

(2) For the first test following the extended outage, the CO_2 capture efficiency was lower than expected when compared to similar tests conducted before the outage. The CO_2 loading of the lean solvent leaving the regenerator was higher than previous levels (0.08 mole fraction compared to 0.02), and this was limiting the amount of CO_2 that could be absorbed for a given solvent flow rate and thereby raised the heat of regeneration. These observations were explained by the regenerator bottom temperature being approximately 8ºF lower than previous. The regenerator equipment was closely scrutinized and water was found to be leaking through a faulty valve isolating the reboiler from the regenerator mist eliminator.

Throughout the campaign, NCCC staff took solvent samples and forwarded them to Yokohama for analysis. The solvent composition was not measured on site but is known to have varied during the run. No make-up for the individual components was provided.

NCCC staff prepared the heat and mass balances for the test periods and supplied then to the Chiyoda test team for verification.

3.1 Foaming in the Wash Tower

Flue gas was introduced into the absorber on December 14, but after several hours of operation, foaming occurred in the wash tower (see Figure 6), resulting in a high pressure drop across the packing and carry-over of solvent with the CO_2-depleted flue gas. Occasionally the pressure drop fell but rose again to the previous level. Figure 7 shows the normal wash tower pressure drop to be 2-inches of water rising to as high as 14-inches of water.

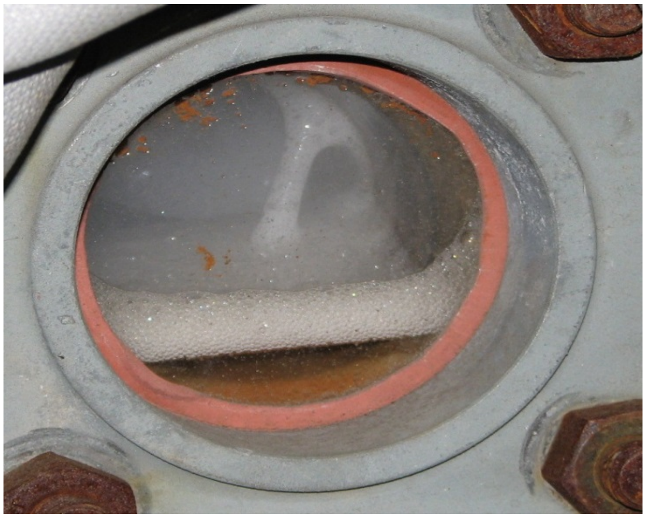


Figure 6. Foaming Observed through Wash Tower Port

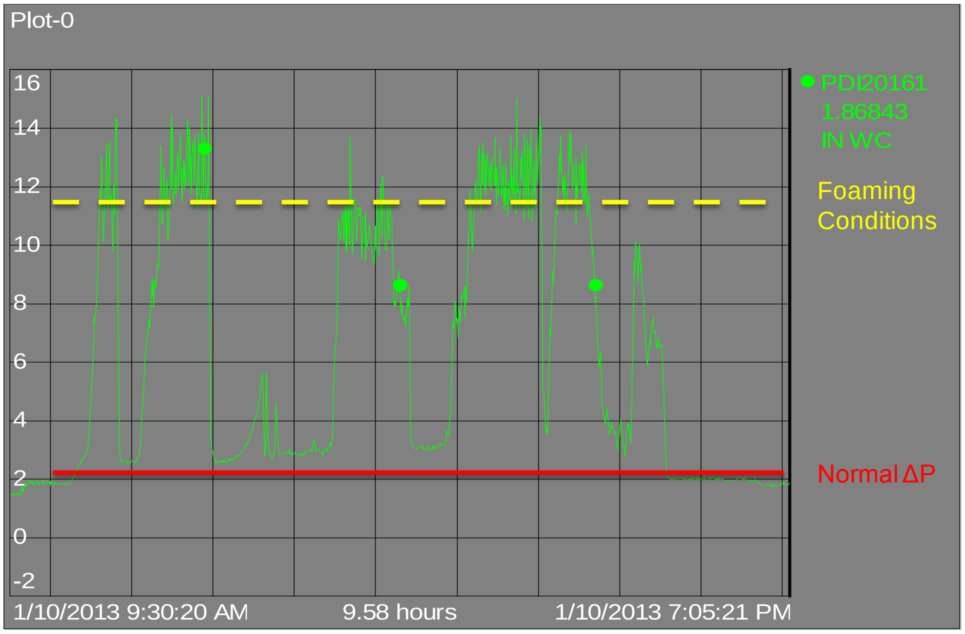


Figure 7. Wash Tower Pressure Drops during Foaming Event

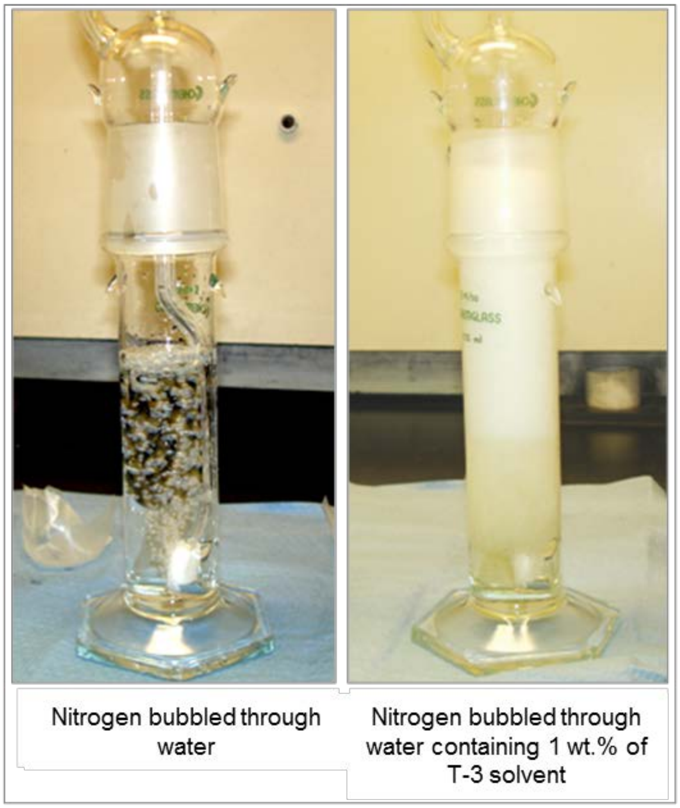
The foam was believed to prevent the wash water from flowing through the packing, and the buildup of water accounted for the increased pressure drop. At a certain water level, the head was sufficient to overcome the resistance offered by the foam and the pressure drop fell. Foaming was not observed in the absorber or regenerator. The plant was shut down, but foaming was seen again during a second test on December 17.

The foaming was unexpected as it had not been observed in past tests. The cause of the foaming is not clear but the on-site gas chromatograph indicated that the wash water contained up to 5 wt. % of T-3 solvent.

As operation was untenable, it was jointly agreed to postpone further testing until a means of eliminating the foam was identified. To test the efficacy of potential defoaming agents, a test apparatus, shown in Figure 8, was set up in the NCCC on-site laboratory. With the set-up, a known height of water is placed in a clear glass gas-wash bottle and nitrogen bubbled through it using a sintered glass frit. As indicated in the Figure, foaming, which approached 3 inches in height, was formed in a solution of water with 1-wt% T-3 solvent. Figure 9 plots foam height versus solvent concentration in water. If foaming is to be avoided, the tests indicated that the solvent concentration in the wash water would have to be reduced to below 0.1-wt. %.

NCCC staff tested several defoaming agents and showed that Shin-Etsu's KS-540 recommended by Chiyoda was the most effective. The manufacturer recommended using the agent with a concentration of 50 ppmw in the wash water, although the lab tests showed the agent was effective at lower concentrations.

The PSTU restarted on January 7, and testing was performed with several operating parameters (gas flow rate, wash-water flow rate, and wash-water temperature) around the PSTU wash tower to see if they reduced the foaming tendency. Variation of the operating parameters did not reduce foaming, and a modification to introduce the anti-foam agent into the wash tower was installed by NCCC staff. After an amount to achieve 50 ppmw was introduced on January 15, the foaming stopped immediately (see Figure 10) and pressure drops remained low and stable. It was expected that as the wash tower collected condensate and its concentration was reduced that more defoaming agent would have to be added, but no further additions were required.



Nitrogen bubbled through water

Nitrogen bubbled through water containing 1 wt.% of T-3 solvent

Figure 8. Laboratory Foaming Test Apparatus

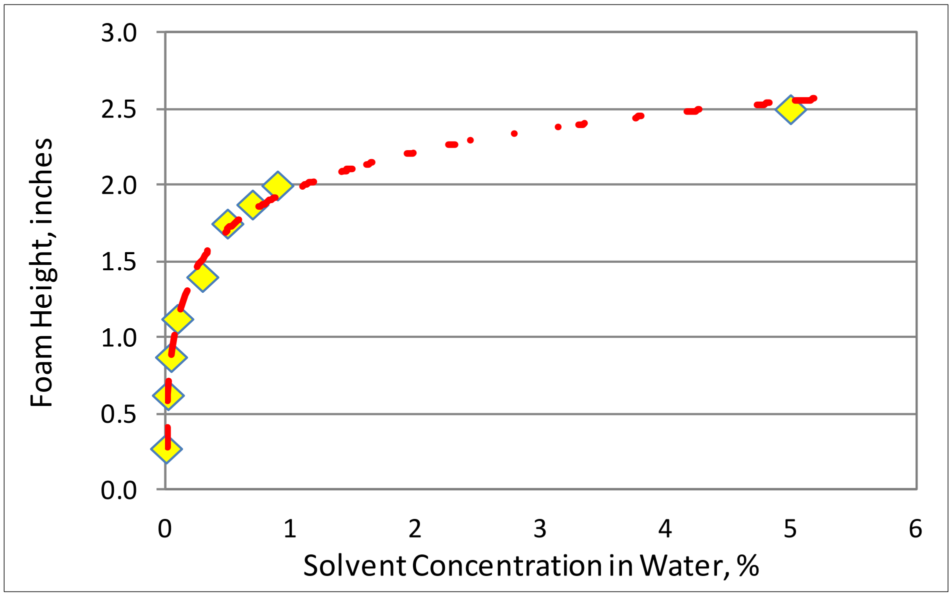


Figure 9. Variation of Foam Height in Test Apparatus with T-3 Solvent Concentration

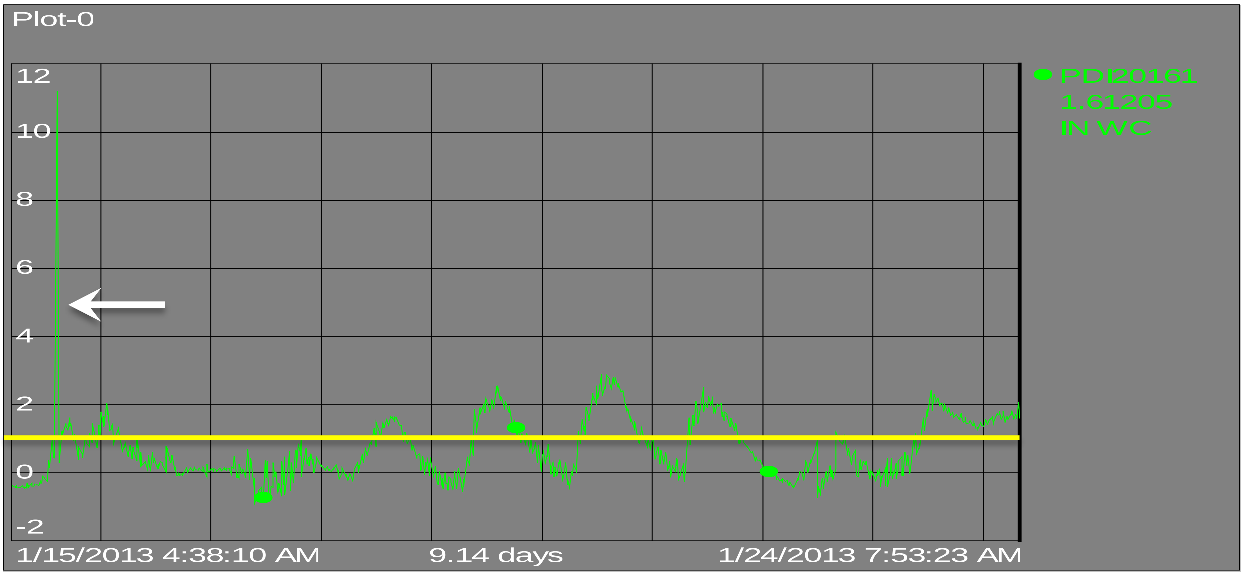


Figure 10. Wash Tower Pressure Drop Following Injection of Anti-Foaming Agent

Once stable operation was established without foaming, the Chiyoda test campaign started on January 17, and parametric tests to determine the optimal operating conditions to maximize the solvent's performance were conducted.

3.2 Absorber L/G Optimization Tests

The conditions for these tests are presented in Table 1. The variation in regeneration energy with L/G ratio is presented in Figure 11, which shows the optimum L/G ratio to be around 2.4 L/Nm^3. At the conditions tested the minimum regeneration energy for a CO_2 capture efficiency of 98.5 is 2.86 GJ/tonne of CO_2, which is comparable to results from previous tests at coal-fired power plants. Appendix 1 presents examples of mass balances collected during the parametric testing.

Once determined, regeneration energies were measured at conditions around the optimum L/G ratio. Figure 12 compares these values for T-3 solvent with results for 30-wt% MEA collected at the NCCC in 2011. The optimum L/G ratio for T-3 of 2.4 is around 50 percent lower than for the MEA and for 90% CO_2 capture the regeneration energy of around 2.6-GJ/tonne for T-3 is around 26 percent lower than the 3.5-GJ/tonne for MEA.

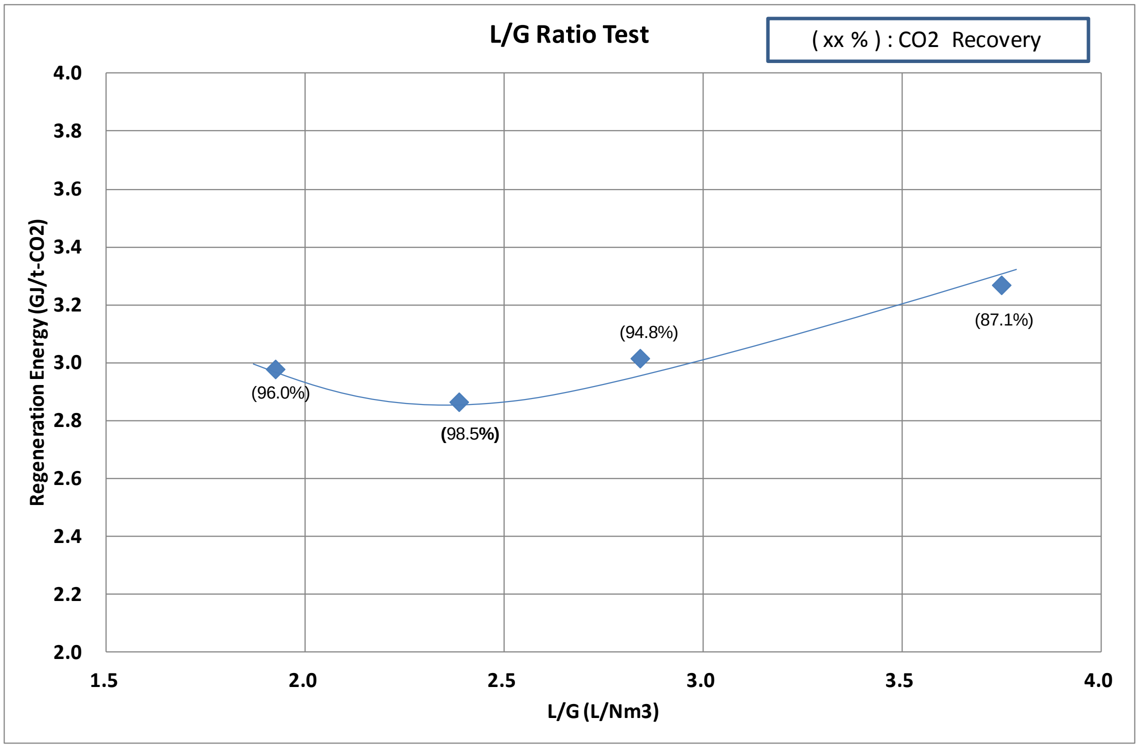


Figure 11. Variation of T-3 Regeneration Energy with Absorber L/G Ratio

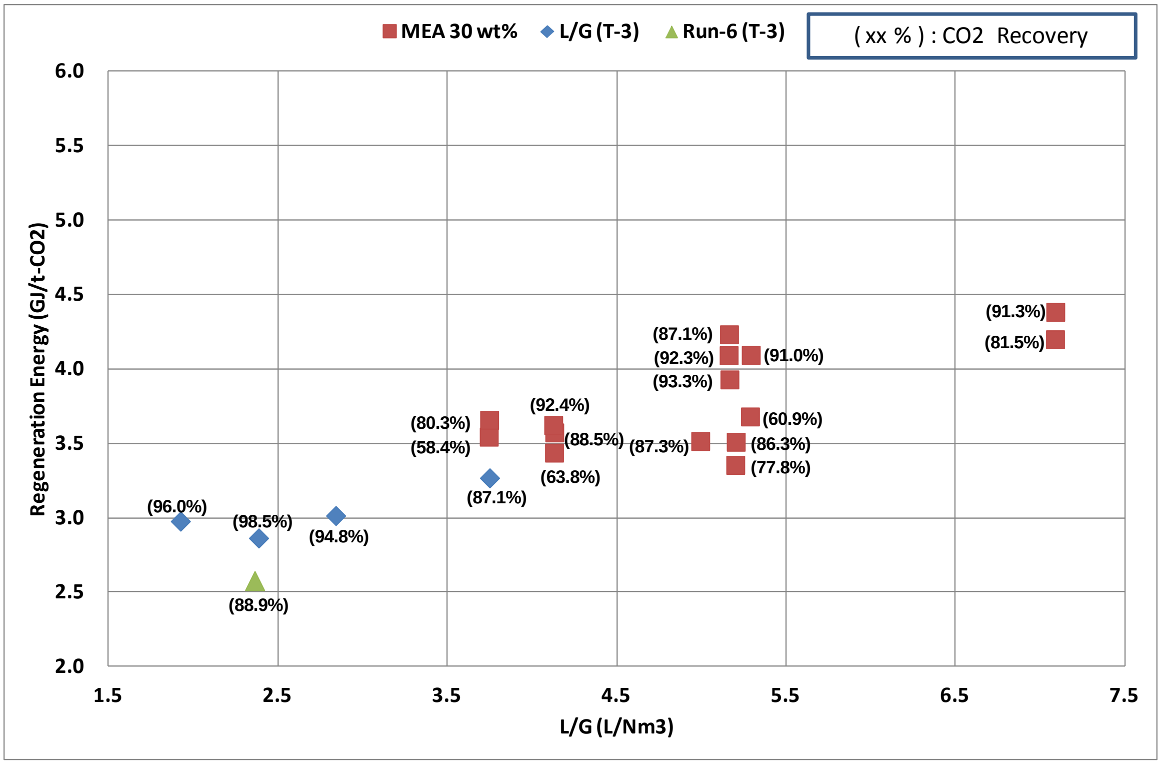


Figure 12. Performance of T-3 Compared to 30 wt. % MEA

3.3 Regeneration Operating Pressure tests

The regenerator pressure was varied to understand how CO_2 recovery is influenced by regenerator bottom temperature. The L/G ratio was set at the optimum value of 2.4 L/Nm^3 and the regenerator pressure and steam flow rate were varied as specified in Table 1. Figure 13 shows that for each regenerator pressure, the CO_2 recovery was highest at the higher bottom temperature. Although there is scatter in the data, CO_2 recovery appears to decrease at higher pressures despite the regenerator bottom temperature increasing. However, the higher pressure lowers the compression ratio required by the CO_2 compressor, and hence the energy consumed and the size of compressor required. The optimal regenerator pressure will be determined by the combined economics of regeneration and CO_2 compression.

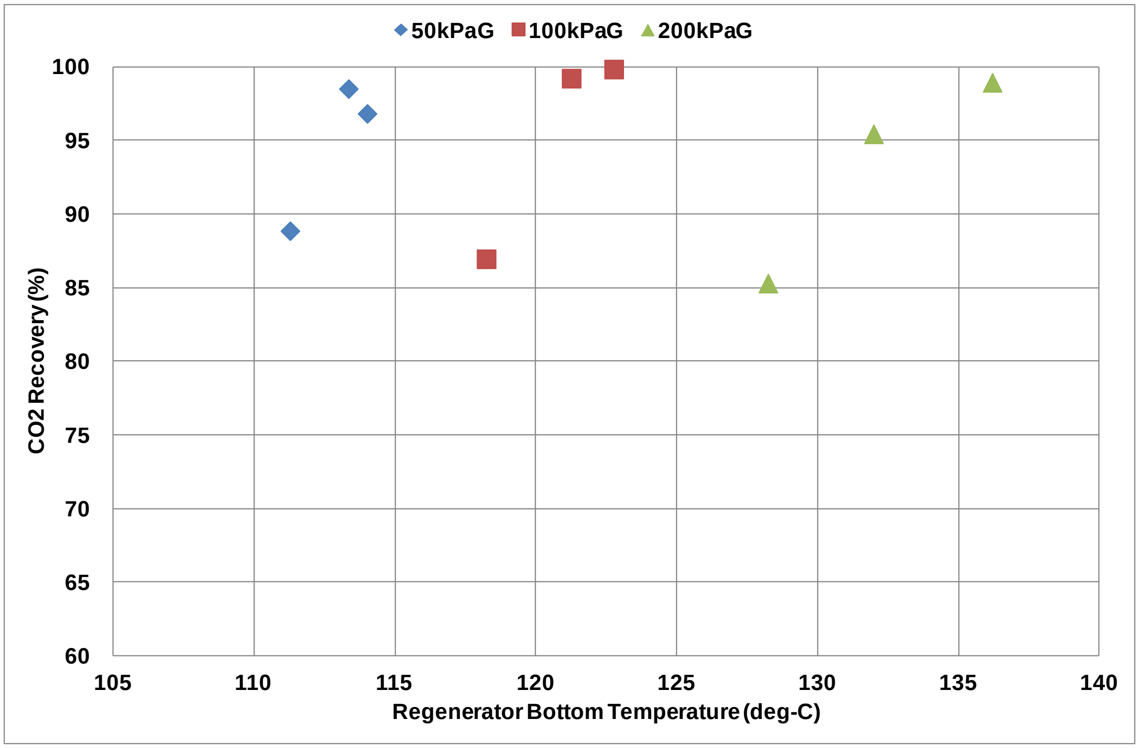


Figure 13. Regenerator Pressure Test

3.4 Absorber Intercooler Tests

To moderate the absorber temperature profile, intercoolers are available between the first and second, and second and third beds. Lowering the mean solvent temperature in this way increases CO_2 absorption efficiency, increasing CO_2 capture for a given solvent flow rate, and subsequently lowering the regeneration energy. A pan at the base of the second and third beds collects the solvent for redistribution; from here the hot solvent is pumped to the cooler and the cooled solvent is returned to the bed below by gravity. The original plan called for two tests collecting 50 and 100 percent of the down-flowing solvent. However, the only control for solvent flow is pump speed and this did not provide a sufficiently steady flow for accurate measurement. Hence only the 100 percent test was completed using both intercooling loops.

The test was completed at the optimum L/G ratio of 2.4 L/Nm^3. As anticipated the rich loading leaving the absorber and the CO_2 capture efficiency were both higher with the intercoolers in service (see Figure 14). The absorber temperature profile with and without intercooling is shown in Figure 15.

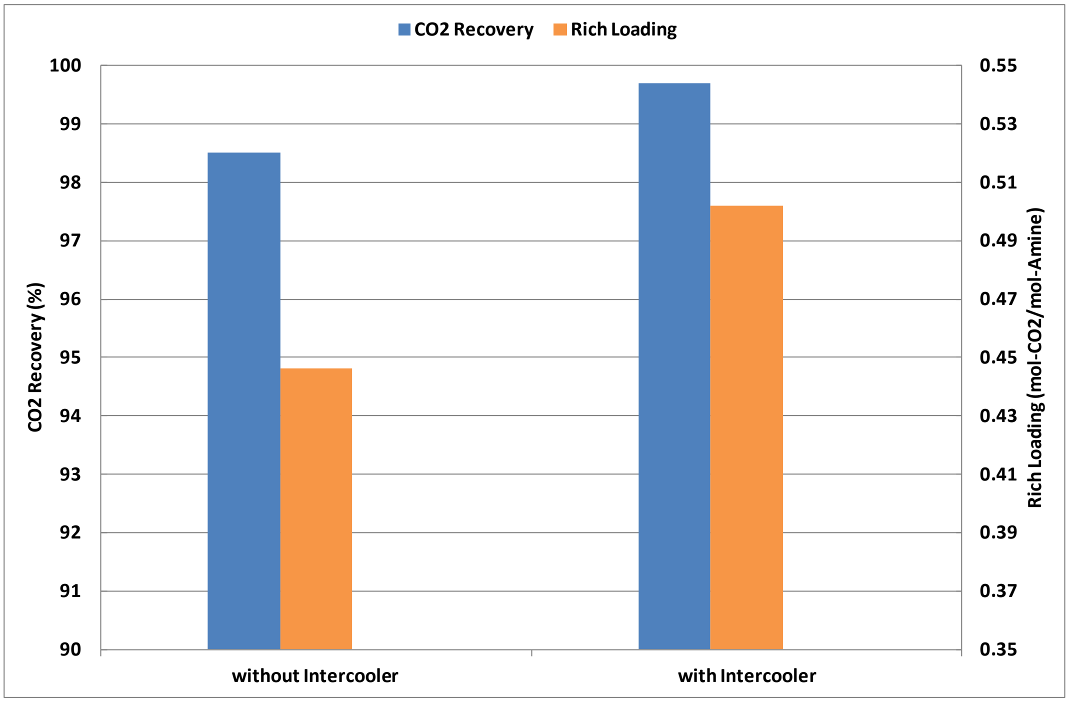


Figure 14. Effect of Intercoolers on Absorber Performance

3.5 Rich-Solvent Recirculation to Absorber

Rich solvent circulation tests were completed to increase the rich loading for a given circulation rate. Again the tests were completed at the optimum L/G ratio of 2.4 L/Nm^3, and two intercoolers were used to moderate the temperature profile. Figure 16 shows how the location at which the recirculated solvent was introduced (above the lower or middle bed) influenced CO_2 recovery and rich loading. Unfortunately, the solvent concentration for Cases B and C with recirculation was around 10 percent lower than for Case A, without recirculation. This might be expected to lower the capture efficiency and loading to approximately 90% and 0.40, respectively, but the corresponding values for Case A and B where higher (92% and 0.462, and 91.5% and 0.455, respectively). On this basis it appears that recirculation benefits the performance of T-3, although this conclusion still needs to be confirmed experimentally.

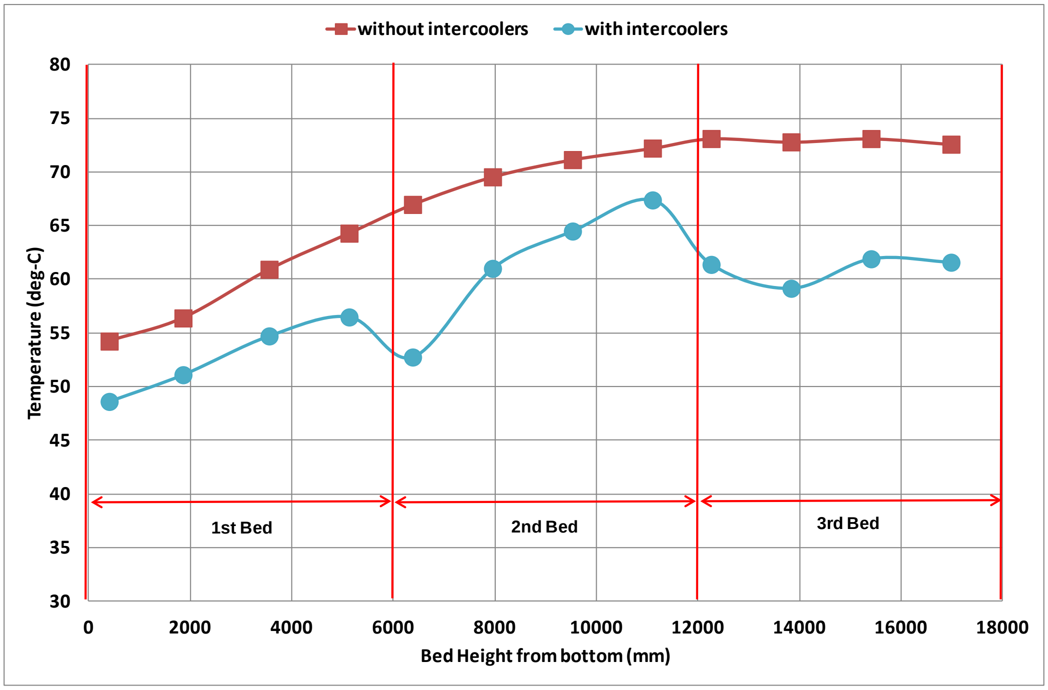


Figure 15. Absorber Temperature Profile with and without Intercooling

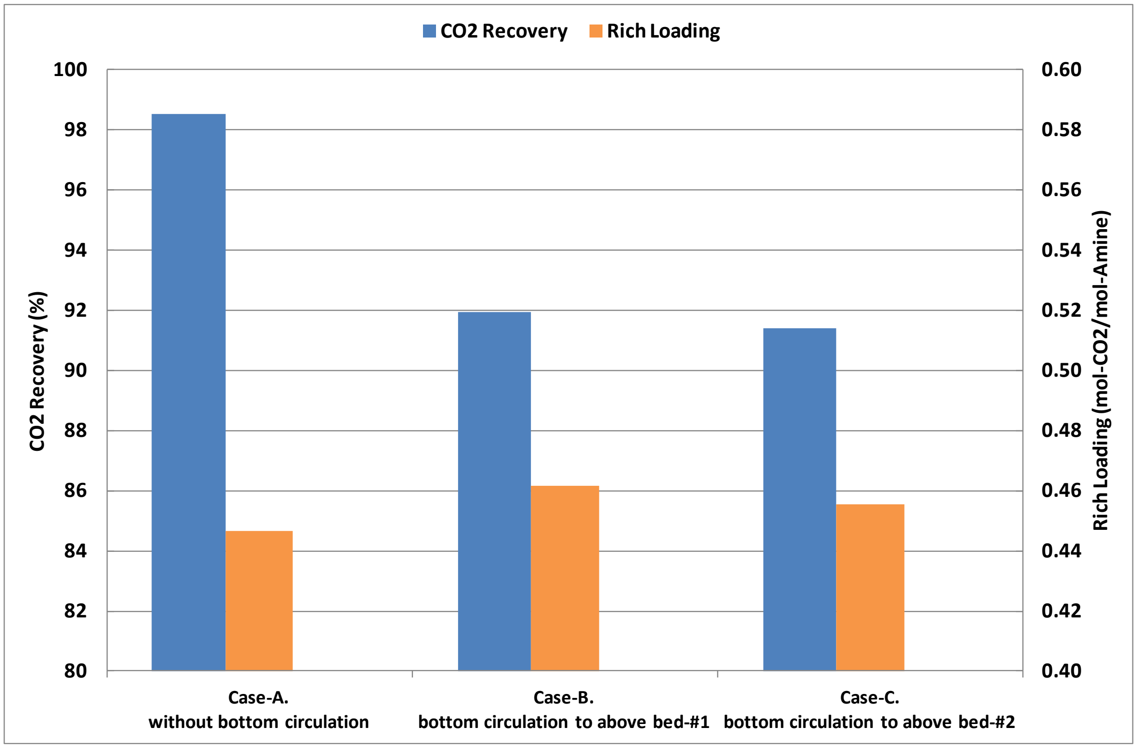


Figure 16. Effect of Recirculating Rich Solvent back to the Absorber

3.6 Extended Duration Test

An extended duration test run of 550 hours was completed at the optimum operating conditions determined during parametric testing. The CO_2 capture efficiency varied from 90.5 to 92.7 percent and regeneration energy from 3.25 to 3.31 GJ/tonne of CO_2. This regeneration energy was approximately 20 percent higher than for earlier runs at similar operating conditions. For example for Run 6, for which the CO_2 capture efficiency was comparable (88.9 percent), the regeneration energy was 2.58 GJ/tonne of CO_2. This increase in regeneration energy is explained by a decrease in T-3 solvent concentration, which at the end of the extended run was approximately 20 percent below the optimum value. There was insufficient solvent inventory to meet fully the makeup requirements. To maintain the same capture efficiency, more aqueous solvent solution was circulated increasing the sensible heat duty of the regenerator. Additionally, liquid analysis revealed that the composition of the solvent blend changed with time, which will also have affected T-3 performance.

As the T-3 solvent was diluted with water, the regeneration energy was increased at the same L/G condition. Furthermore, as a result of liquid analysis, it was determined that the ratio of amine components was changing with time due to the differing chemical characteristics of the individual solvent components. Consequently, this would have affected the solvent performance over time compounded by the number of impurities accumulated during the test campaign. Although the impurities were very dilute in the solvent, their effect on solvent performance is unknown so far. The compounded effect of varying concentrations and compositions was critical in this test campaign.

3.7 Solvent Losses during Test Campaign

The reduction in T-3 solvent concentration arose from higher-than-expected solvent losses arising primarily from solvent carried over with the CO_2-depleted flue gas. Similar solvent losses occurred during the MEA base-line tests. SO_3 aerosol present in the flue gas entering the absorber provides nucleation sites for the formation of droplets consisting primarily of water with a solvent concentration determine by vapor pressure equilibrium. The solvent losses occur as follows.

- The majority of droplets greater than around 3 microns are collected by the wash water. Most of the wash water is circulated back to the absorber to maintain the water balance, but when excess water accumulates this is discharged from the system resulting in solvent loss.
- The high wash water concentration will also result in the loss of T-3 solvent as vapor.
- The majority of droplets less than 3 microns are carried through the wash tower and passes to the inlet of the power plant FGD.

- Solvent was also carried over with the CO_2 released in the regenerator although this was mostly removed in the reflux condenser and returned to the absorber as part of water make up. Nevertheless, some solvent will have left with the CO_2 discharged back to the FGD inlet.
- Solvent was also lost when the PSTU system was drained and flushed through with water ahead of the extend outage and at the end of the test campaign. High losses, albeit for relatively short duration, were incurred during the foaming event.

Further investigation of solvent losses is required to evaluate the environmental and economic impact on commercial CO_2 capture processes.

APPENDIX A. SELECTED MASS BALANCES

The mass balances are prepared using the instrumentation discussed in Section 2. Experience shows that a minimum of three lean and rich solvent samples are required to achieve total CO_2 closures (CO_2 in inlet and outlet gas and liquid streams) of better than 1 percent. This sets the minimum balance period duration at 3 hours.

To illustrate the quality of data collected five balance periods are presented showing how the heat of regeneration varied with L/G ratio for capture efficiency around 90 percent. The data are tabulated in a form that complies with Chiyoda's confidentiality requirements. The minimum energy of 1050 Btu/lb of CO_2 (2.45 GJ/tonne of CO_2) [achieved with two of the balance periods presented] occurs around a mean L/G ratio of 1.81 on a mass basis or 2.17 on a L/Nm^3 basis.

Table A-1. Balance Period 1

Start and end dates and times	05:00, 10th Feb 2013 to 15:30, 10th Feb 2013
Duration, hours and minutes	10:30

Absorber Gas Flows

	Inlet	Wash Tower Outlet	Closure, %
Nitrogen, lb/hr	3510	3500	0.29
Oxygen, lb/hr	372	374	0.53
CO_2, lb/hr	815	38.7	
Moisture, lb/hr	279	231	
TOTAL, lb/hr	4976	4144	
Temperature, ºF	115	111	

Absorber Liquid Flows

	Inlet	Outlet
Water + solvent, lb/hr	10,620	10,410
CO_2, lb/hr	209	978
TOTAL, lb/hr	10,829	11,399
Temperature, ºF	106	127
Liquid/gas ratio, -	2.18	

Absorber CO_2 Flows (in liquid and in gas), lb/hr

	Inlet	Outlet	Closure, %
CO_2	1024	1017	0.69

CO_2 Flow Cross Checks

	Rates, lb/hr	Capture efficiency, %
CO_2 removed from flue gas	776	95.2
CO_2 absorbed by solvent	769	
CO_2 released from regenerator	770	

Lean-Rich Heat Exchanger Temperatures

	In	Out
Lean	233	136
Rich	128	221

Regenerator Data

Steam flow to reboiler, lb/hr	1070
Steam pressure, psia	41.4
Steam temperature, ºF	271
Regenerator bottom temperature, ºF	233
Heat of regeneration, Btu/lb (measured)	1290
Heat of regeneration, Btu/lb (adjusted) (1)	1250

(1) Allowing for heat losses (estimated at 30,600 Btu/hr)

Table A-2. Balance Period 2

Start and end dates and times	16:15, 10th Feb 2013 to 07:40, 11th Feb 2013
Duration, hours and minutes	15:25

Absorber Gas Flows

	Inlet	Wash Tower Outlet	Closure, %
Nitrogen, lb/hr	3510	3480	0.86
Oxygen, lb/hr	376	373	0.80
CO_2, lb/hr	813	97.2	
Moisture, lb/hr	278	193	
TOTAL, lb/hr	4977	4143	
Temperature, ºF	115	105	

Absorber Liquid Flows

	Inlet	Outlet
Water + solvent, lb/hr	14,040	13,990
CO_2, lb/hr	405	1120
TOTAL, lb/hr	14,445	15,110
Temperature, ºF	106	134
Liquid/gas ratio, -	2.90	

Absorber CO_2 Flows (in liquid and in gas), lb/hr

	Inlet	Outlet	Closure, %
CO_2	1218	1217	0.08

CO_2 Flow Cross Checks

	Rates, lb/hr	Capture efficiency, %
CO_2 removed from flue gas	716	88.1
CO_2 absorbed by solvent	715	
CO_2 released from regenerator	701	

Lean-Rich Heat Exchanger Temperatures

	In	Out
Lean	229	139
Rich	131	218

Regenerator Data

Steam flow to reboiler, lb/hr	1070
Steam pressure, psia	39.8
Steam temperature, ºF	269
Regenerator bottom temperature, ºF	229
Heat of regeneration, Btu/lb (measured)	1390
Heat of regeneration, Btu/lb (adjusted) (1)	1350

(1) Allowing for heat losses (estimated at 30,400 Btu/hr)

Table A-3. Balance Period 3

Start and end dates and times	12:15, 11th Feb 2013 to 00:00, 12th Feb 2013
Duration, hours and minutes	11:45

Absorber Gas Flows

	Inlet	Wash Tower Outlet	Closure, %
Nitrogen, lb/hr	3490	3440	1.45
Oxygen, lb/hr	369	368	0.27
CO_2, lb/hr	842	79.1	
Moisture, lb/hr	280	245	
TOTAL, lb/hr	4981	4132	
Temperature, ºF	115	113	

Absorber Liquid Flows

	Inlet	Outlet
Water + solvent, lb/hr	8820	8550
CO_2, lb/hr	207	971
TOTAL, lb/hr	9027	9521
Temperature, ºF	107	129
Liquid/gas ratio, -	1.81	

Absorber CO_2 Flows (in liquid and in gas), lb/hr

	Inlet	Outlet	Closure, %
CO_2	1049	1050	0.10

CO_2 Flow Cross Checks

	Rates, lb/hr	Capture efficiency, %
CO_2 removed from flue gas	763	90.6
CO_2 absorbed by solvent	764	
CO_2 released from regenerator	734	

Lean-Rich Heat Exchanger Temperatures

	In	Out
Lean	232	134
Rich	125	220

Regenerator Data

Steam flow to reboiler, lb/hr	893
Steam pressure, psia	38.9
Steam temperature, ºF	267
Regenerator bottom temperature, ºF	232
Heat of regeneration, Btu/lb (measured)	1090
Heat of regeneration, Btu/lb (adjusted) (1)	1050

(2) Allowing for heat losses (estimated at 30,400 Btu/hr)

Table A-4. Balance Period 4

Start and end dates and times	15:20, 13th Feb 2013 to 03:50, 14th Feb 2013
Duration, hours and minutes	12:30

Absorber Gas Flows

	Inlet	Wash Tower Outlet	Closure, %
Nitrogen, lb/hr	3510	3460	1.45
Oxygen, lb/hr	360	358	0.56
CO_2, lb/hr	830	102	
Moisture, lb/hr	281	261	
TOTAL, lb/hr	4981	4181	
Temperature, ºF	115	115	

Absorber Liquid Flows

	Inlet	Outlet
Water + solvent, lb/hr	8810	8580
CO_2, lb/hr	223	935
TOTAL, lb/hr	9033	9515
Temperature, ºF	107	125
Liquid/gas ratio, -	1.81	

Absorber CO_2 Flows (in liquid and in gas), lb/hr

	Inlet	Outlet	Closure, %
CO_2	1053	1037	1.54

CO_2 Flow Cross Checks

	Rates, lb/hr	Capture efficiency, %
CO_2 removed from flue gas	728	87.7
CO_2 absorbed by solvent	712	
CO_2 released from regenerator	789	

Lean-Rich Heat Exchanger Temperatures

	In	Out
Lean	262	135
Rich	124	238

Regenerator Data

Steam flow to reboiler, lb/hr	880
Steam pressure, psia	62.8
Steam temperature, ºF	297
Regenerator bottom temperature, ºF	263
Heat of regeneration, Btu/lb (measured)	1100
Heat of regeneration, Btu/lb (adjusted) (1)	1050

(1) Allowing for heat losses (estimated at 37,200 Btu/hr)

Table A-5. Balance Period 5

Start and end dates and times	05:00, 20th Feb 2013 to 15:30, 20th Feb 2013
Duration, hours and minutes	10:30

Absorber Gas Flows

	Inlet	Wash Tower Outlet	Closure, %
Nitrogen, lb/hr	3590	3570	0.56
Oxygen, lb/hr	381	380	0.26
CO_2, lb/hr	829	97.9	
Moisture, lb/hr	200	148	
TOTAL, lb/hr	5000	4196	
Temperature, ºF	104	96	

Absorber Liquid Flows

	Inlet	Outlet
Water + solvent, lb/hr	7190	7210
CO_2, lb/hr	37.8	763
TOTAL, lb/hr	7228	7973
Temperature, ºF	106	122
Liquid/gas ratio, -	1.45	

Absorber CO_2 Flows (in liquid and in gas), lb/hr

	Inlet	Outlet	Closure, %
CO_2	867	861	0.70

CO_2 Flow Cross Checks

	Rates, lb/hr	Capture efficiency, %
CO_2 removed from flue gas	731	88.2
CO_2 absorbed by solvent	725	
CO_2 released from regenerator	718	

Lean-Rich Heat Exchanger Temperatures

	In	Out
Lean	235	129
Rich	121	222

Regenerator Data

Steam flow to reboiler, lb/hr	1090
Steam pressure, psia	42.0
Steam temperature, ºF	271
Regenerator bottom temperature, ºF	237
Heat of regeneration, Btu/lb (measured)	1390
Heat of regeneration, Btu/lb (adjusted) (1)	1340

(1) Allowing for heat losses (estimated at 35,700 Btu/hr)