Testing of Hitachi H3-1 Solvent at the National Carbon Capture Center:
Final Report

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Abstract

The National Carbon Capture Center (NCCC) at the Power Systems Development Facility supports the Department of Energy goal of promoting the United States' energy security through reliable, clean, and affordable energy produced from coal. The NCCC facilities provide adaptable slipstreams that allow technology development of CO_2 capture concepts using coal-derived syngas and flue gas 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 path to commercialization.

The Hitachi H3-1 solvent for post-combustion CO_2 capture was tested during a three-month test campaign in the NCCC's Pilot Solvent Test Unit. Operation began on April 24, 2012, and ended on July 16, 2012 achieving about 1,400 hours of testing for a range of parametric and plant operating conditions. The subjects investigated include CO_2 capture performance, regeneration energy, and corrosion, among others. Studies show a favorable comparison of the H3-1 solvent with monoethanolamine, a standard amine solvent, a result consistent with previous findings by Hitachi. The NCCC test campaign results are a valuable resource for Hitachi to further its commercialization efforts on post-combustion CO_2 capture.

Acknowledgement

Table of Contents

List of Figures

List of Tables

List of Abbreviations and Acronyms

BOP	Balance-of-Plant
CCS	CO_2 Capture and Storage
DCS	Distributed Control System
DOE	Department of Energy
ER	Electrical Resistance
FGD	Flue Gas Desulfurization
FRP	Fiberglass Reinforced Piping
MEA	Monoethanolamine
NCCC	National Carbon Capture Center
NDIR	Non-Dispersive Infrared
PC4	Post-Combustion Carbon Capture Center
ppmv	Parts per million by volume
ppmw	Parts per million by weight
PSDF	Power Systems Development Facility
PSTU	Pilot Solvent Test Unit
RCRA	Resource Conservation and Recovery Act
SCR	Selective Catalytic Reduction
SCU	Syngas Conditioning Unit

1.0 INTRODUCTION

The National Carbon Capture Center (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 1-1, 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 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.
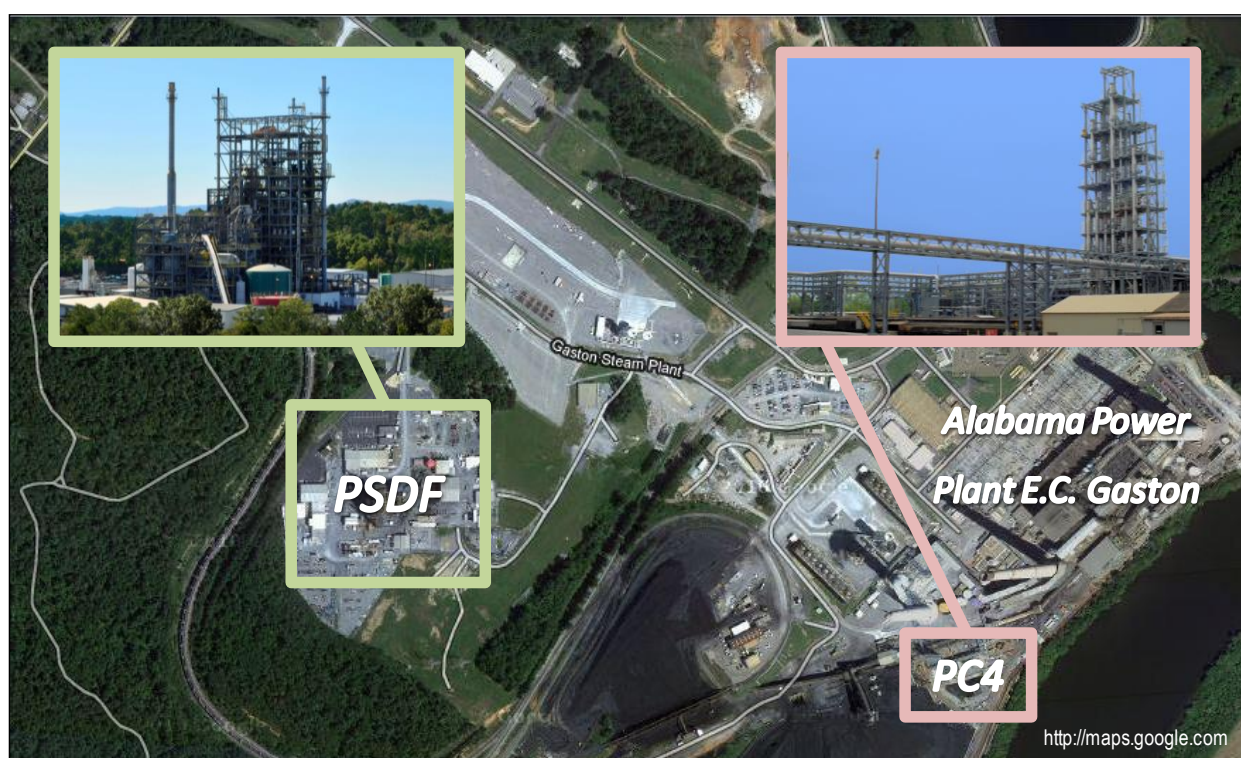
Figure 1-1 - NCCC/PSDF Facilities

One of the cornerstones of the PSDF testing was the development of the Transport Integrated Gasification process, which will be demonstrated on a 540-MW scale at Mississippi Power's Kemper County Energy Facility. Additionally, in support of the DOE's coal development projects, the PSDF worked with over 70 organizations testing a number of different technologies. Providing test facilities with commercially representative operating conditions at a scale sufficiently large to provide meaningful data enabled processes to progress rapidly to the next stage of development. In some instances, technologies were found to be insufficiently robust to progress further, which is another way that the PSDF provided value.

The major objectives of the NCCC are to:

- Provide a flexible test facility with commercially representative test conditions to support testing of technologies that will reduce the cost of integrating CO_2 capture and storage (CCS) with coal-based power plants
- Solicit and incorporate activities from a wide range of participants and promote innovation through collaborative research
- Accelerate the development of cost-effective CO_2 capture technologies and facilitate their scale-up and commercialization.

The two parts of the facility offer multiple slipstream capabilities for testing candidate processes in parallel and at different scales. Long-term testing is also available to establish the durability and reliability of new technologies. The Transport Gasifier utilized at the PSDF can process different ranks of coal and biomass co-feed. Plant Gaston is on commercial dispatch firing Alabama bituminous coal, the coal supply possibly varying as a result of competitive pricing.

Project Partners

Co-funding partners of the NCCC include the Electric Power Research Institute and leaders in the power and coal industries, including American Electric Power, Luminant, NRG Energy, Southern Company, Arch Coal, Peabody Energy, and Rio Tinto. Other participants are expected to join as the project evolves.

1.1   Scope of Work

The NCCC provides state-of-the-art facilities to test developers' technologies for extended periods under commercially representative conditions with coal-derived flue gas and syngas, thereby accelerating development of cost-effective CO_2 capture technologies. Support includes:

- All necessary infrastructure to support testing of developers' technologies
- Operations and maintenance staff dedicated to supporting testing activities
- Access to advanced analytical techniques at local universities.
- Comprehensive data collection and analysis capability to validate performance.
- Technical staff who ensure acceptable heat and mass balance closures are achieved and support developers' data analyses when required
- Flexible facilities to allow for scale-up from bench- to engineering-scale

This support is provided at limited cost to the developer. The developer must provide raw materials, such as CO_2 solvent. Some charges may be incurred for unusual interconnection requirements and for non-standard chemical analyses.

Figure 1-2 presents the approached being used to support developers. Innovative ideas under investigation at the laboratory scale will progress without NCCC involvement. Those ideas that emerge successfully and require testing at a larger scale using commercially representative coal-derived flue gas and syngas are candidates for testing at the NCCC. Testing can be at the bench or pilot scale and the data collected used to support more detailed evaluation of the technology. The technologies considered most feasible may proceed to the

demonstration phase at other locations, although NCCC could support development activities if required.
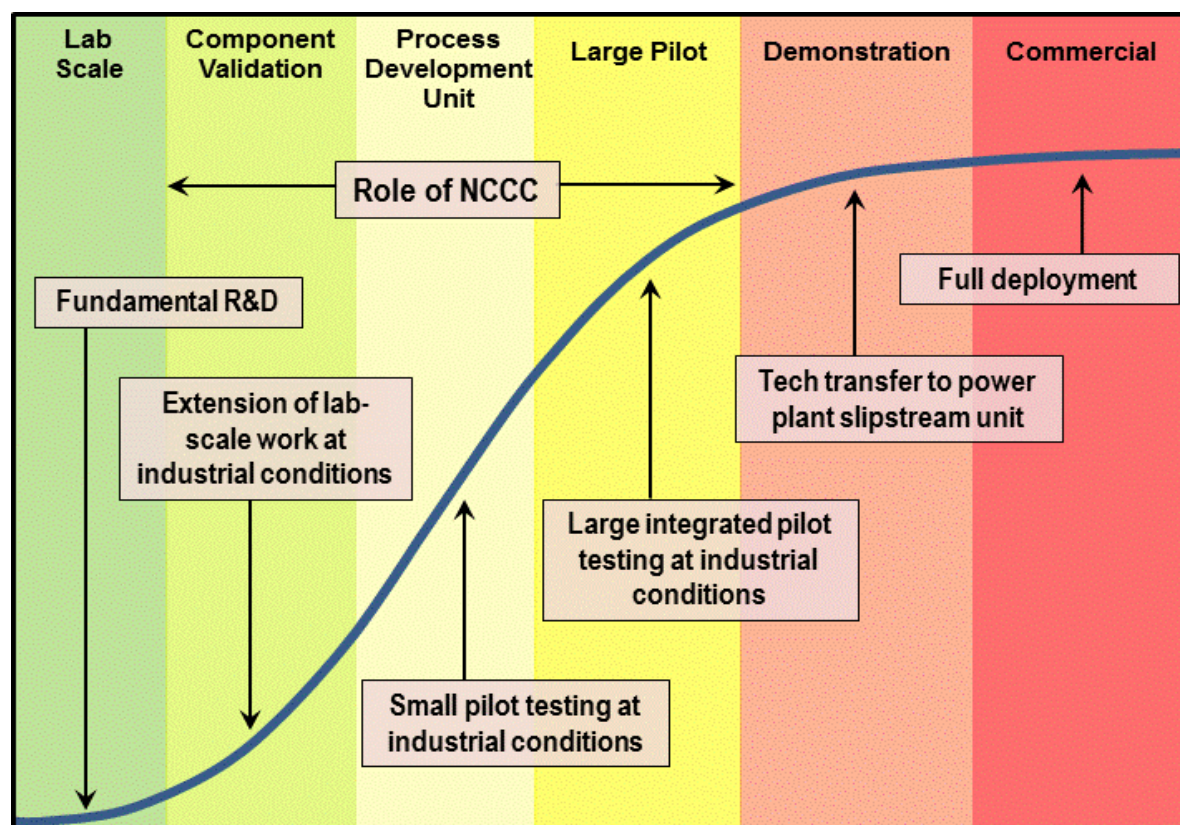
Figure 1-2 - Focus of NCCC Test Support

Selection criteria are used to prioritize testing and derive the greatest benefit with respect to time and cost. A means of assessing the state-of-readiness of individual technologies has been developed to aid the selection of those to be tested and to determine what level of support is most appropriate. A technology in the conceptual stage might be best suited for being tested at the bench scale, while one that has already been tested at the bench scale might be ready for pilot-scale testing. Criteria will also be developed to select a technology in those instances where two or more technologies are competing for the same slot.

1.2 Pre-Combustion CO$_2$ Capture

To allow for the testing and development of systems that improve the thermodynamic and economic performance of pre-combustion CO$_2$ capture technologies, the NCCC provides slipstreams of coal-derived syngas at around 650°F drawn from the Transport Gasifier exit duct downstream of a high-temperature, high-pressure filter. Figure 1-3 shows the flow arrangements for testing these technologies. The 1,500-lb/hr slipstream supplies the Syngas Conditioning Unit (SCU) with two test streams: one for bench-scale units each using up to 100 lb/hr of syngas, and one for a pilot-scale unit using up to 1000 lb/hr of syngas. The 1,000 lb/hr slipstream supplies syngas to a second pilot-scale unit.
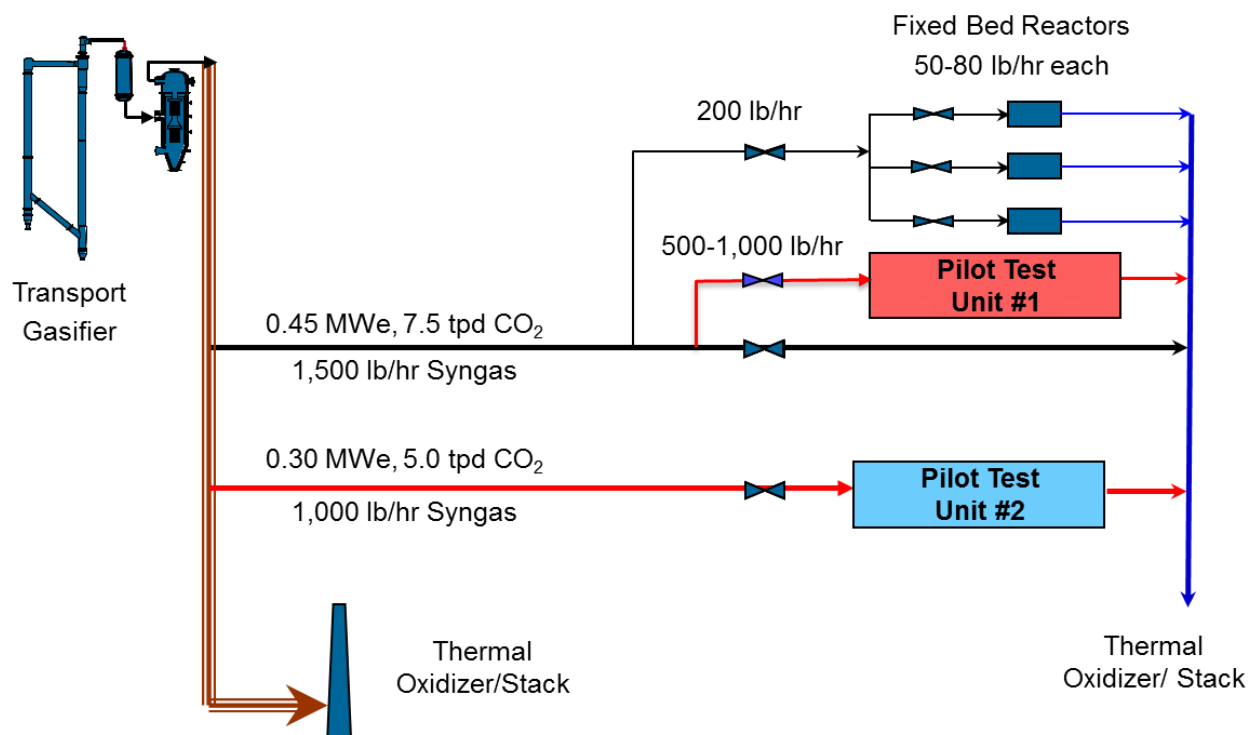
Figure 1-3 - Slipstream Arrangement for Pre-Combustion Technology Development

Information is collected and stored in the data acquisition system, and various gas analyzers are available to determine the composition of inlet and outlet gas streams. The syngas leaving the test vessels is treated in an atmospheric syngas combustor prior to stack discharge. The bench-scale SCU slipstream has been used to evaluate emerging technologies for a range of flow rates. Currently the NCCC provides a bench-scale stirred batch reactor and three pressure vessels to support testing. To date, technology testing has included:

- Water gas shift catalysts
- High-temperature adsorption of mercury and heavy metals
- Chemical and physical solvents for the absorption of CO_2 and hydrogen sulfide

The NCCC vessels have also been used to provide shifted and sulfur-free syngas to developers' test skids. The skids tested incorporated the following technologies:

- High-temperature adsorption of CO_2
- Carbon-, palladium-, and polymer-based hydrogen separation membranes
- Polymer-based CO_2 separation membranes

The two 1,000 lb/hr slipstreams are also in service. Pilot Test Unit #1 is MTR's polymer-based CO_2 separation membrane, processing 500 lb/hr of syngas at 100°F. Pilot Test Unit #2 is Ohio State's Syngas Chemical Looping Unit, processing 800 lb/hr of syngas at 600°F. Discussions are in progress with other developers to test their technologies at both the bench- and the pilot-scale.

1.3   Post-Combustion CO$_2$ Capture

The flue gas utilized 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 NOx control, dry electrostatic precipitators for particulate control, and a single Chiyoda wet flue gas desulfurization (FGD) unit 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 1-4.

Figure 1-4 - Alabama Power Gaston Steam Plant with PC4 Location

The arrangement of PC4 is shown in Figure 1-5 as of April 2014. A slipstream of coal-derived flue gas at around 130°F is drawn from the FGD exit duct. After passing through the test equipment, the spent flue gas is returned to the FGD inlet to remove any contaminants such as dust or solvent vapor from the processed flue gas before it is discharged to the stack. By avoiding additional point-source emissions, the power plant's air permit is not infringed.
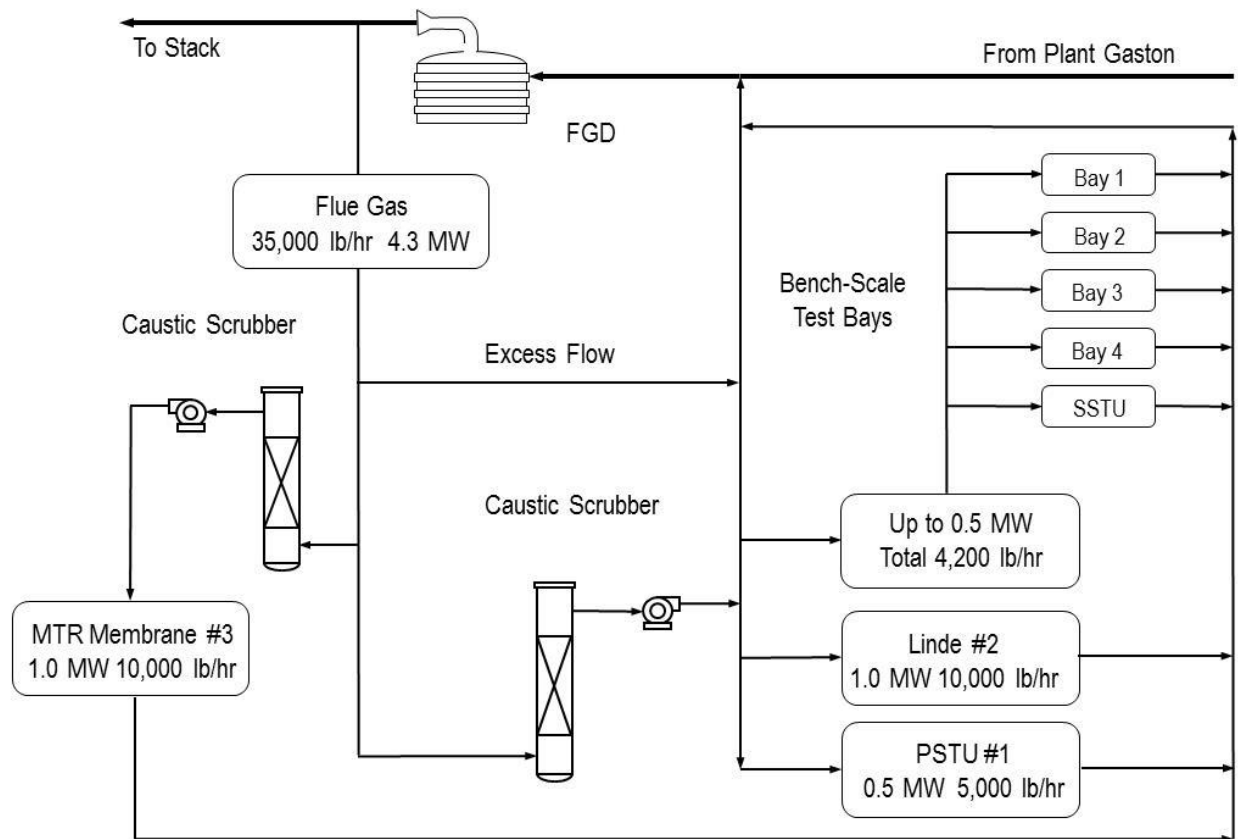
Figure 1-5 - Flue Gas Slipstream Arrangement for PC4

Around 35,000 lb/hr of flue gas is extracted to help maintain flue gas temperature and limit the amount of condensation occurring in the delivery header. Up to 29,200 lb/hr is used for testing.

The bench-scale modules receive up to 4,200 lb/hr of flue gas, allowing up to five technologies to be tested simultaneously. The Pilot Solvent Test Unit (PSTU) is a permanent fixture processing up to 6,000 lb/hr of desulfurized flue gas to test developers' solvents. Test campaigns have been completed with monoethanolamine (MEA), a standard industrial solvent, to provide baseline data to compare with the performance of the developers' solvents. Two large pilot bays each process up to 10,000 lb/hr of desulfurized flue gas. As of April 2014 these two bays were occupied by Linde's 1-MW solvent pilot plant and MTR's 1-MW membrane pilot plant.

PC4 has its own control room and data acquisition and control system. Operations, maintenance, and test support are provided by NCCC staff with only limited participation from Plant Gaston staff.

2.0 HITACHI CO_2 CAPTURE SOLVENT TECHNOLOGY DEVELOPMENT

Hitachi has been engaged in the development of CO_2 capture technologies for coal-fired power plants since the early 1990's, when the first bench-scale studies and pilot-scale demonstration were conducted. Since then, Hitachi has been continually improving process designs and technologies for full-scale power plant applications through research and development, and demonstrations. Hitachi has developed an advanced amine solvent, H3-1, capable of capturing 90 percent of CO_2 generated from a coal-fired power plant while eliminating shortcomings of commercial amines. Key attributes of the H3-1 solvent are:

- Low regeneration energy demand resulting in low steam consumption
- High net cycle carbon absorption capacity resulting in low solvent circulation flow
- Low solvent degradation and low amine loss resulting in longer service life
- Low corrosivity

2.1   Technology History

Bench-Scale R&D

At Hitachi's Kure Research Laboratory near Hiroshima, Japan, bench-scale studies with simulated flue gas are performed on a small test rig, absorber ID 2 inches, and a larger rig with a 12-inch ID vessel. These test rigs were used to screen over 30 different combinations of amines and additives to identify promising absorbents for maximum CO_2 removal efficiencies while keeping solvent degradation and energy consumption low. Figure 2-1 shows the 2-inch diameter test rig including the absorber, desorber, heat exchangers, and pumps.

Long-Term Pilot Plant Testing

Figure 2-2 shows Hitachi's first CO_2 capture pilot plant built at Yokosuka Thermal Power Plant Unit 2 in cooperation with Tokyo Electric Power Company in 1994, three years before the Kyoto Protocol in 1997. A slipstream of 620 scfm (~ 1 MWth) of flue gas from the combustion of coal – oil mixture was treated for CO_2 removal. During the two-year demonstration period, Hitachi tested several solvent solutions including commercial MEA as a benchmark and three proprietary amine-based solvent formulations, H1, H2, and H3. The best performing solvent, H3, achieved an average CO_2 removal of more than 90 percent in over 2,000 hours of continuous operation. The energy for solvent regeneration was much lower than that required for the commercial MEA. The liquid-to-gas ratio needed for 90-percent capture was significantly lower than that for MEA because of H3 solvent's high absorption capacity.

Figure 2-1 - Bench-Scale Test Rig
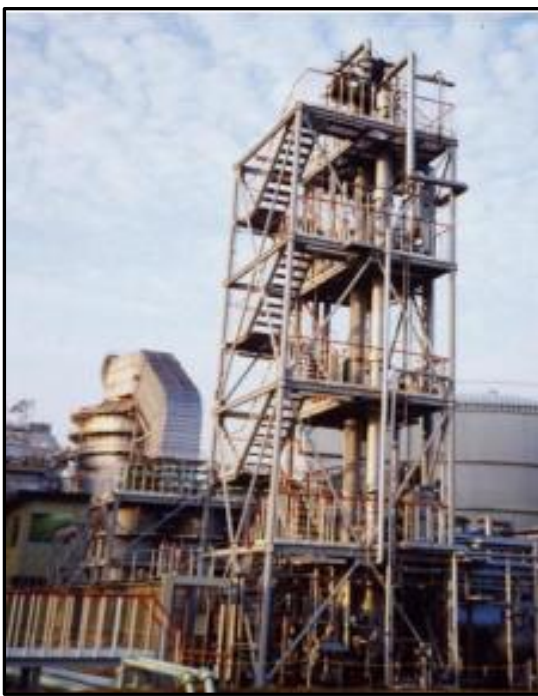
Figure 2-2 - Pilot Plant at Yokosuka Power Plant

Development of the H3-1 solvent

To reduce amine loss and degradation, the H3 solvent formulation was improved and its performance enhanced further[1]. This latest advanced solvent, H3-1, has the same high absorption capacity and low regeneration heat as H3. Figure 2-3 and Figure 2-4 compare solvent performance based on third-party test data, including those by a government research institute in Japan. H3 and H3-1 have the lowest regeneration heat compared to MEA and two advanced amine solutions by other developers (A solv and B solv). H3-1 also has the lowest amine loss, which is 86 percent lower than that of MEA. The reduced level of solvent losses and lower heat requirement of H3-1 translate to significant savings in utility and operating costs.

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[1] Kikkawa, H.; et al. *Hitachi's Carbon Dioxide Scrubbing Technology with New Absorbent for Coal-Fired Power Plants.* Power Plant Air Pollutant Control "MEGA" Symposium, Baltimore, MD. August 30-September 2, 2010
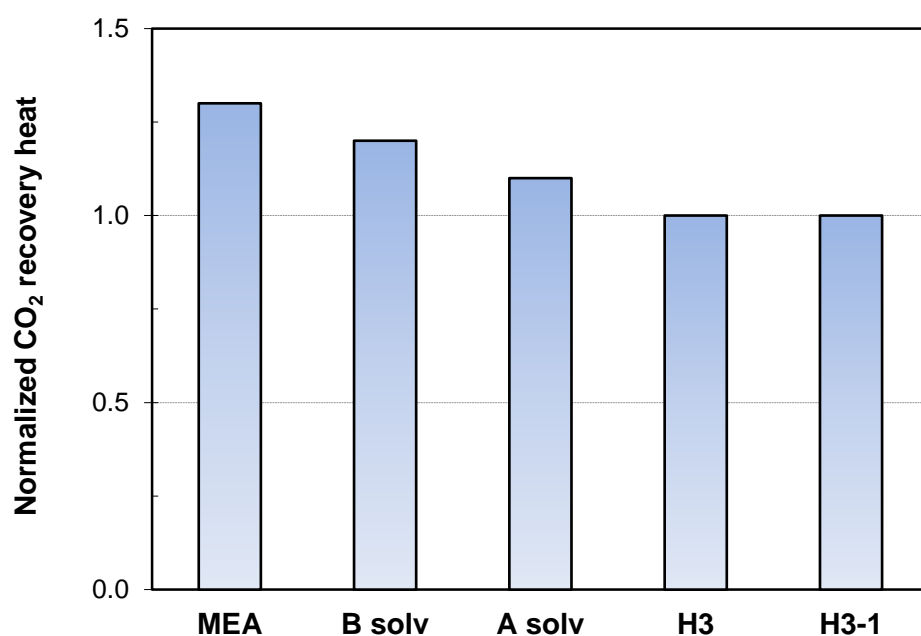
Figure 2-3 - Comparison of CO$_2$ Heats of Regeneration for Different Solvents
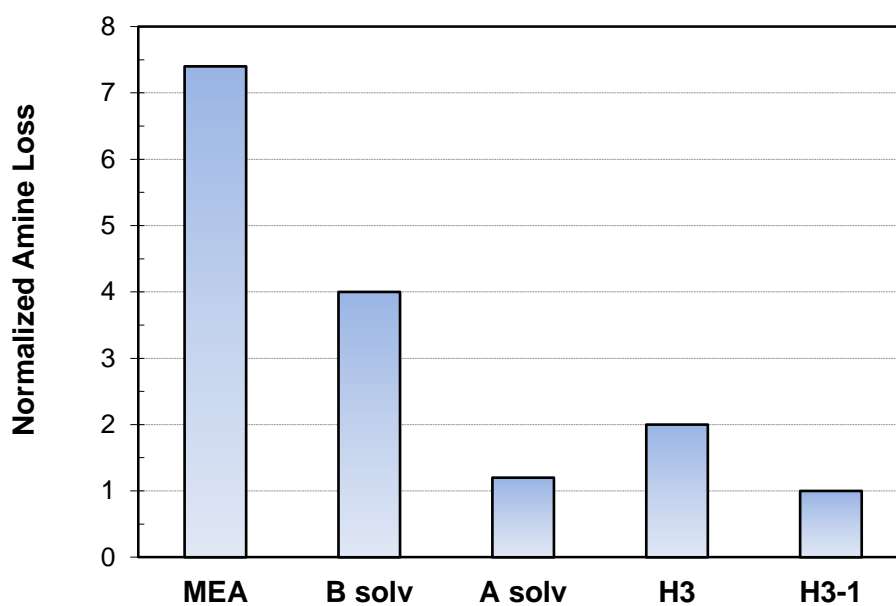
Figure 2-4 - Comparison of Amine Losses for Different Solvents

2.2   Pilot Test at EERC

The H3-1 solvent was tested in early 2010 at the 120 scfm CO_2 capture pilot plant at the Energy and Environmental Research Center (EERC), University of North Dakota[2]. The pilot plant, shown in Figure 2-5, comprises of a pulverized-coal combustion furnace, selective catalytic reduction unit, electrostatic precipitator, wet flue gas desulfurizer, and a CO_2 capture system. This study is a part of the DOE – Industry co-sponsored "Partnership for CO_2 Capture" program in collaboration with 15 private sector partners including utilities, engineering companies and technology providers. Hitachi has been a member of this partnership program since the beginning.

Figure 2-5 - CO$_2$ Capture Pilot Facility at EERC

Figure 2-6 shows the relationship between solvent flow rate and CO_2 removal efficiency for H3-1 and MEA from testing at the EERC. At 90 percent CO_2 capture, the required solvent flow rate for H3-1 was 45 percent lower than that of MEA. Figure 2-7 shows that for the tests at EERC the heat requirement of H3-1 was about 30 percent lower than that for the 30 wt% MEA solution. The durability of H3-1 absorbent was also confirmed by the absence of detectable anions in the used solvent.

2.3   20-MWth Test Facility

In collaboration with SaskPower, a utility company in Saskatchewan, Canada, Hitachi has designed a 20-MWth Carbon Capture Test Facility at SaskPower's coal-fired Shand Power Station. The test facility is currently being installed and testing of the H3-1 solvent is scheduled to begin in 2014. The demonstration unit will treat approximately 13,500 scfm of slipstream flue gas from the power plant.

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[2] Pavlish, B. *Partnership for CO$_2$ Capture: Results of the Pilot-Scale Solvent Evaluations*. 2010 NETL CO$_2$ Capture Technology Meeting, Pittsburgh, PA. September 13–17, 2010
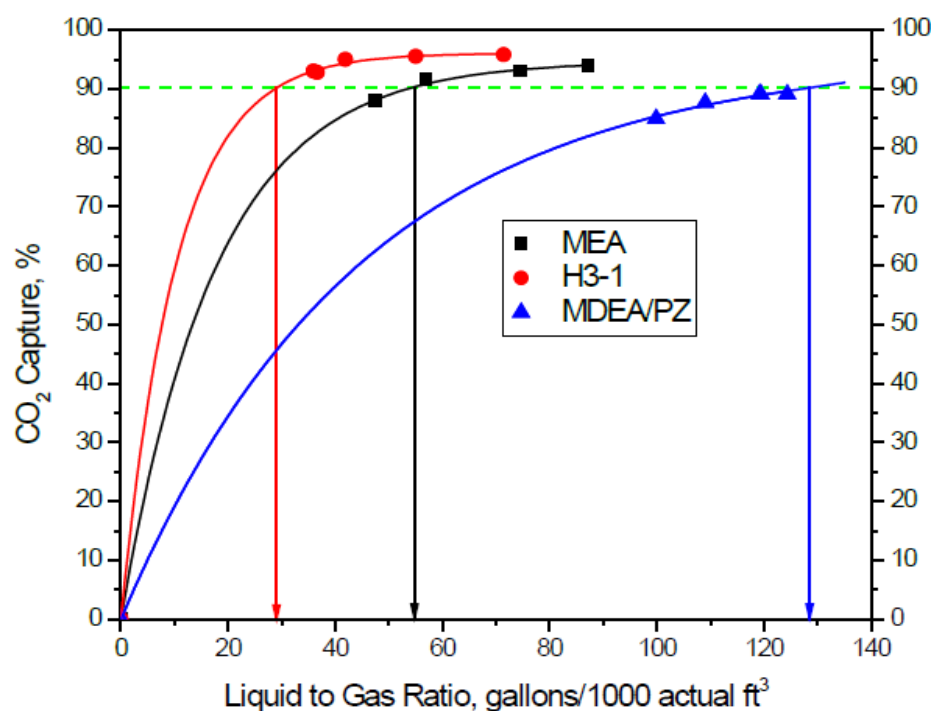
Figure 2-6 - Comparison of the Effect of L/G of Various Solvents
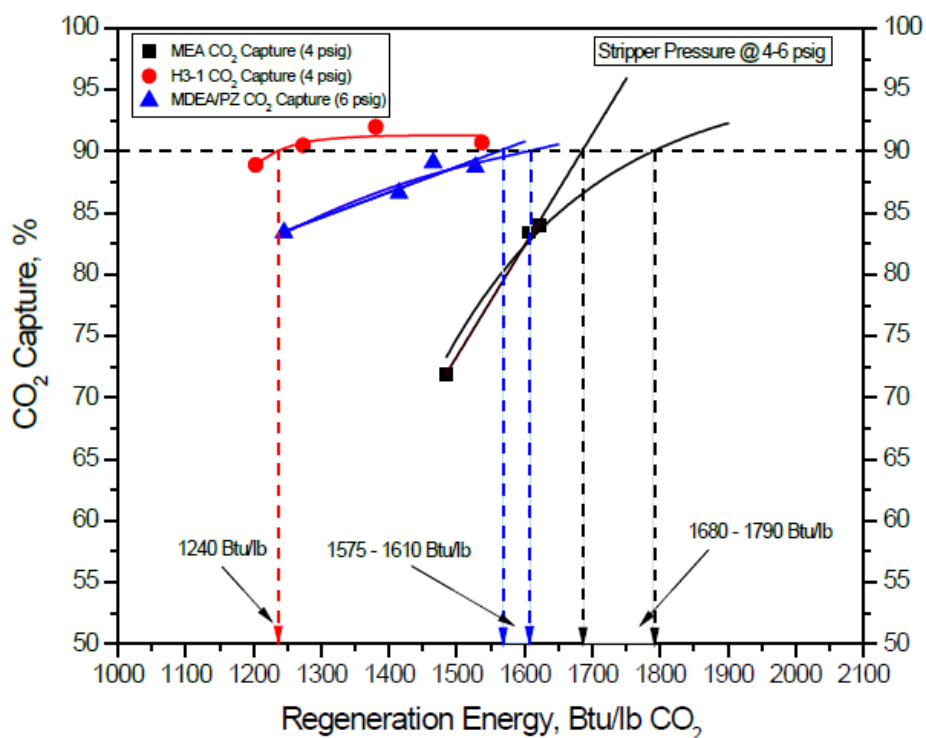
Figure 2-7 - Comparison of Regeneration Energy of Various Solvents

3.0 DESCRIPTION OF THE PILOT SOLVENT TEST UNIT

Figure 3-1 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 3-1 is a photograph of the PSTU.
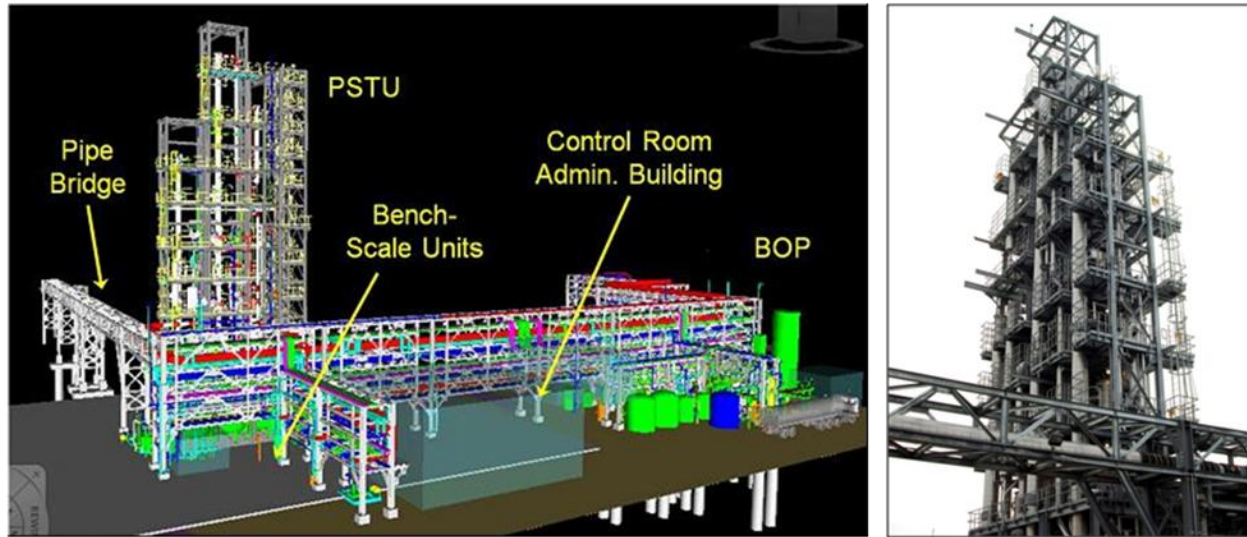
Figure 3-1 - Views of the PSTU

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.
- 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 3-2. Up to 35,000 lb/hr of flue gas is extracted from downstream of the power plant FGD for PC4 testing. Of this amount, 5,000 lb/hr is used in the PSTU. There are five major PSTU sub-systems (shown in green in Figure 3-2), and their functions will be discussed individually. Table 3-1 lists the dimensions of each of the columns and the type of packing currently being used.
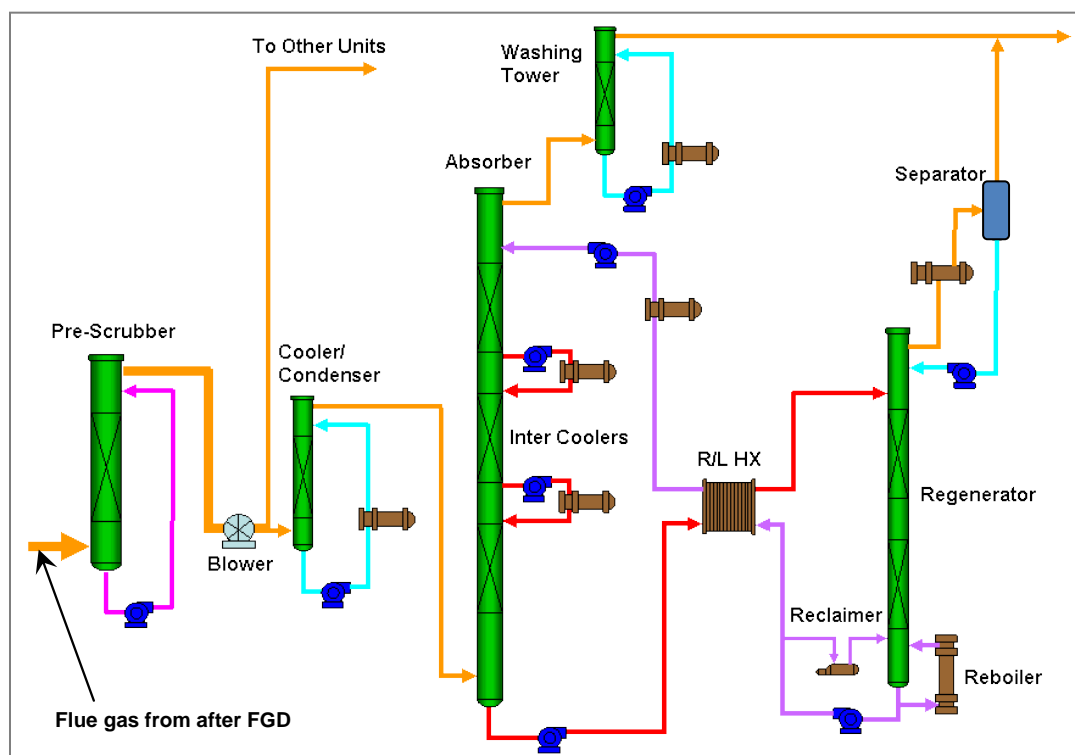
Figure 3-2 - Schematic of PSTU

Table 3-1 - Dimensions and Packing Used in PSTU Columns

Column	Height, ft	Outer Diameter, inches	Number of Beds	Packing Type
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

Pre-Scrubber

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 to the PC4 balance-of-plant (BOP) 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.

Cooler/Condenser

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.

Intermittently a small stream (about 4 percent) of the hot-lean solvent is 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 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 location are presented in Table 3-2. 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 3-2 - 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_2	Ultra violet
Wash Tower Outlet	
Oxygen	Paramagnetic
CO_2	NDIR
Moisture	Calculated
NO_X/NO_2	Ultra violet
Regenerator Outlet	
Moisture	Calculated
CO_2	By difference

The NOx/NO_2 meters were installed at Hitachi's request prior to testing their solvent. NO_2 could react with amines to form nitrosamines, and the additional information was required to assist data evaluation. 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 approximately 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 first diluted with pH-adjusted methanol and then titrated with potassium hydroxide to determine the CO_2 loading 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, making 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, and possibly some CO_2 was being released at the higher temperature 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.

4.0 HITACHI TEST CAMPAIGN

4.1   Test Plan and Test Conditions

The test campaign with Hitachi's H3-1 solvent at the NCCC began on April 24, 2012, and ended on July 16, 2012, achieving about 1,400 hours of testing. During this period, parametric tests with a wide range of conditions were conducted. The parameters tested were flow rate and temperature of inlet flue gas and solvent, reboiler steam flow rate, pressure in the regenerator, temperature at the outlet of the wash tower, the effect of the intercoolers, and the effect of the number of packing beds in the absorber. Table 4-1 presents the range of operating conditions covered during testing.

Table 4-1 - Operating Parameters for Hitachi Solvent Testing

Operating Parameter	Range
Absorber Flue Gas Flow Rate (G), lb/hr	4,000 to 6,000
Solvent Flow Rate (L), lb/hr	7,000 to 17,000
Reboiler Steam Flow Rate, lb/hr	700 to 1,100
Absorber Inlet Flue Gas Temperature, °F	96 to 122
Absorber Inlet Solvent Temperature, °F	96 to 114
Wash Tower Exit Temperature, °F	107 to 123
Regenerator Pressure, psig	3 to 22
Inlet Flue Gas CO_2 Content, vol%	11 to 13
Number of Absorber Beds	1, 2, and 3
Intercoolers	On and Off

Screenshots from the Distributed Control System (DCS) showing typical process conditions of the overall system, absorber, wash tower, and regenerator are shown in Figure 4-1, Figure 4-2, Figure 4-3, and Figure 4-4, respectively.
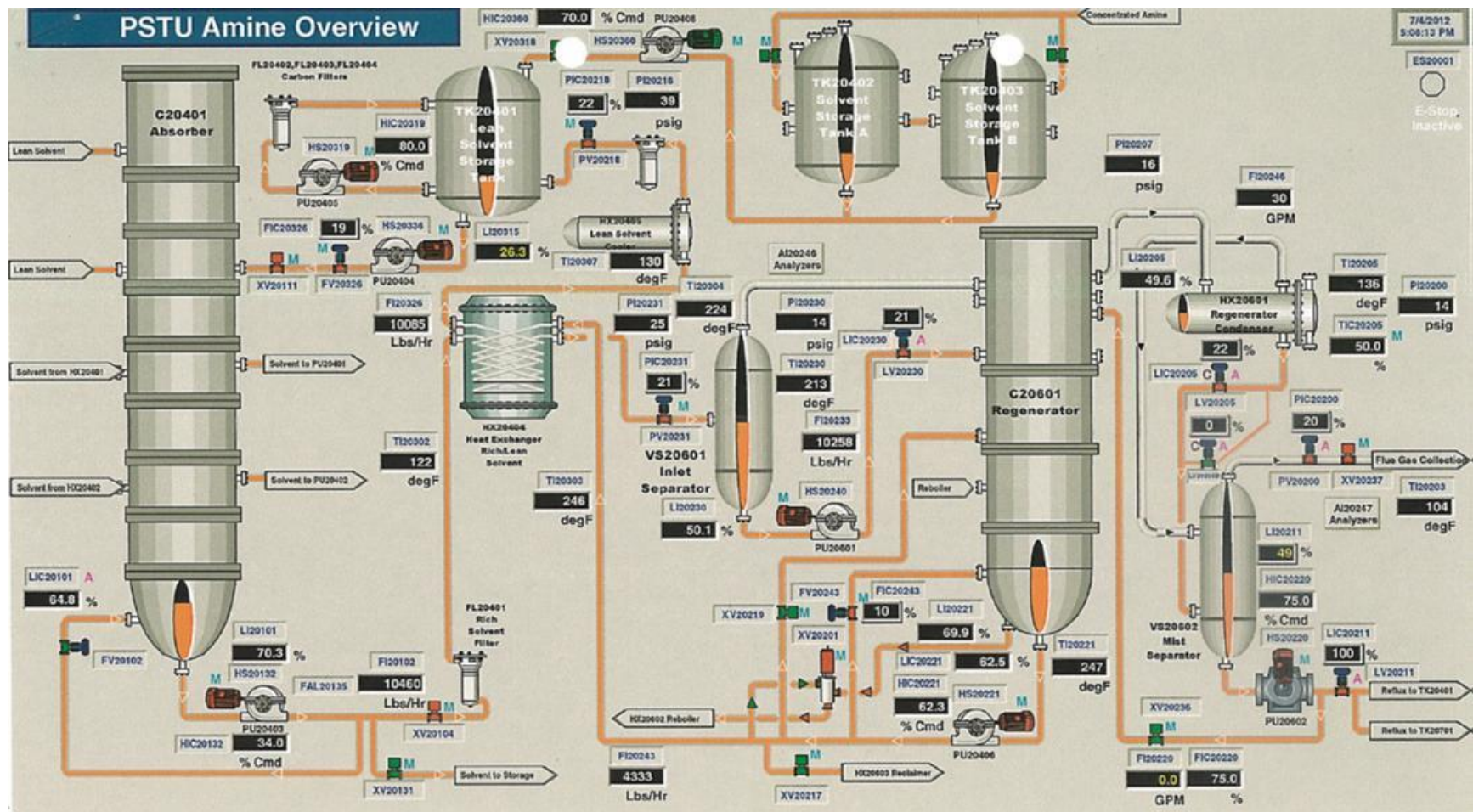
Figure 4-1- Typical PSTU Operating Conditions
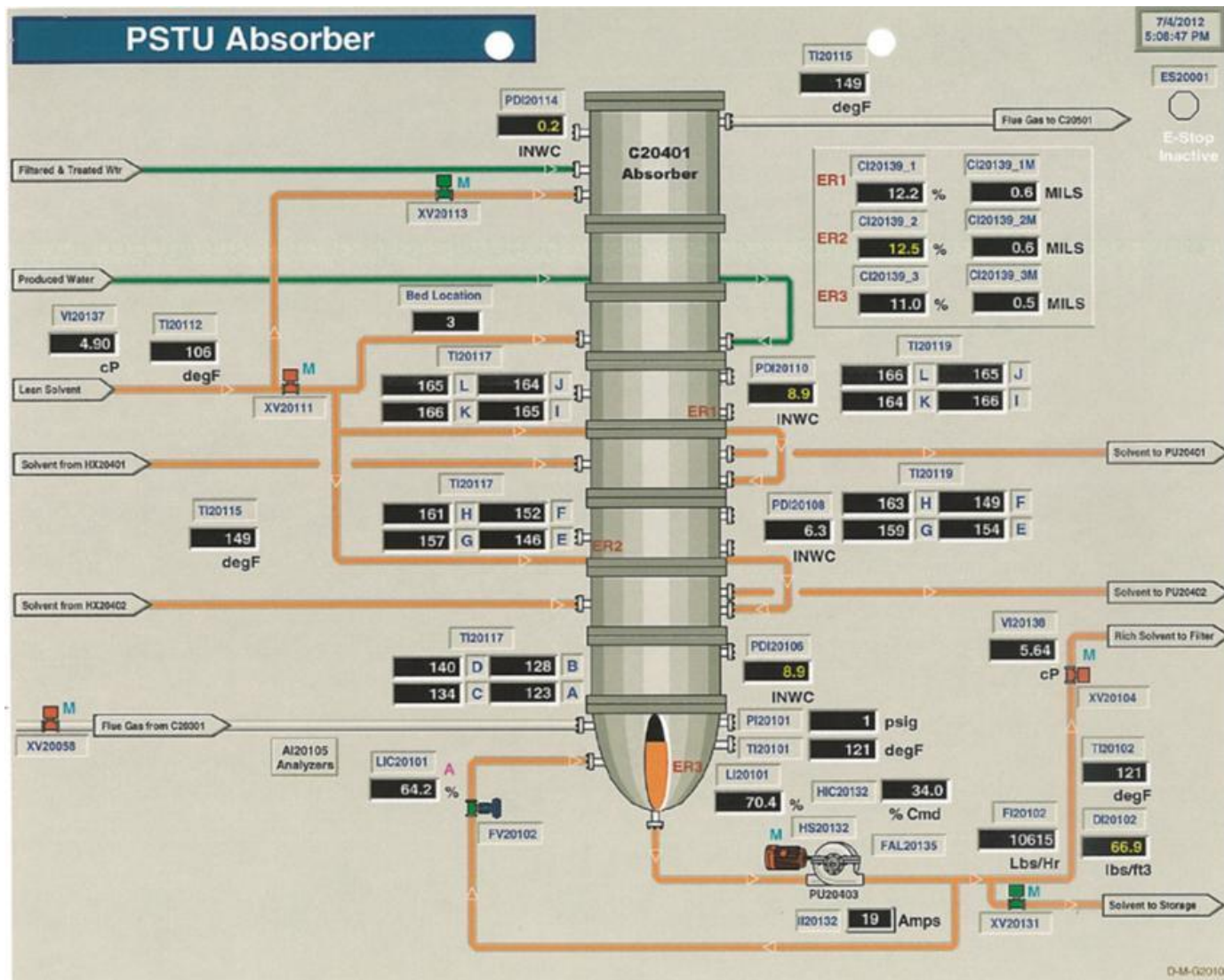
Figure 4-2 - Typical Absorber Process Conditions

Figure 4-3 - Typical Wash Tower Process Conditions

Figure 4-4 - Typical Regenerator Process Conditions

4.2   CO$_2$ Capture Performance

Figure 4-5 shows the CO$_2$ capture performance of the H3-1 solvent during the test campaign averaging around 91 percent over a range of boiler loads, flue gas compositions, and test conditions. The low values of CO$_2$ removal marked by 'A' in Figure 4-5 were completed to extend the range of data collected and include parametric tests carried out to generate trend data over a wide range of test conditions rather than to achieve high CO$_2$ removal.
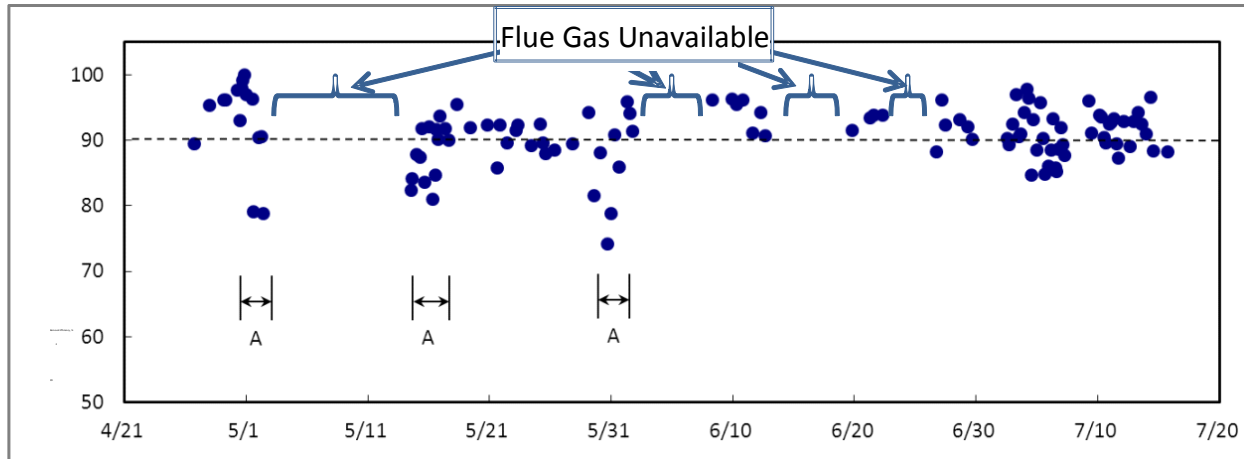
Figure 4-5 - Overall CO$_2$ Capture Performance

Figure 4-6 plots the concentrations of CO$_2$ and O$_2$, which varied with boiler load between 11 and 13 vol% on a dry basis and between 5.5 and 8 vol% on a wet basis, respectively.
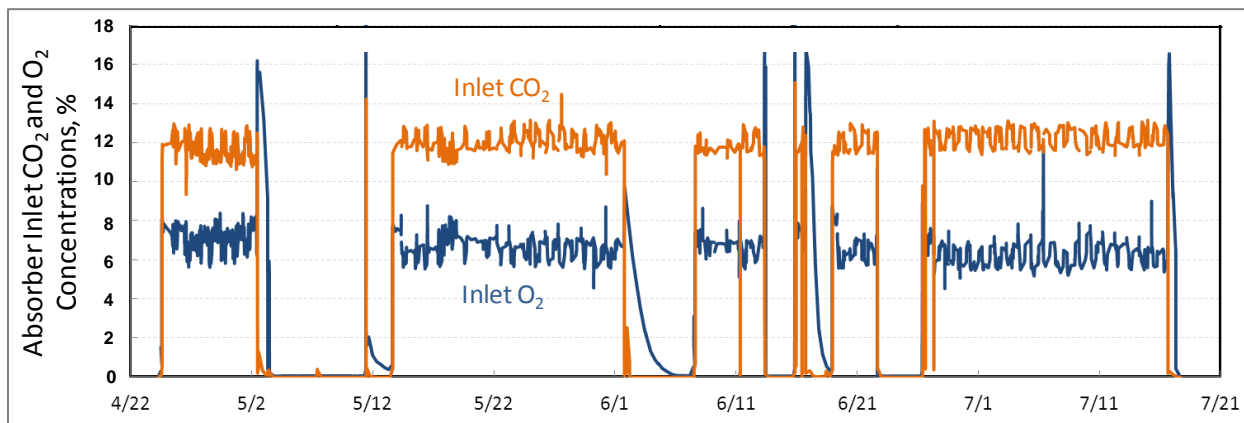
Figure 4-6 - CO$_2$ and O$_2$ Concentration at Absorber Inlet

The concentrations of SO$_2$ and NO/NO$_2$ in flue gas entering the absorber are shown in Figure 4-7 and Figure 4-8, respectively. SO$_2$ can cause solvent degradation and NO$_2$ could react with the amine solvent to form secondary products. The concentration of caustic in the pre-scrubber was adjusted regularly to maintain an SO$_2$ concentration of 1 ppmv or lower in the flue gas entering the absorber. During early testing, inlet NO varied between 20 and 50 ppmv, and NO$_2$ between 5 and 7 ppmv. Towards the end of the test campaign, inlet NO increased to about 100 ppmv and inlet SO$_2$ to between 2 and 3 ppmv.
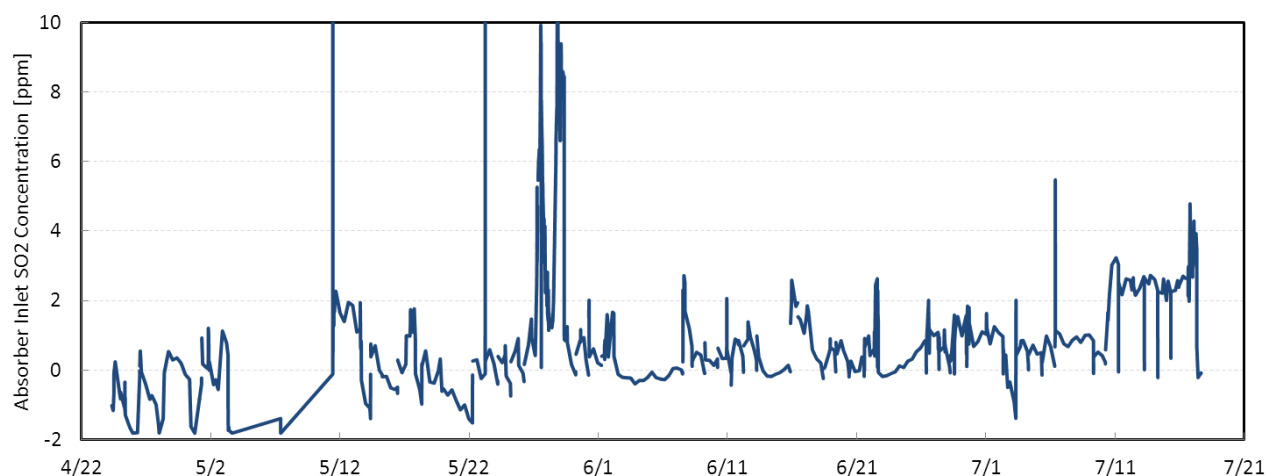
Figure 4-7 - SO$_2$ Concentration at Absorber Inlet
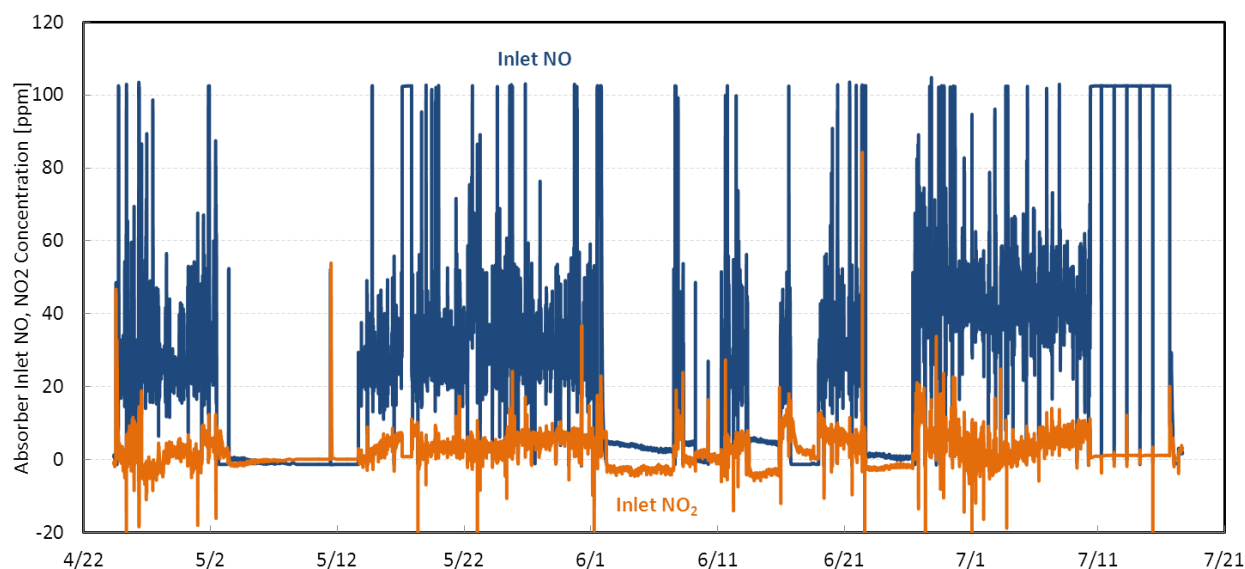
Figure 4-8 - NO and NO$_2$ Concentration at Absorber Inlet

During testing, the power plant load varied between 900 MW and about 700 MW during the day and typically remained at 700 MW at night in response to power demand. As inlet CO$_2$ concentration varied with boiler load, it was challenging to collect data at stable conditions for extended periods at a particular boiler load.

4.3   Absorber Pressure Drop

During the first week of testing, baseline tests were conducted to verify the range of operability and to check if flooding could occur within the absorber. The maximum superficial velocity of flue gas tested was 6 ft/sec. Figure 4-9 shows the effect of absorber pressure drop at different superficial velocities. Pressure drop did not increase rapidly with increasing gas flow rate, and within this test range, flooding in the absorber was not observed.
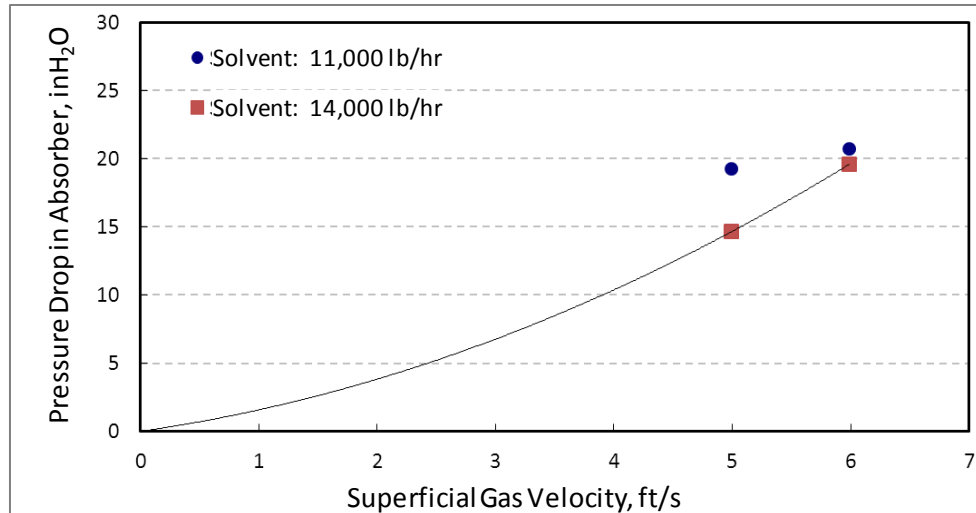
Figure 4-9 - Variation of Absorber Pressure Drop with Gas Flow Rate

4.4 Solvent Circulation Rate and Regeneration Energy

CO_2 removal efficiency for a particular solvent circulation rate varies with the absorber inlet CO_2 concentration, which depends on the plant boiler load. During the test campaign, the inlet CO_2 concentration was typically below 12 vol% at 700 MW, the low load level, and above 12 vol% at the full boiler load of 900 MW. Figure 4-10 shows the effect of solvent flow rate on CO_2 capture performance at low load conditions. As the solvent circulation rate increased to 7,000 lb/hr, the CO_2 removal efficiency increased to a maximum value of about 96 percent. As solvent flow rate increased further, CO_2 capture efficiency began to decrease.
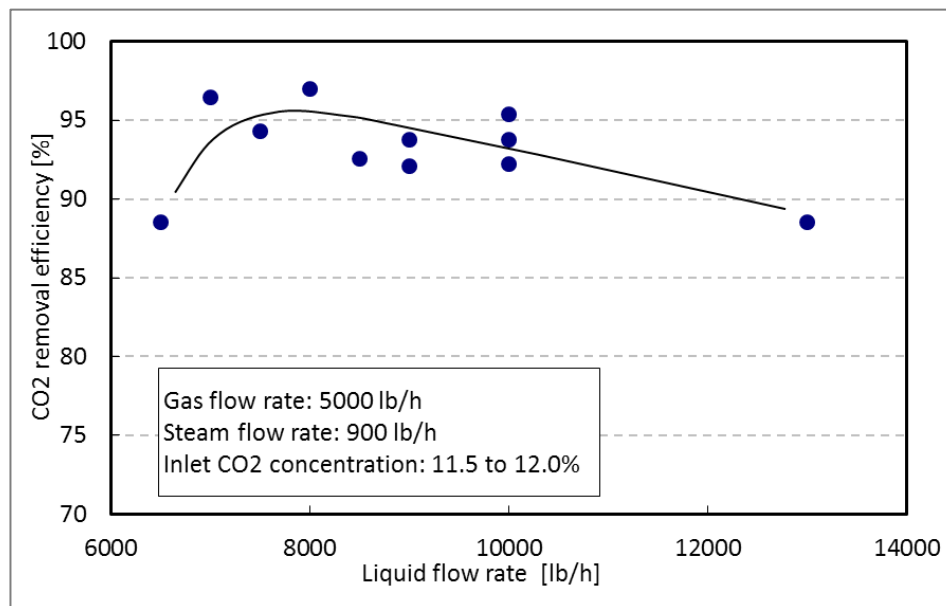
Figure 4-10 - Variation of CO$_2$ Removal Efficiency with Solvent Flow Rate at Low Boiler Load

This observation is explained by the trends in CO_2 loading for the rich and lean solvent shown in Figure 4-11. At lower solvent flows, the difference in CO_2 loading between the rich and lean solvent was large, enabling high CO_2 removal efficiencies. As the solvent flow rate increased, the lean loading also increased because the heat provided to release the CO_2 from the rich solvent was insufficient (the reboiler steam flow was held constant during these tests). At the same time, the rich loading decreased due to increasing liquid flow in the absorber. The net CO_2 loading (rich minus lean loading) at high solvent circulation rates decreased significantly, thereby reducing CO_2 removal efficiency.
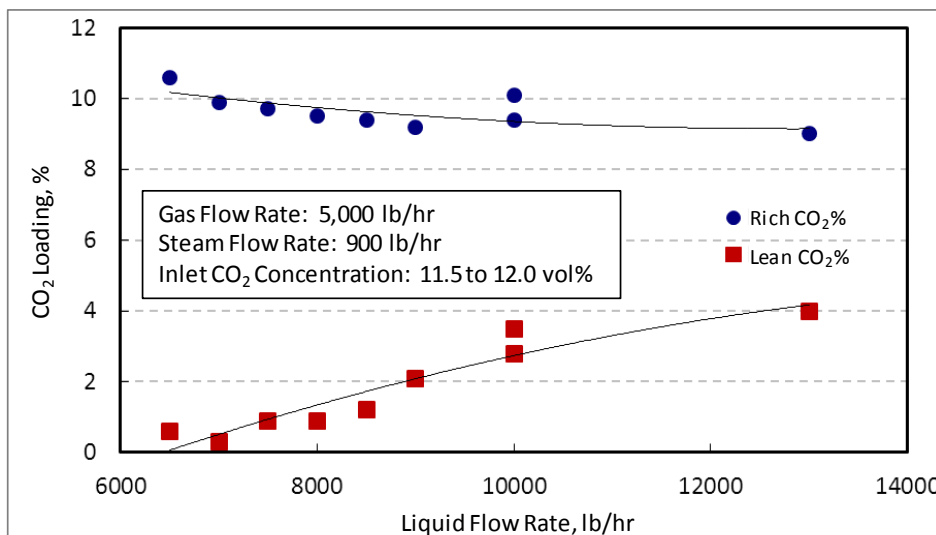
Figure 4-11 - Variation of CO_2 Loading Effect with Solvent Flow Rate at Low Boiler Load

Regeneration energy is the amount of energy required, which is the reboiler duty, to release a given amount of CO_2. As reboiler steam flow was constant and the amount of CO_2 captured decreased at solvent flow rates greater than the optimal value of 7,000 lb/hr, the regeneration energy increased correspondingly, as shown in Figure 4-12. At the optimal flow rate of H3-1 solvent the CO_2 capture was its maximum, about 96 percent, and the regeneration energy was at its minimum value of approximately 2.4 GJ/tonne of CO_2 or 1,030 Btu/lb of CO_2.
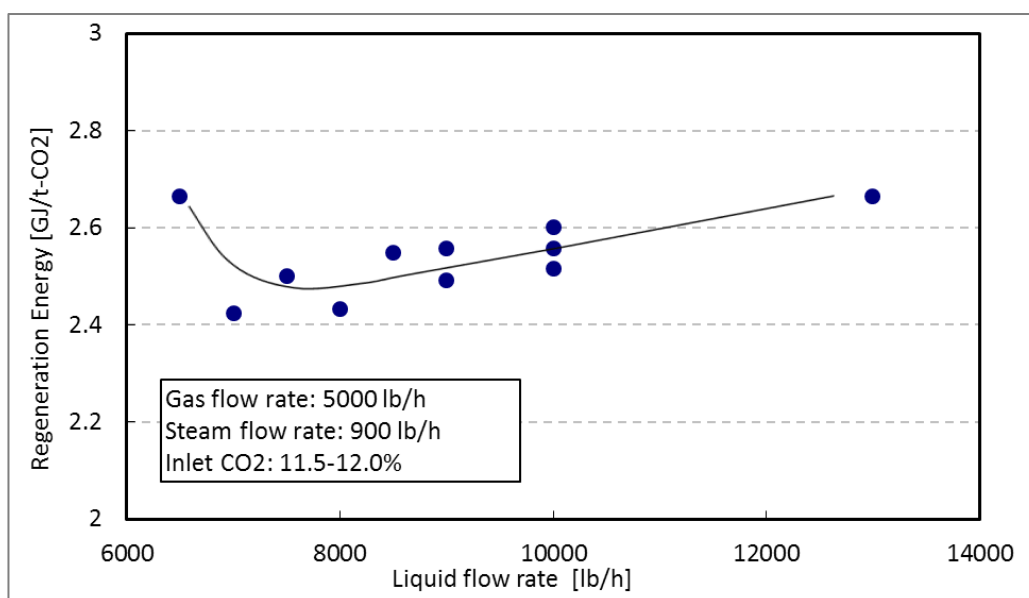
Figure 4-12 - Variation of Regeneration Energy with Solvent Flow Rate at Low Boiler Load

Figure 4-13 shows the effect of solvent flow rate on CO_2 capture performance at full-load conditions. Showing a similar trend to the partial load case, the amount of CO_2 captured increased with solvent flow rate up to an optimal value of about 10,000 lb/hr, beyond which capture efficiency decreased. The trends for the rich and lean loadings for the full-load case are shown in Figure 4-14.
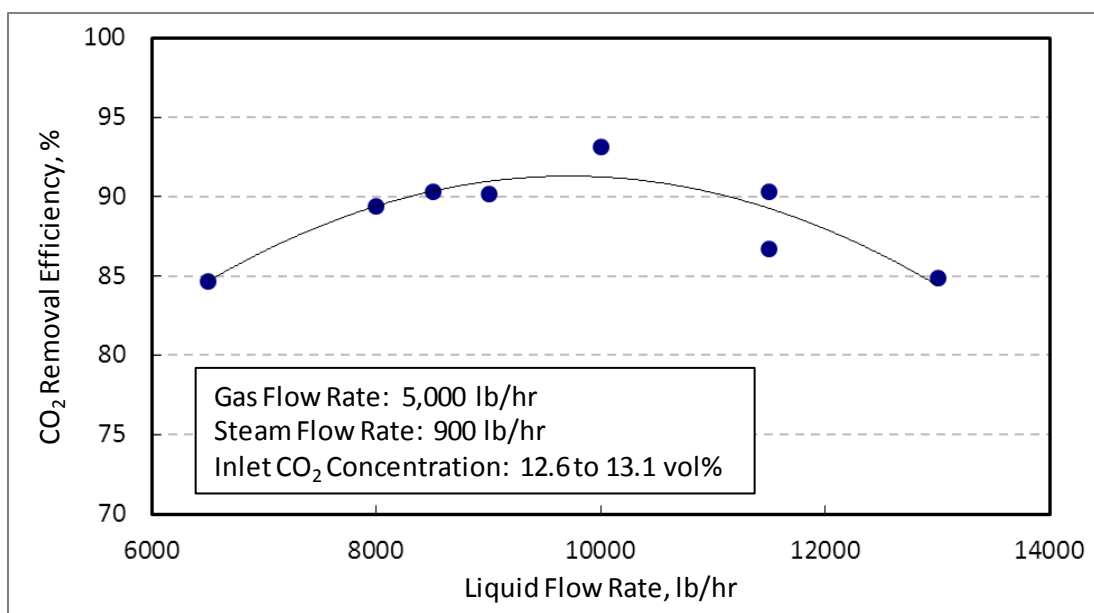
Figure 4-13 - Variation of CO₂ Removal Efficiency with Solvent Flow Rate at Full Boiler Load
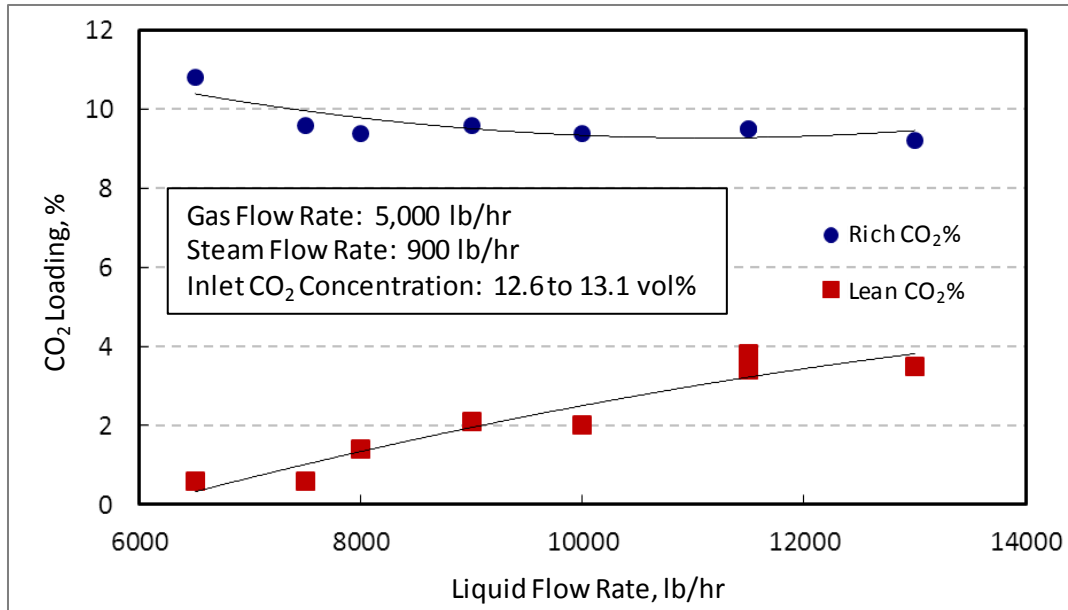
Figure 4-14 - Variation of CO₂ Loading with Solvent Flow Rate at Full Boiler Load

As shown in Figure 4-15, at a solvent flow rate of 10,000 lb/hr, the regeneration energy is lowest. Based on the test data and trend curve, the minimum value of regeneration energy at full load conditions is approximately 2.4 GJ/tonne of CO_2 or 1,030 Btu/lb of CO_2, similar to that observed at partial load conditions.
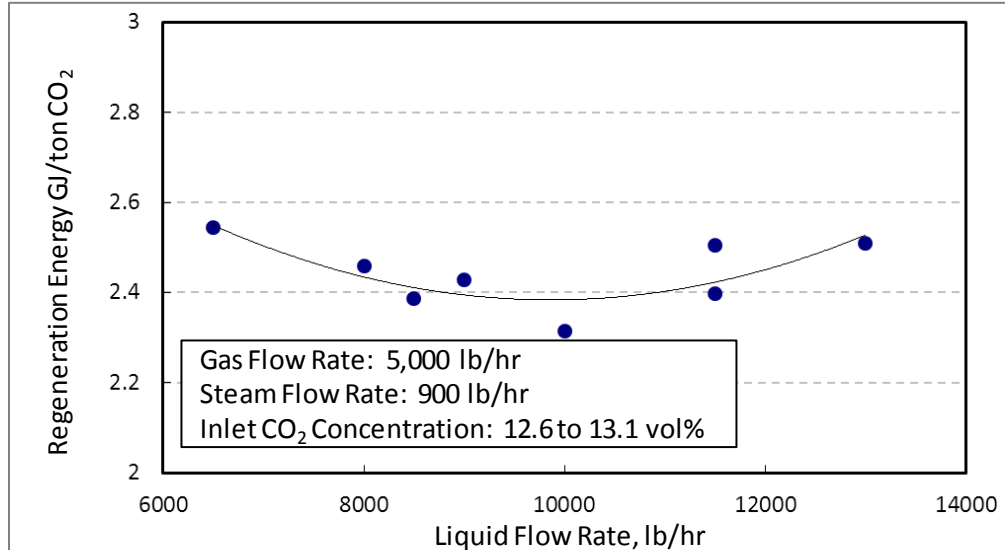
Figure 4-15 - Variation of Regeneration Energy with Solvent Flow Rate at Full Boiler Load

4.5   CO₂ Mass Balance

CO_2 mass balance was checked by comparing CO_2 removed from the flue gas with CO_2 produced at the regenerator. CO_2 released from the regenerator was measured at the outlet of the mist separator. Figure 4-16 shows that over the duration of testing, the CO_2 concentration in the gas

phase between the absorber and regenerator correlate reasonably well. Due to the relative lack of consistency of CO_2 concentration in the liquid side and the reliable measurements in the gas-phase, regeneration energy for the H3-1 testing was determined using the gas-phase CO_2 concentrations.
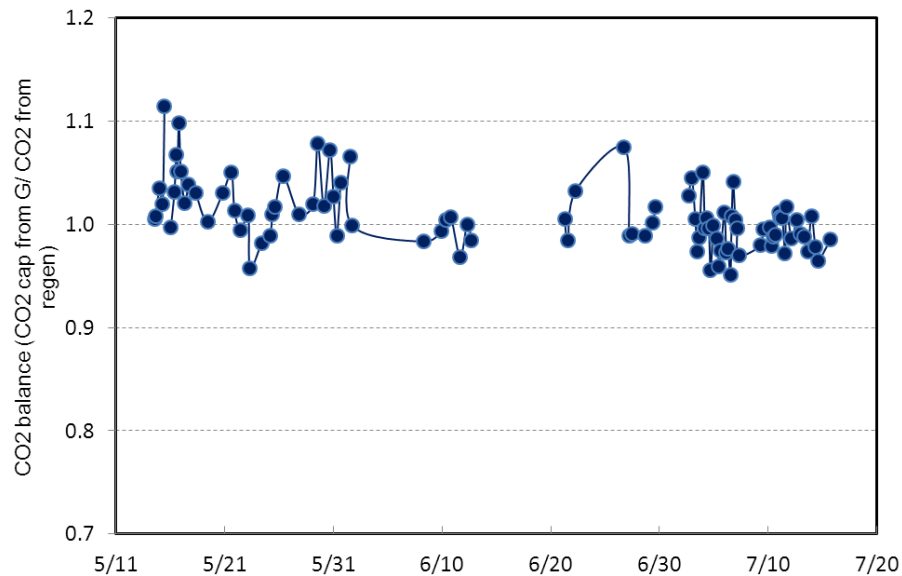
Figure 4-16 - CO$_2$ Balance on the Gas-side

4.6   Reboiler Steam Flow Rate

Figure 4-17 shows results from testing the influence of steam flow rate on CO_2 removal efficiency. The inlet flue gas flow and solvent circulation rates were kept constant at 5,000 lb/hr and 10,000 lb/hr, respectively. Generally, the CO_2 removal efficiency increases with the reboiler steam flow rate. At the partial load condition when the inlet CO_2 concentration was low, the CO_2 removal efficiency was higher than that of the full load condition.
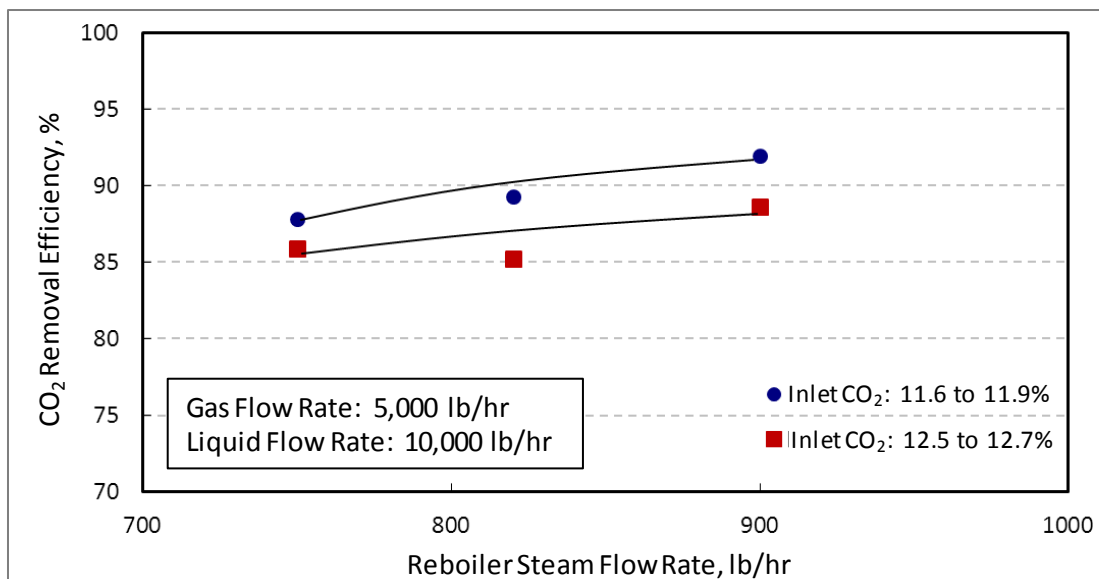
Figure 4-17 - Variation of CO$_2$ Removal Efficiency with Reboiler Steam Flow Rate

Figure 4-18 plots the rich and lean loading of the solvent for the tests shown in Figure 4-17. CO_2 loading in the rich solvent was not affected by reboiler steam flow rate, but the lean solvent loading decreased slightly with increasing steam flow rate. Leaner solvent in the absorber and correspondingly, higher net working capacity, resulted in higher CO_2 removal efficiency at a steam flow rate of 900 lb/hr.
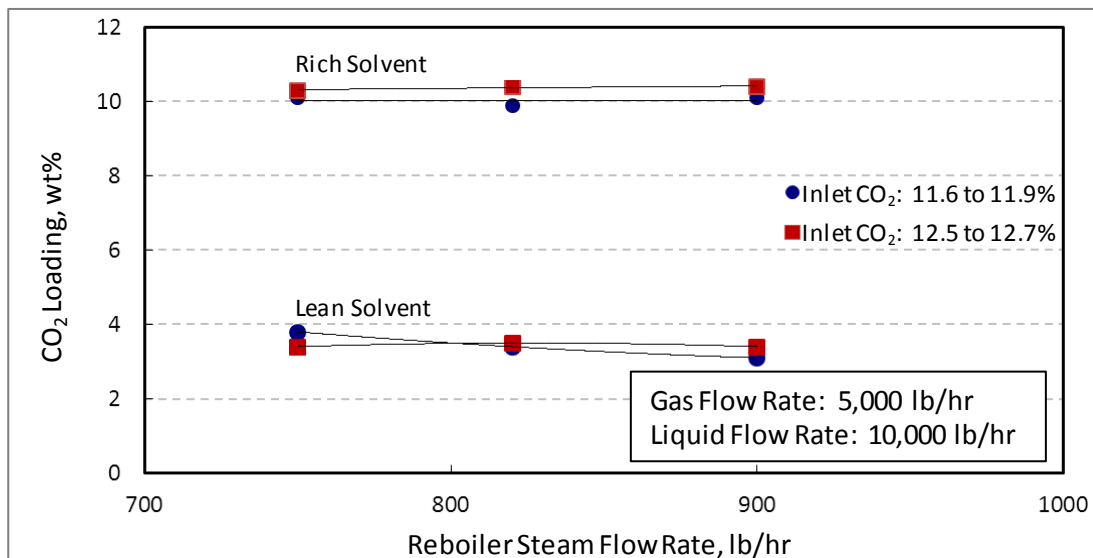
Figure 4-18 - Variation of CO_2 Loading with Reboiler Steam Flow Rate

4.7 Temperature of Flue Gas and Solvent at Absorber Inlet

The effect of temperature of the lean solvent and flue gas at the absorber inlet were verified during the parametric tests. Inlet solvent temperature was controlled using the lean solvent cooler located upstream of the lean solvent storage tank. From the lean solvent storage tank, solvent is fed to the absorber. A wide range of temperatures was tested, but the lower end of the range was limited by the cooling water temperature, which could not be reduced below 96°F (even during night) due to warm ambient conditions. Figure 4-19 shows the CO_2 removal efficiencies for the tests performed by changing the absorber inlet temperature of the solvent, at both partial load and full load conditions. The effect of inlet solvent temperature on CO_2 removal efficiency was small for the tested range.

Inlet flue gas temperature was maintained by controlling the cooling water flow to the cooler/condenser located upstream of the absorber. As shown in Figure 4-20, CO_2 removal efficiency decreased slightly with increasing temperature at temperatures below 104°F. As the temperature of the inlet gas increased beyond this value, there was no appreciable effect on the CO_2 removal efficiency. The impact of flue gas temperature at the absorber inlet on CO_2 capture was small for the range tested.
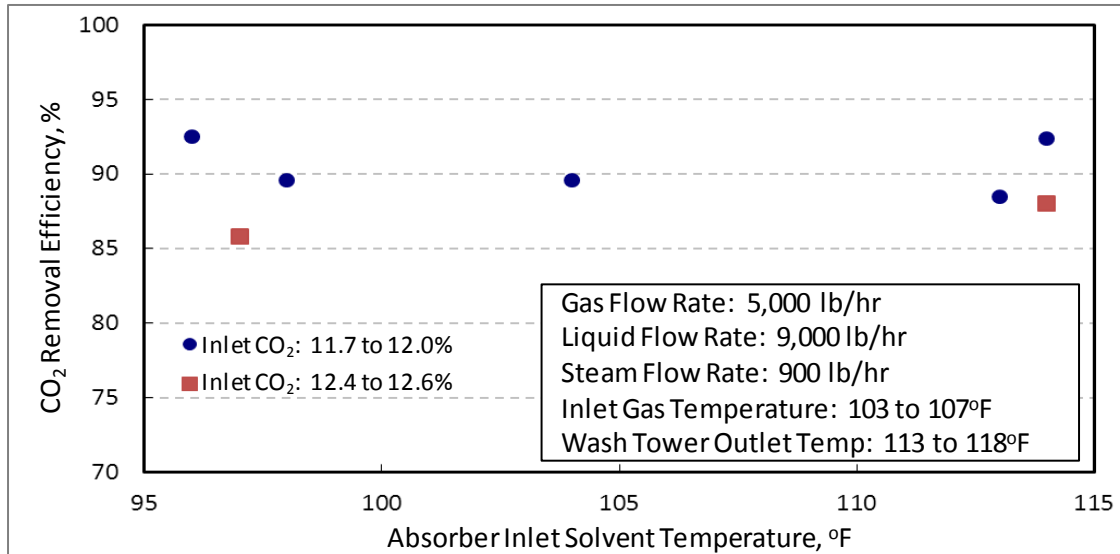
Figure 4-19 - Variation of CO$_2$ Removal Efficiency with Absorber Inlet Solvent Temperature
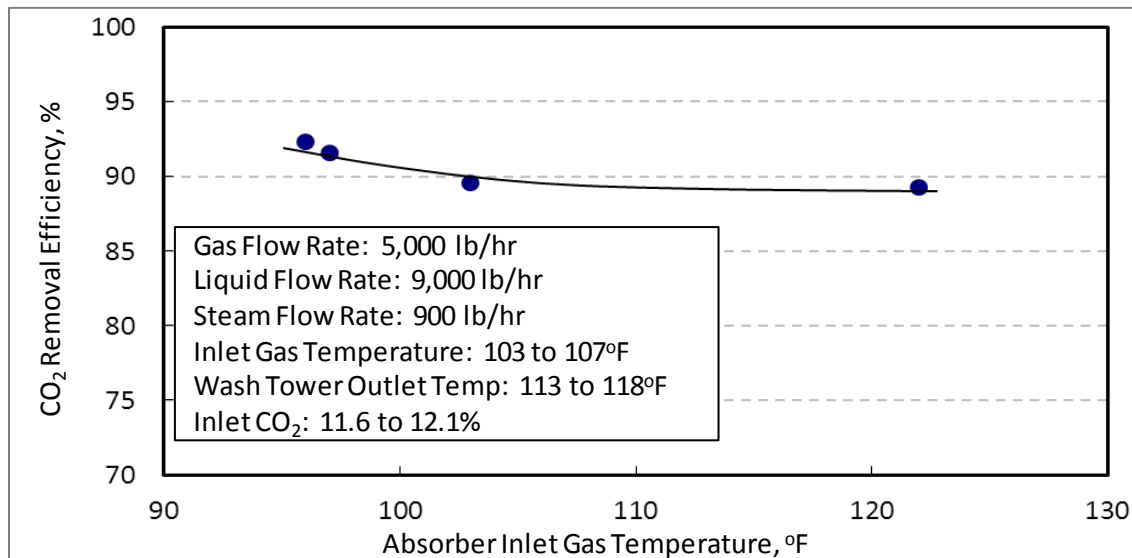
Figure 4-20 - Variation of CO$_2$ Removal Efficiency with Absorber Inlet Flue Gas Temperature

4.8   Number of Absorber Beds

The PSTU absorber contains three stages of packed beds with structured packing. The effect of the number of absorber beds was investigated during the H3-1 testing, and the results are given in Figure 4-21. During one-bed operation, the bottom bed was in service, and during two-bed operation, the bottom two beds were in service. As expected, with an increasing number of packed beds, greater CO$_2$ removal efficiency was achieved. At the operating test conditions with only two packing stages in service, close to 90 percent of the CO$_2$ was captured. With all three packing stages in operation, CO$_2$ removal efficiency increased further but with a smaller increment.
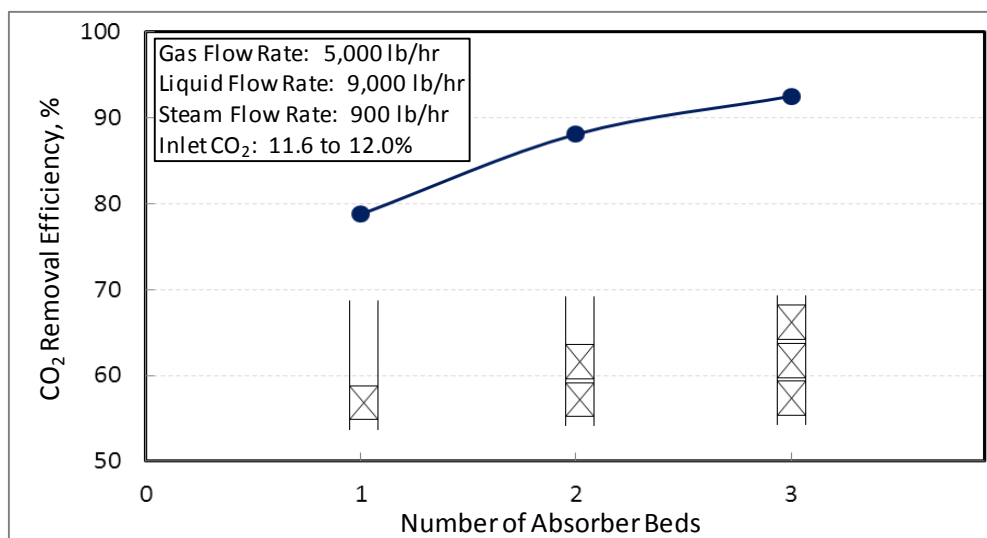
Figure 4-21 - Variation of CO$_2$ Removal Efficiency with Number of Absorber Beds in Service

4.9   Intercoolers

CO$_2$ absorption in amine is an exothermic reaction, resulting in increased temperature along the flue gas path. Therefore, the influence of solvent cooling in the absorber on the CO$_2$ capture efficiency was examined by operating with the intercoolers. The absorber includes two intercoolers located between the three packed beds. Both intercoolers were used when the intercooler was in service, and the entire solvent flow was routed through each intercooler before being re-distributed over the next packed bed in the absorber. Figure 4-22 shows the results of the tests with and without the intercoolers in service. For these tests, flue gas flow rate was 5000 lb/hr, solvent circulation rate was 9,000 lb/hr, and the reboiler steam flow rate was 900 lb/hr. Without the use of intercoolers, about 90 percent CO$_2$ removal was achieved. With the intercoolers in service, a 6 percentage-point improvement in the CO$_2$ removal efficiency was achieved at the same test conditions. This is because at low temperatures, the CO$_2$ carrying capacity of the solvent is greater than at higher temperatures.
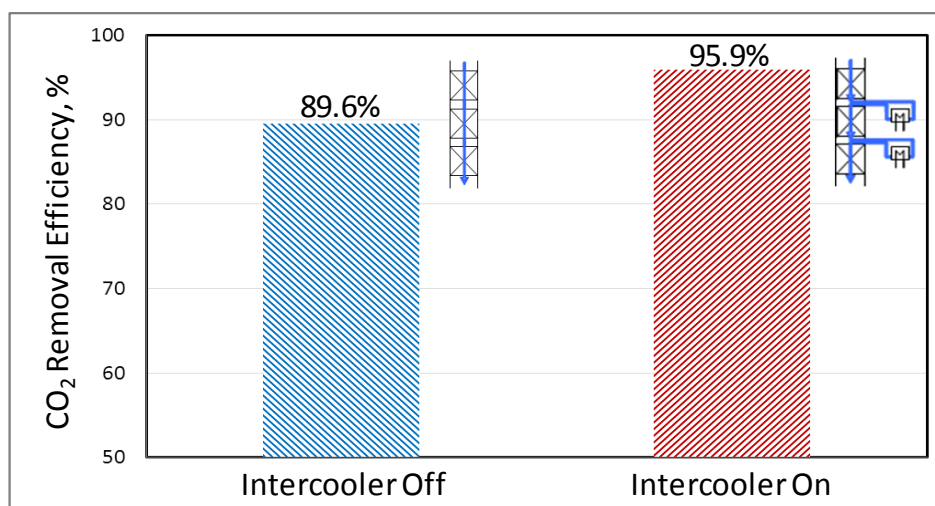
Figure 4-22 - Effect of Intercoolers on CO$_2$ Removal Efficiency

Figure 4-23 provides the temperature profiles along the height of the absorber for the two tests with and without intercoolers. With the intercooler in service, the absorber internal temperature was lower by 10 to 20°F within the packing stages. By lowering the temperature within the absorber, the amount of CO_2 absorbed can be increased without changing the solvent circulation rate or reboiler duty.
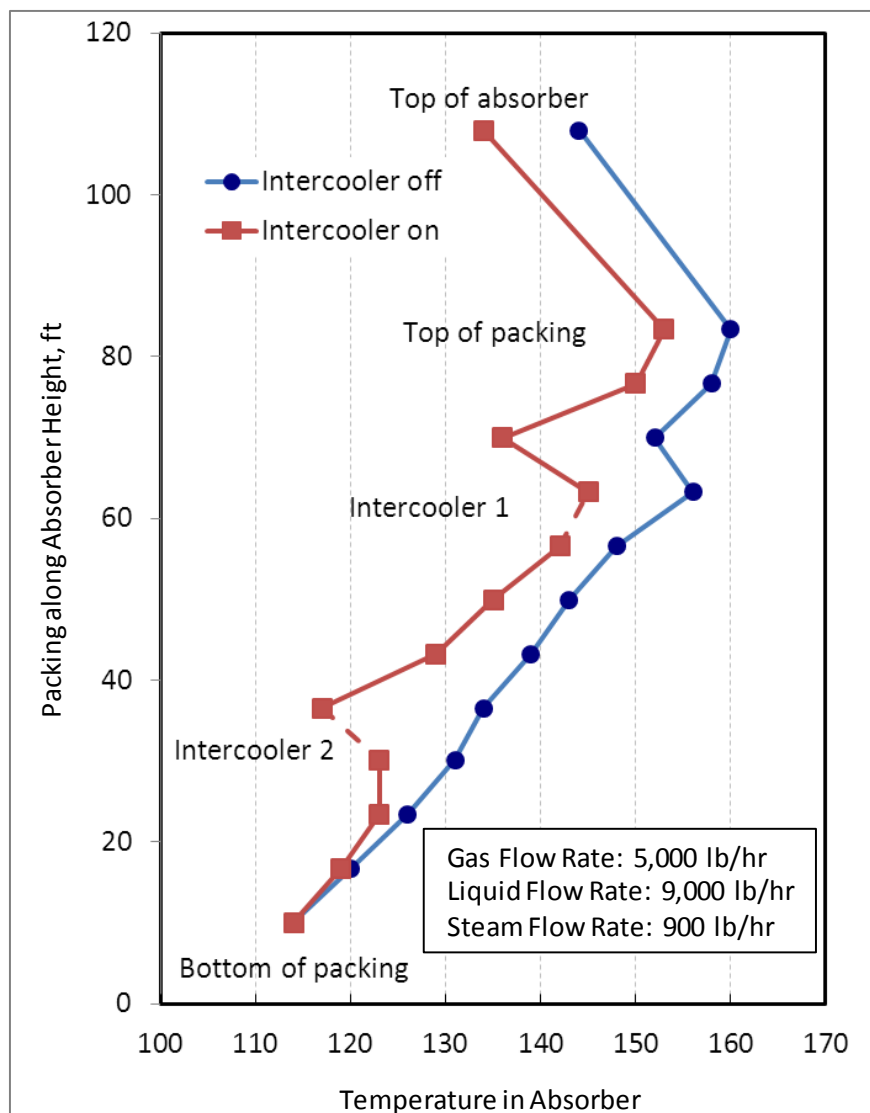
Figure 4-23 - Absorber Temperature Profile With and Without Intercoolers in Service

4.10   Comparison of H3-1 Performance with MEA

The performance of H3-1 was compared with results for MEA tested at the NCCC under similar operating conditions. All three absorber beds were in service, but intercoolers were not used. Figure 4-24 shows a comparison of the liquid-gas ratio for both solvents to achieve greater than 90 percent CO_2 capture. Compared to 30 wt% MEA, the solvent flow rate for H3-1 is about 37 percent lower. For a new CO_2 capture system, this would translate to savings in capital cost since smaller equipment (heat exchangers, pumps, etc.) would be sufficient to achieve high

removal efficiencies, and in operating cost since a smaller amount of solvent would be pumped through the process loop.
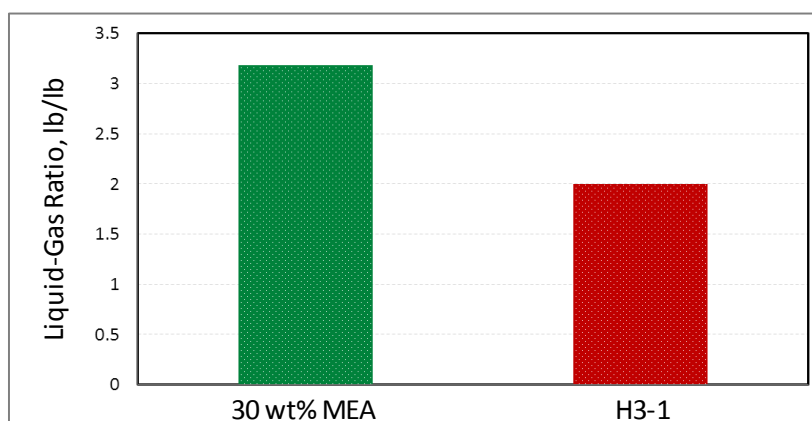
Figure 4-24 - Liquid-Gas Ratio of MEA Compared with H3-1

Data for 30 wt% MEA and H3-1 is summarized in Table 4-2, and regeneration energy for the two solvents is shown in Figure 4-25. At 2.4 GJ/tonne CO_2 or 1,030 Btu/lb CO_2, the regeneration energy required for H3-1 is about 34 percent lower than that for MEA.

Table 4-2 - Comparison of H3-1 Performance with MEA

Solvent	Liquid-Gas Ratio, lb/lb	CO_2 Removal Efficiency, %	Inlet CO_2 Conc'n, %	Regeneration Energy, GJ/tonne CO_2
30 wt% MEA	3.2	92	12.5 - 13.0	3.6
H3-1	2.0	93	12.8	2.4
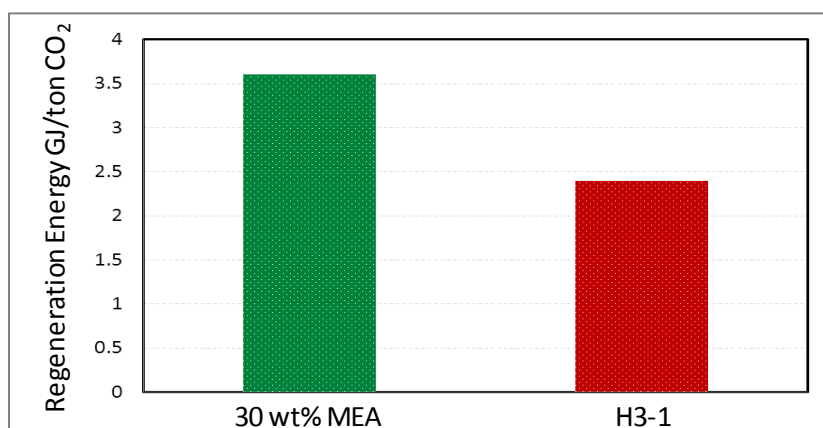
Figure 4-25 - Regeneration Energy of MEA Compared with H3-1

4.11   NCCC Cross Check Calculations

At the request of the DOE, NCCC performed mass balances for select test conditions to compare the results with those obtained by Hitachi. The mass balance information developed is present in

Appendix 1 along with some plots of the data developed. The results are summarized below for test cases with three absorber beds in operation.

	Minimum Heat of Regeneration, Btu/lb	Liquid-to Gas Ratio, -	Capture Efficiency, %
Hitachi	1030	2.0	93.0
NCCC	1010	1.9	93.0

The values are very close together and the variation seen is considered to be within the scatter of the data collected. Hence it is concluded that the two sets of values are in agreement.

4.12   Amine Carryover and Secondary Products

Amine carryover was measured by collecting gas samples at the outlet of the wash tower. Figure 4-26is a schematic of the set-up for the gas sampling method developed by Southern Research Institute comprising mainly of a polytetrafluoroethylene (PTFE) sample line, a knock-out trap in an ice bath, and a volumetric flow meter. Gas was sampled using an isokinetic sample probe. The sample port was located on a vertical pipe at the outlet of the wash tower with the outlet gas flowing in the downward direction. The same sampling set-up and location have been used to measure amine carryover during the MEA tests.
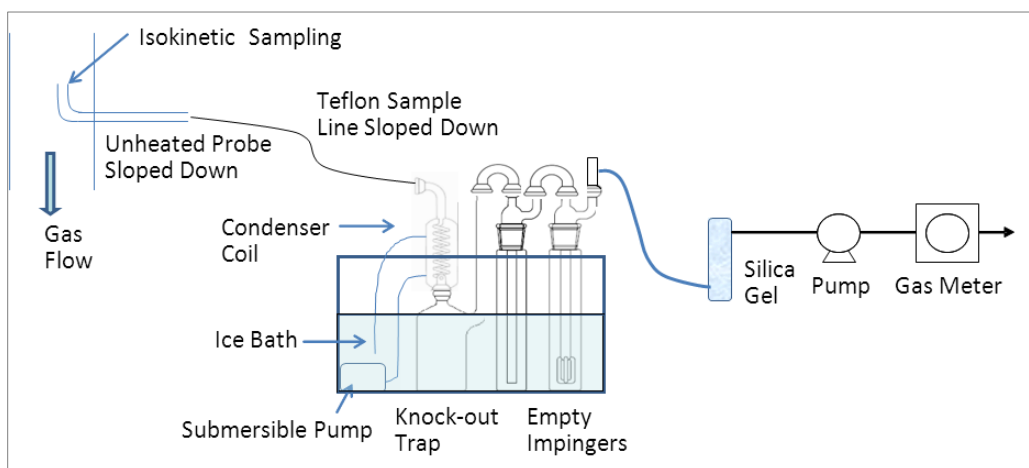
Figure 4-26 - Gas Sampling Method for Amine Carryover using Knock-out Trap

Three samples were collected during parametric tests in May and July 2012. The amine carryover from these tests was estimated to be 66, 55, and 68 ppmw with an average of 63 ppmw (in the wet flue gas). This is about half the value of amine carryover measured when operating with MEA, which was about 135 ppmw. This value for MEA was measured under test conditions that NCCC had determined to generate the lowest amine carryover rate (two absorber beds in service with no intercoolers).

Although the extent of carryover is less for H3-1 compared to 30 wt% MEA, the amount of amine carryover for both solvents is high. Since the concentration of SO_3 in the flue gas is small (measured value of less than 3 ppmv during the Hitachi solvent testing), amine mist formed due to the presence of SO_3 aerosol in the flue gas is expected to be small. Test results indicate that

amine carryover is not only contingent upon the type of solvent, but strongly depends on the design and operation of the absorber and the wash tower. The wash tower at NCCC is a single-stage packed tower. Wash water sprayed from the top of the tower absorbs amine from the absorber exhaust gas that flows in a counter-current manner through the packing section. The water leaving the bottom of the wash tower is collected in a buffer tank from where it is recirculated back to the top of the wash tower. The addition of make-up water is based on the level of the buffer tank, and not determined by the process conditions such as concentration of amine in the wash water. Additionally, the ranges of temperature and flow rate of the recirculating wash water are limited. Taking into consideration the single-stage design and operating conditions of the wash tower at NCCC, such high values of amine carryover are not unexpected.

Based on Hitachi's pilot plant experience, a single-stage wash tower is not sufficient to reduce amine carryover to very low levels. For effective emissions control, multiple washing stages are required. The mechanism in a wash tower can be explained using Figure 4-27, which shows the relation between amine concentration in the outlet gas and in the wash water, at equilibrium. The plot is based on tests conducted at Hitachi's in-house pilot facility over a wide range of amine concentrations in the gas entering the wash tower. Following the expected trend as per Henry's law, the concentration of amine in the outlet gas is proportional to the amine concentration in the wash water. In a single-stage wash tower similar to the one at NCCC, the concentration of amine in the wash water is quite high resulting in high carryover.
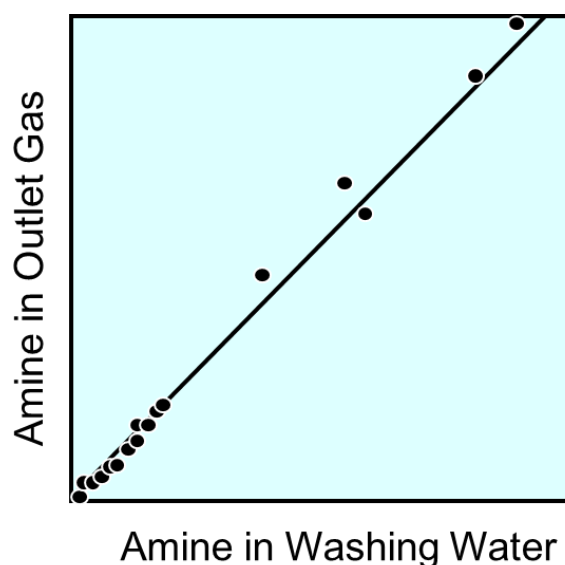
Figure 4-27 - Correlation between Amine in Wash Water and Gas-Phase

In a multi-stage wash tower, the concentration of amine in the wash water of the top stage can be controlled to very low levels while maintaining the water balance in the CO_2 capture system, to produce an outlet gas with very low amine carryover. For the NCCC system, Hitachi recommends a three-stage wash tower along with reducing the temperature of the wash water to minimize the amount of amine mist and vapor leaving the wash tower.

Gas samples at the outlet of the wash tower were also collected using a different method, which is shown in Figure 4-28. This sampling set-up mainly consisted of a heated PTFE sampling line;

two impingers in an ice bath, one containing water and the other, an organic solvent (xylene); and a rotameter. Amine carryover measured by this method was higher than that measured by the knock-out trap method, but in the same order of magnitude. This difference in the concentrations between the two methods could be due to the differences in the sampling techniques. In the knock-out trap method, when the sample gas was rapidly chilled, amine mist may have been generated that passed through the empty impinger. Due to the absence of a water impinger, any mist that may have formed was not collected. The discrepancy of carryover results in the two methods shows the need for standardized sampling and analysis methods to be developed in order to determine the amine carryover especially at low emissions.
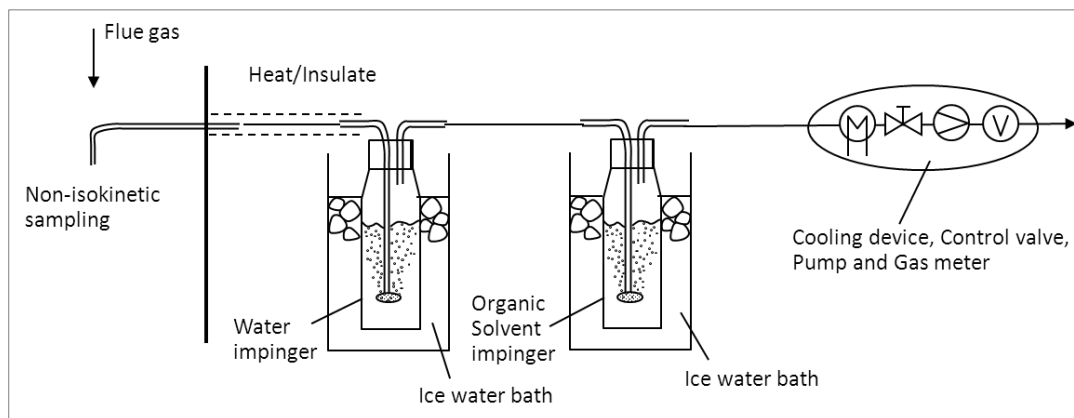
Figure 4-28 - Gas Sampling Method for Amine Carryover using Organic Solvent

Gas samples were also collected at the outlet of the wash tower to analyze for nitrosamine emissions. Nitrosamines can be formed in the gas when the amine reacts with NO_2 present in the flue gas. NO_2 is typically a small fraction of the total NOx emissions exiting the SCR. The sampling method for nitrosamine emissions, shown in Figure 4-29 includes a heated PTFE sample line and an acid impinger to suppress further reactions between NO_2 and amine in the sampling train. The gas sample passes through a Thermosorb/N sorbent cartridge to adsorb any nitrosamine present: the heater is used to evaporate any liquid as wetting the adsorbent reduces its activity. Three samples were collected at different times during the test campaign and the temperature at the outlet of the wash tower was different for each of these tests.

The sorbent cartridges were sent to an external lab for analysis of nitrosamine. As indicated in Table 4-3, nitrosamine was not detected in the gas samples collected at the outlet of the wash tower. The detection limit was 0.05 micrograms/cartridge, or about 0.25 micrograms/m^3.
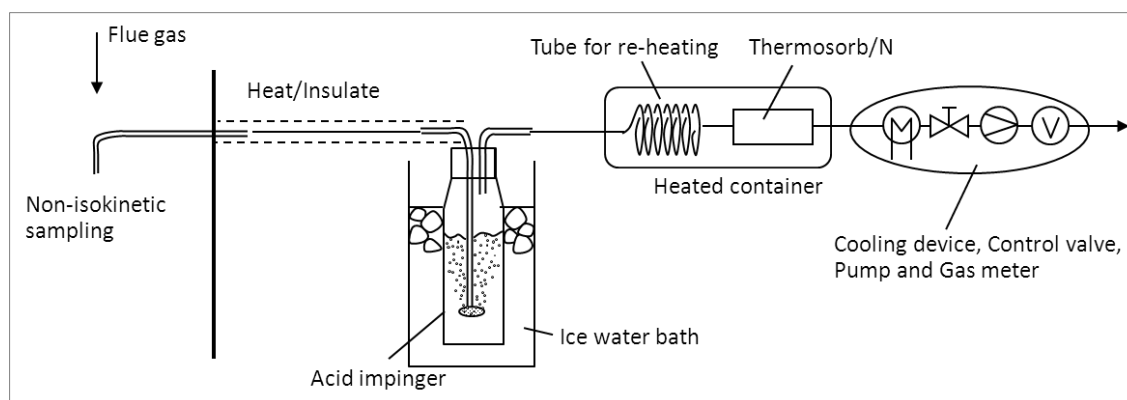
Figure 4-29 - Gas Sampling Method for Nitrosamine Emissions

Table 4-3 - Nitrosamine Sample Results from the Wash Tower Outlet

Operating Hours	Nitrosamine Conc., ppm	Gas Temperature, °F
843	Not Detected	117
936	Not Detected	121
1,272	Not Detected	113

4.13   Solvent Degradation

Solvent samples from the outlet of the absorber (CO_2-rich) and inlet to the absorber (CO_2-lean) were collected regularly (roughly one set per test) to perform manual titration for verification of the amine and CO_2 concentrations measured by the auto-titrator. Some of the samples were analyzed to check for degradation products, and the results are plotted for formic acid and oxalic acid formation over operating time in Figure 4-30.

As expected, the concentration of the degradation products was very low, in the range of 10 to 15 ppmw, after 1,000 hours of testing. Over a similar duration of testing with MEA (during the MEA baseline campaign conducted in March 2012) the concentration of oxalates and formates measured were much higher, at 393 ppmw and 1,820 ppmw, respectively. It is noted that oxidation inhibitors were not used when testing either MEA or H3-1. Figure 4-30 also shows that as H3-1 testing progressed, the concentration of formic acid and oxalic acid in the solvent slightly increased. The reduction in acid concentration at about 950 hours was due to the introduction of fresh solvent to the process loop after about 750 hours. This was done to maintain sufficient liquid level in the process solvent tank for the lean solvent pump to work effectively. The formation of heat stable salts as sulfates in the solvent was also measured by analyzing lean solvent samples taken at various intervals of testing. Sulfate compounds are formed due to the reaction of the amine and SO_2 in the flue gas. During most of the H3-1 testing, the inlet SO_2 concentration was controlled in the pre-scrubber and maintained below 2 ppmv (lower detection limit of the analyzer), except for a few fluctuations (see Figure 4-7). Towards the latter part of the test campaign, the inlet SO_2 concentration increased to 3 to 4 ppm. Figure 4-31 is a plot of the concentration of sulfates in the solvent at different test durations. The formation of degradation products increased with time, and after 1,200 hours, the sulfate

38

concentration was around 900 ppmw. After about 1,000 hours of testing with MEA during 2012 MEA baseline testing, the sulfate concentration in the rich MEA solvent as reported by NCCC was 1,010 ppmw. The presence of sodium, calcium, and magnesium in the solvent indicates that at least in part the sulfate detected originates from carryover from the PSTU caustic scrubber and Plant Gaston's limestone-based FGD.
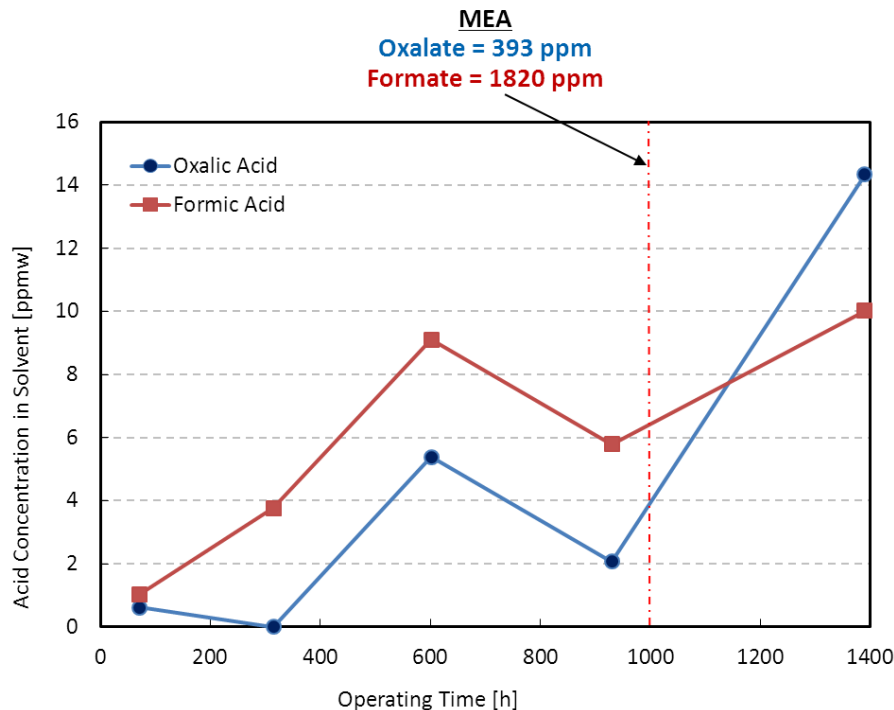
Figure 4-30 - Products of Degradation in H3-1 Solvent
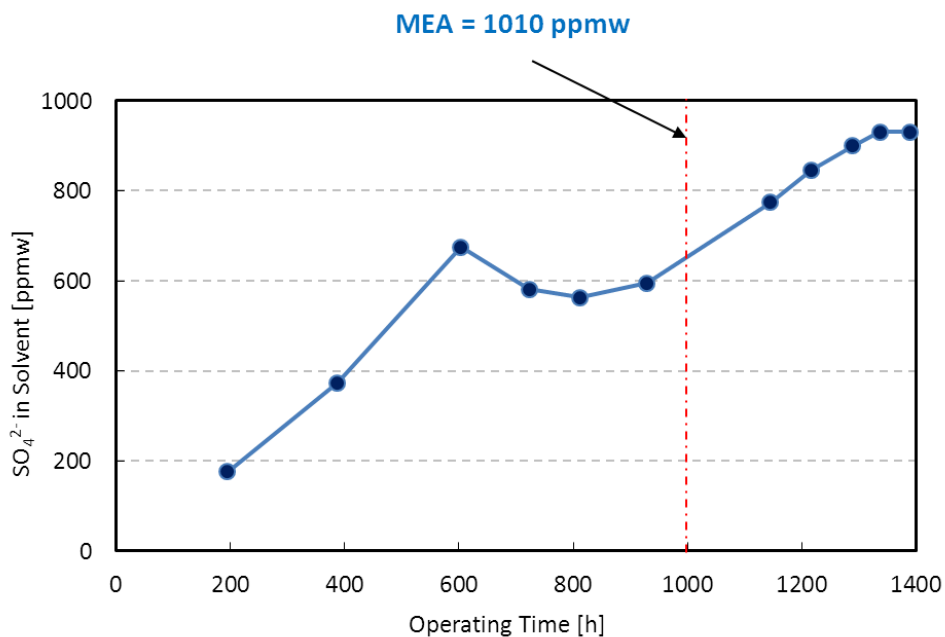
Figure 4-31 - Sulfate Concentration in H3-1 Solvent

4.14   Corrosion

During preliminary discussions between NCCC and Hitachi, it was decided that two types of corrosion measurement techniques would be employed. One was the commonly used method wherein coupons of stainless steel and carbon steel would be placed at different locations in the absorber and regenerator. At the end of testing the weight of each coupon would be measured and verified against the weight of a fresh coupon to check for the rate of corrosion. The other method, suggested by NCCC, used electric resistance (ER) probes to be inserted in many of the same locations as the weight-loss coupons. This method provides a continuous signal that could be read as a measurement and recorded in the DCS. NCCC had procured weight-loss coupons and planned to install them during the first 11-day plant outage in early May. However, at the end of testing in July, when the probes to hold the corrosion coupon were removed, it was found that the corrosions coupons had not been installed.

As shown in Figure 4-32, three ER probes were located in the absorber and one each in the wash tower, inlet separator, regenerator, and mist separator. The ER probes used were made of carbon steel. Figure 4-33 shows the measurements for the three probes located in the absorber, and they are almost constant from the beginning to the end of testing. This shows that corrosion in the absorber was insignificant. The slight change in the readings shown in the Figure occurred during periods of plant outage when flue gas was unavailable.
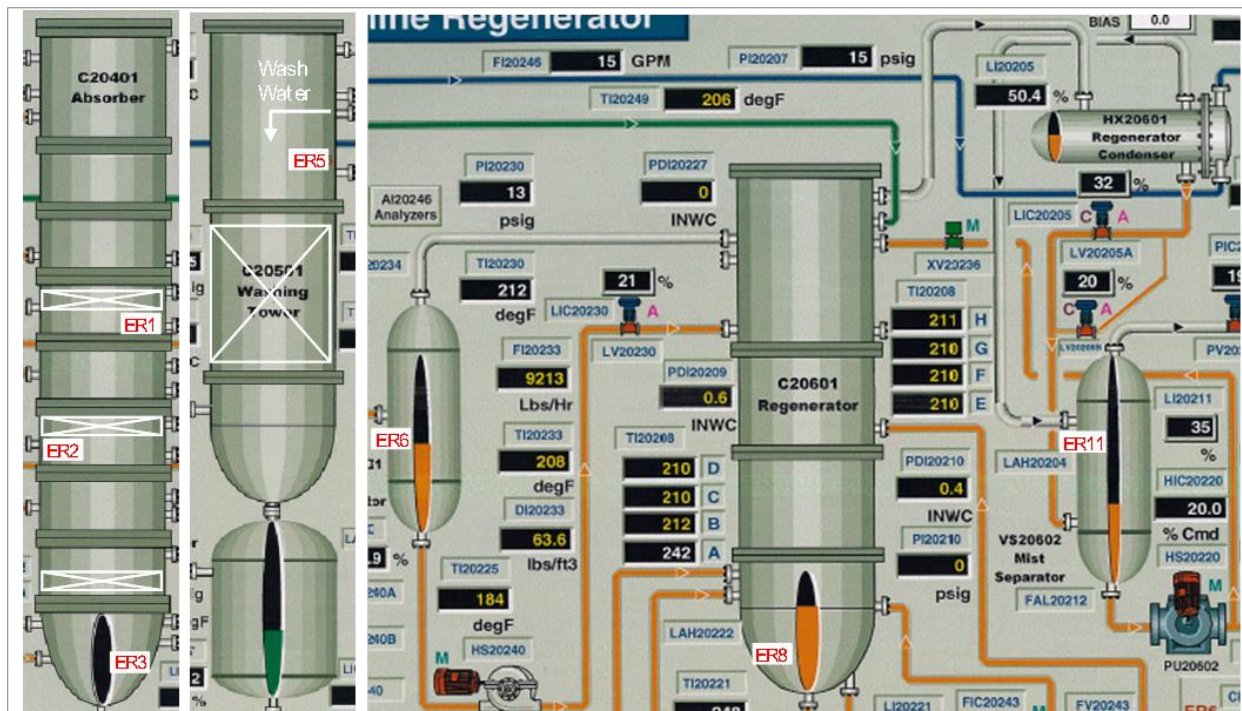
Figure 4-32 - Location of Electric-Resistance Probes in the PSTU

The three probes within the absorber were located at different elevations which are at different temperature regions due to the exothermic nature of the absorption reaction of CO_2 and amine. The ER probe readings at all three locations in the absorber were similar, indicating that from top to bottom there was no significant difference in corrosion.
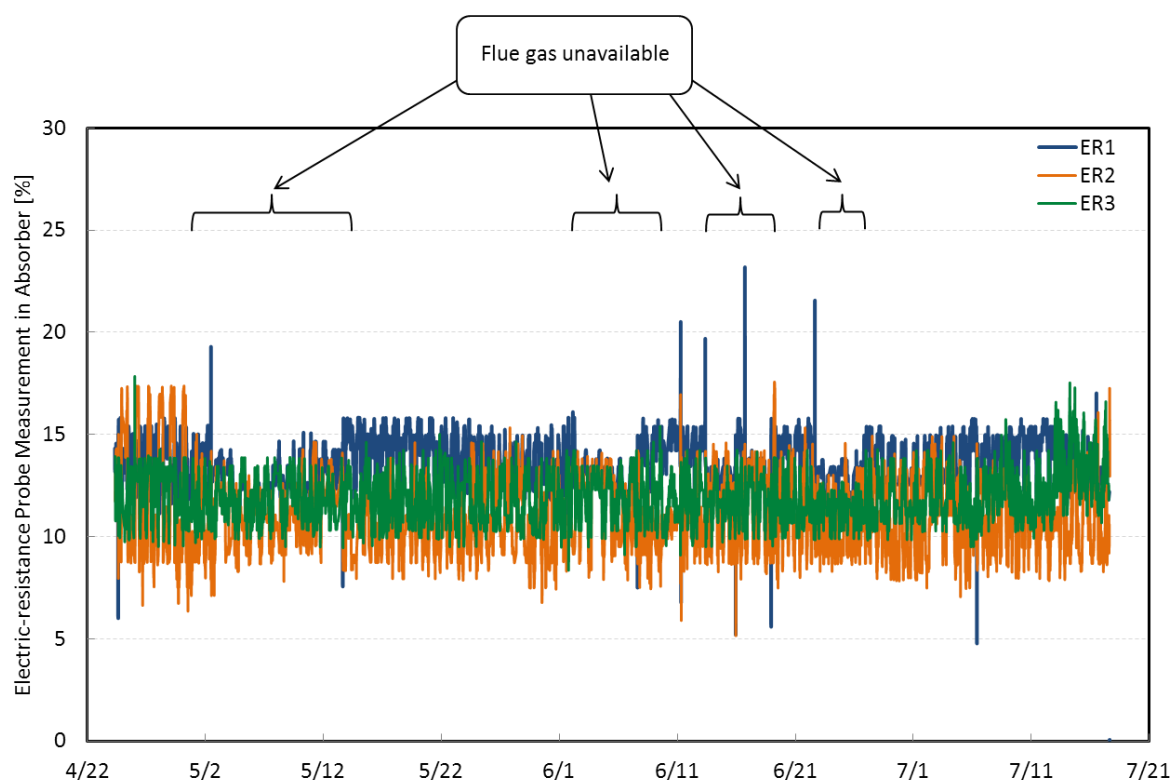
Figure 4-33 - Electric-Resistance Probe Corrosion Measurements in the Absorber

Figure 4-34 shows the measurements for the ER probe in the wash tower. Corrosion is not expected in the wash tower due to the large amount of water in the vessel, low temperatures and low concentration of amine. As expected, the readings were almost the same throughout the test campaign, indicating no corrosion or insignificant corrosion. Unlike the absorber, the measurements did not change during plant outages.

Figure 4-35 shows the measurements of ER probes in the inlet separator, at the bottom of the regenerator, and in the mist separator. At all three locations, the ER probe measurements were almost constant from the beginning of the test campaign till the end, 1400 hours later. The readings from the ER probes at the bottom of the regenerator and in the mist separator were higher than those from the inlet separator, absorber, and wash tower. The bottom of the regenerator and the mist separator are both at high temperature with a mixture of CO_2 and water/steam present that create an acidic environment resulting in increased corrosion potential. The intervals during which the ER probe readings are highest are during plant outages when flue gas was unavailable.
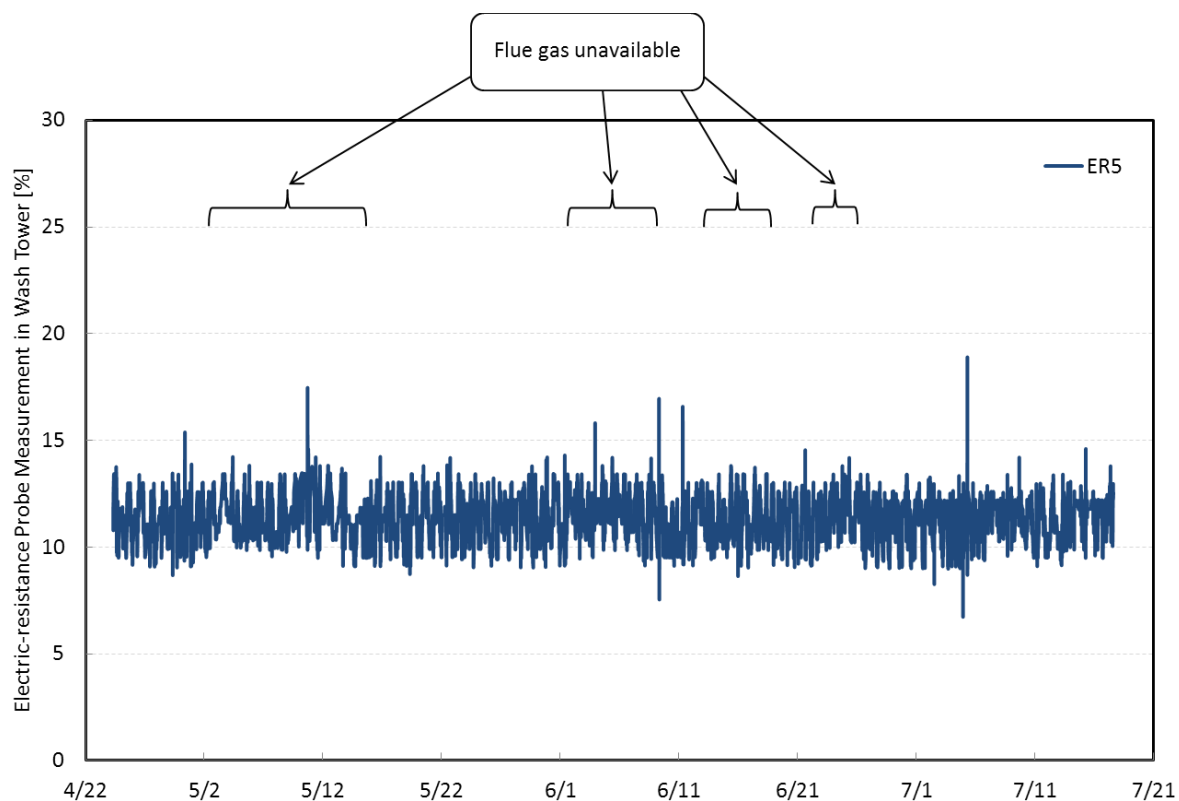
Figure 4-34 - Electric-Resistance Probe Corrosion Measurements in the Wash Tower
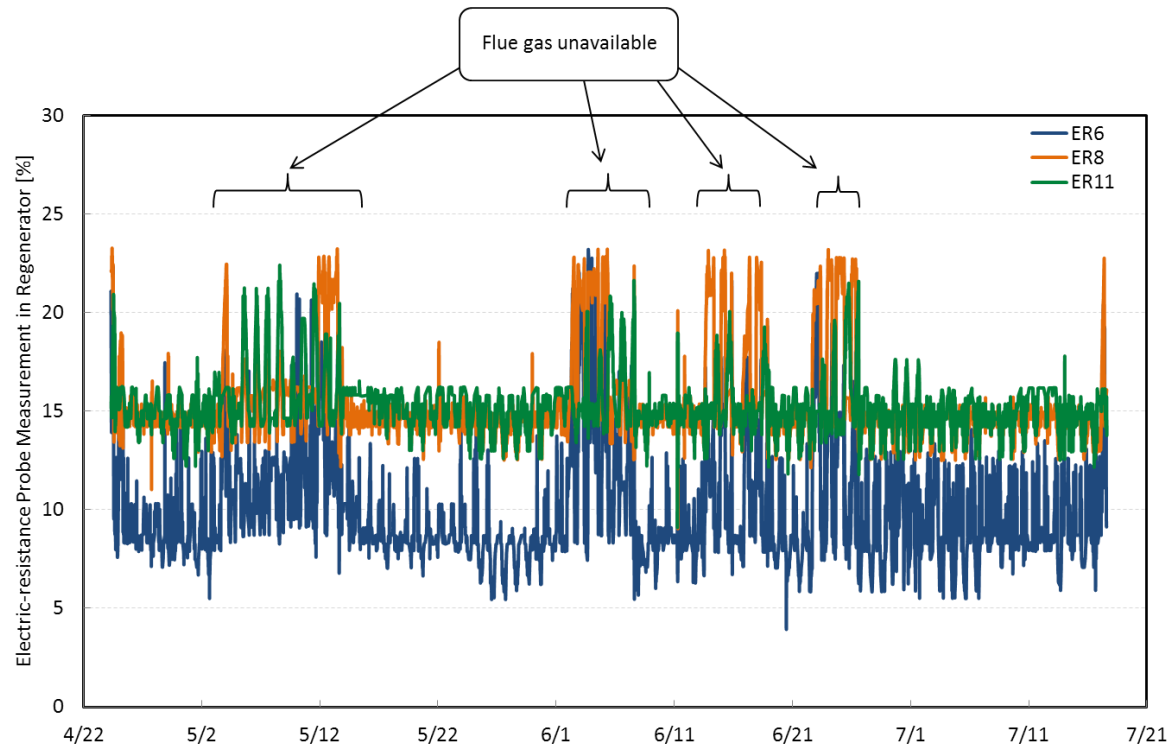
Figure 4-35 - Electric-resistance Probe Corrosion Measurements in the Inlet Separator, Regenerator, and Mist Separator

4.15 Metals in Solvent

The concentration of metals in the H3-1 solvent was analyzed to check for accumulation of metals that are present in the flue gas and to verify corrosion effects. Table 4-4 shows the results of the analysis of H3-1 and MEA. The H3-1 samples were analyzed by two labs—an independent laboratory in Japan that analyzed samples taken after 900 hours and 1,350 hours of testing, and Alabama Power's General Test Laboratory that analyzed samples after the completion of testing. NCCC provided the data for MEA samples that were analyzed after 1,000 hours of testing. The limits set by the U.S. Environmental Protection Agency Resource Conservation and Recovery Act (RCRA) for some of the metals are also listed in the Table.

Table 4-4 - Concentration of Metals in Solvent

Metal	H3-1, Lab Analysis, mg/L		H3-1, TCLP Analysis, mg/L	MEA from NCCC, mg/L	RCRA Limit, mg/L
	900 hr	1,350 hr	1,350 hr	1,000 hr	
Ba	<0.01	<0.01	<1	0.27	100
Cr	0.63	0.84	<1	45.09	5
Se	3.3	5.4	2.9	1.95	1
As	0.42	0.68	2.3	0.22	5
Cd	0.05	0.01	<1	<0.01	1
Pb	<0.01	<0.01	<1	<0.01	5
Hg	<0.1	<0.1	<0.05	<0.005	0.2
Ag	0.01	<0.01	<0.2	<0.5	5
Fe	0.61	0.58	-	137.20	-
Ni	0.10	0.17	-	28.77	-
Mn	0.01	0.01	-	5.62	-
Co	<0.01	<0.01	-	1.02	-

Metals such as barium, selenium, arsenic, cadmium, lead, mercury, and silver are typically present in the flue gas. The concentration of these metals in the H3-1 solvent was similar to that found in MEA. The presence of these metals does not affect the CO_2 capture performance of the solvent or energy requirement for the process.

Chromium, iron, nickel, manganese, and cobalt are metals that are present in the 316L stainless steel material used in absorber and regenerator construction and are generally not likely to be present in the flue gas in significant quantities. The presence of these metals in the solvent indicates the occurrence of corrosion in the process equipment. As shown in Table 4-4, the concentration of these metals in H3-1 is insignificant and orders of magnitude lower than that measured in MEA (which did not contain corrosion inhibitor). Such low concentrations confirm results from the ER probe measurements and Hitachi's previous pilot- and lab-scale results that the H3-1 solvent has a very low corrosivity.

Furthermore, the proportion of metals in the solvent was compared with that in stainless steel. Table 4-5 gives the composition of 316L stainless steel. The ratios of chromium to iron and nickel to iron in 316L are in the range of 0.23-0.29 and 0.14-0.23, respectively. The ratio of metals in the MEA solvent after about 1,000 hours of operation were 0.33 and 0.21, respectively, similar to the proportion of metals in 316L indicating that the material is being removed corroded uniformly by the MEA.

Table 4-5 - Composition of 316L Stainless Steel

Component	Content, %
C	0.03
Mn	2
P	0.045
S	0.03
Si	0.75
Cr	16 - 18
Ni	10 - 14
Mo	2
Ni	0.1
Fe	Remaining

In comparison, the proportion of chromium to iron after 900 hours and 1,350 hours of H3-1 solvent testing were 1.03 and 1.45, respectively. The proportion of nickel to iron in the H3-1 solvent after 900 hours and 1,350 hours of testing were 0.16 and 0.29, respectively. The higher proportion of chromium in the solvent suggests that only the protective layer of chromium oxide formed on the steel is being removed by the H3-1 solvent, not the bulk of the metal. It is understood that if the loss rate of the outer surface layer is low, it is renewed using available chromium in the steel and the corrosion-protective film is restored. It should be noted that the actual concentrations of all three metals in H3-1 is insignificant, indicating that the corrosion potential of H3-1 is much lower than that of MEA.

5.0 SUMMARY

The Hitachi H3-1 solvent was successfully tested from April 24, 2012 to July 16, 2012 in the pilot-scale test facility at NCCC using a flue gas slipstream from Plant Gaston's Unit 5. The solvent was supplied by Hitachi and the pilot plant was operated by Southern Company. No modifications were required to the pilot plant to accommodate the Hitachi solvent. Hitachi personnel were present on-site to observe testing and coordinate the test plan.

The solvent was operated at the PSTU for about 1,400 hours under various parametric test conditions and boiler loads. The parameters tested include flow rate and temperature of flue gas and solvent, reboiler steam flow rate, the effect of the intercoolers, and the effect of the number of packing beds in the absorber. An average of about 91 percent CO_2 was captured over the duration of testing under the various test conditions. The effect of solvent circulation rate on CO_2 capture efficiency and regeneration energy was verified and optimal operating conditions for the Hitachi solvent were identified at different boiler load conditions. To achieve 90 percent CO_2 capture, the solvent circulation rate was about 30 percent lower than that required for MEA at the same facility. The regeneration energy for the Hitachi solvent at this condition was 2.4 GJ/tonne of CO_2 or 1,030 Btu/lb-CO_2 and about 34 percent lower than that observed for MEA.

Parametric tests using different packed beds in the absorber showed that close to 90 percent of the CO_2 was removed with only the bottom two packed beds in service. With all three absorber beds in the service, CO_2 removal efficiency was about 93 percent. Intercooling of the solvent in the absorber had a considerable effect on the CO_2 capture performance. A 6 percentage point improvement in the CO_2 removal efficiency was achieved under the same test conditions as those without the intercoolers.

Amine carryover during the Hitachi solvent testing was about half of that from MEA testing. However, both values were relatively high. Based on Hitachi's experience, amine carryover depends heavily on the design and operation of the wash tower and the single-stage wash tower currently installed at NCCC is inadequate. A multiple-stage wash tower is recommended to reduce amine carryover to very low levels. Nitrosamines were not detected in any of the three samples taken during the test campaign. The concentration of degradation products in the solvent such as formate and oxalate were measured to be very low at 10-15 ppmw, which is one to two orders of magnitude lower than that measured in MEA.

Corrosion was measured using carbon steel electric-resistance probes placed at various locations in the PSTU including the absorber, wash tower, inlet separator, regenerator, and mist separator. At the end of about 1,400 hours of testing under various parametric conditions and boiler loads, the electric-resistance probe measurements at all the locations were little changed from the initial value at the start of the test campaign, indicating that corrosion due to the Hitachi solvent was insignificant. Solvent samples at the completion of testing were analyzed and the results showed that the concentration of metals typically present in flue gas such as barium, cadmium, selenium, arsenic, lead, mercury and silver was similar to that in MEA. The concentration of metals typically present in the stainless steel material such as iron, nickel, chromium, manganese and cobalt was much lower than that in MEA tested at NCCC. Such insignificant levels of metals that are originated from vessel construction materials at the end of the test campaign confirm the low corrosive tendency of the Hitachi solvent.

6.0 APPENDIX A: NCCC MASS BALANCES

The mass balances are prepared using the instrumentation discussed in Section 3. 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.

The data are tabulated in a form that complies with Hitachi's confidentiality requirements.

- Tables A-1 through A-6 present data collected with three beds for liquid-to-gas ratios from 1.3 to 2.6.
- Tables A-3, A-7, and A-8 present data collected with a liquid-to-gas ratio of 1.8 for 3, 2, and 1 bed(s), respectively.

Based on data contained in these eight tables, four graphs are prepared as follows:

- Figure A-1 shows how the heat of regeneration varies with L/G ratio with three absorber beds in service. A simple curve fit indicates that the minimum value of 1010 Btu/lb occurs at an L/G ratio of 1.9. From Figure A-2, the corresponding CO_2 capture efficiency is 93 percent.
- Figure A-2 shows how CO_2 capture efficiency varies with L/G ratio with three absorber beds in service. A simple curve fit indicates that the maximum value of 94 percent occurs at an L/G ratio of 1.7 for which, from Figure A-1, the corresponding heat of regeneration is 1010 Btu/lb.
- Figure A-3 shows how the heat of regeneration varies with the number of absorber beds in service for an L/G ratio of 1.8. A simple curve fit indicates that the regeneration energy decreases as the number of beds increases, presumably as result of increased CO_2 capture efficiency. See Figure A-4.
- Figure A-4 shows how CO_2 capture efficiency varies with the number of absorber beds in service for an L/G ratio of 1.8.

The optimum operating conditions for three absorber beds as determined by Hitachi and NCCC are tabulated below.

	Minimum Heat of Regeneration, Btu/lb	Liquid-to Gas Ratio, -	CO_2 Capture Efficiency, %
Hitachi	1030	2.0	93.0
NCCC	1010	1.9	93.0

The values are very close together and the variation seen is considered to be within the scatter of the data collected.

Table A-1 - Balance Period 1: Three Absorber Beds

Start and end dates and times	08:10, 4th July 2012 to 13:00, 4th July 2012
Duration, hours and minutes	4:50

Absorber Gas Flows

	Inlet	Wash Tower Outlet	Closure, %
Nitrogen, lb/hr	3560	3540	0.60
Oxygen, lb/hr	335	335	0.00
CO_2, lb/hr	857	101	
Moisture, lb/hr	239	322	
TOTAL, lb/hr	4991	4298	
Temperature, ºF	109	120	

Absorber Liquid Flows

	Inlet	Outlet
Water + solvent, lb/hr	6520	6160
CO_2, lb/hr	19.7	769
TOTAL, lb/hr	6540	6929
Temperature, ºF	107	117
Liquid/gas ratio, -	1.31	

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

	Inlet	Outlet	Closure, %
CO_2	877	870	0.80

CO_2 Flow Cross Checks

	Rates, lb/hr	Capture efficiency, %
CO_2 removed from flue gas	756	88.2
CO_2 absorbed by solvent	749	
CO_2 released from regenerator	747	

Lean-Rich Heat Exchanger Temperatures

	In	Out
Lean	252	124
Rich	117	219

Regenerator Data

Steam flow to reboiler, lb/hr	916
Steam pressure, psia	45.0
Steam temperature, ºF	278
Regenerator bottom temperature, ºF	254
Heat of regeneration, Btu/lb (measured)	1120
Heat of regeneration, Btu/lb (adjusted) (1)	1080

(1) Allowing for heat losses (estimated at 30,040 Btu/hr) and adjusting lean-rich approach temperature (lean out – rich in) from 7 to 6.5ºF.

Table A-2 - Balance Period 2: Three Absorber Beds

Start and end dates and times	16:10, 3rd July 2012 to 23:30, 3rd July 2012
Duration, hours and minutes	7:20

Absorber Gas Flows

	Inlet	Wash Tower Outlet	Closure, %
Nitrogen, lb/hr	3560	3530	0.87
Oxygen, lb/hr	333	334	0.47
CO_2, lb/hr	852	41.3	
Moisture, lb/hr	246	326	
TOTAL, lb/hr	4991	4231	
Temperature, ºF	110	121	

Absorber Liquid Flows

	Inlet	Outlet
Water + solvent, lb/hr	7600	7250
CO_2, lb/hr	34.0	851
TOTAL, lb/hr	7634	8101
Temperature, ºF	107	118
Liquid/gas ratio, -	1.53	

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

	Inlet	Outlet	Closure, %
CO_2	886	892	0.68

CO_2 Flow Cross Checks

	Rates, lb/hr	Capture efficiency, %
CO_2 removed from flue gas	811	95.2
CO_2 absorbed by solvent	817	
CO_2 released from regenerator	802	

Lean-Rich Heat Exchanger Temperatures

	In	Out
Lean	250	126
Rich	118	219

Regenerator Data

Steam flow to reboiler, lb/hr	911
Steam pressure, psia	44.7
Steam temperature, ºF	277
Regenerator bottom temperature, ºF	253
Heat of regeneration, Btu/lb (measured)	1040
Heat of regeneration, Btu/lb (adjusted) (1)	1000

(1) Allowing for heat losses (estimated at 26,700 Btu/hr) and adjusting lean-rich approach temperature (lean out – rich in) from 8 to 6.5ºF.

Table A-3 - Balance Period 3: Three Absorber Beds

Start and end dates and times	01:00, 1st June 2012 to 05:30, 1st June 2012
Duration, hours and minutes	4:30

Absorber Gas Flows

	Inlet	Wash Tower Outlet	Closure, %
Nitrogen, lb/hr	3600	3600	0.00
Oxygen, lb/hr	372	378	1.61
CO_2, lb/hr	815	61.9	
Moisture, lb/hr	207	261	
TOTAL, lb/hr	4994	4301	
Temperature, ºF	104	113	

Absorber Liquid Flows

	Inlet	Outlet
Water + solvent, lb/hr	8760	8630
CO_2, lb/hr	242	1000
TOTAL, lb/hr	9002	9630
Temperature, ºF	107	113
Liquid/gas ratio, -	1.81	

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

	Inlet	Outlet	Closure, %
CO_2	1057	1062	0.47

CO_2 Flow Cross Checks

	Rates, lb/hr	Capture efficiency, %
CO_2 removed from flue gas	753	92.4
CO_2 absorbed by solvent	758	
CO_2 released from regenerator	767	

Lean-Rich Heat Exchanger Temperatures

	In	Out
Lean	245	123
Rich	113	223

Regenerator Data

Steam flow to reboiler, lb/hr	883
Steam pressure, psia	45.5
Steam temperature, ºF	279
Regenerator bottom temperature, ºF	248
Heat of regeneration, Btu/lb (measured)	1080
Heat of regeneration, Btu/lb (adjusted) (1)	1020

(1) Allowing for heat losses (estimated at 29,500 Btu/hr) and adjusting lean-rich approach temperature (lean out – rich in) from 10 to 6.5ºF.

Table A-4 - Balance Period 4: Three Absorber Beds

Start and end dates and times	08:55, 9th July 2012 to 05:35, 10th July 2012
Duration, hours and minutes	20:40

Absorber Gas Flows

	Inlet	Wash Tower Outlet	Closure, %
Nitrogen, lb/hr	3540	3520	0.67
Oxygen, lb/hr	343	338	1.54
CO_2, lb/hr	846	75.8	
Moisture, lb/hr	255	285	
TOTAL, lb/hr	4984	4219	
Temperature, ºF	111	117	

Absorber Liquid Flows

	Inlet	Outlet
Water + solvent, lb/hr	9820	9580
CO_2, lb/hr	295	1080
TOTAL, lb/hr	10,117	10,660
Temperature, ºF	104	122
Liquid/gas ratio, -	2.03	

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

	Inlet	Outlet	Closure, %
CO_2	1141	1156	0.44

CO_2 Flow Cross Checks

	Rates, lb/hr	Capture efficiency, %
CO_2 removed from flue gas	770	91.0
CO_2 absorbed by solvent	785	
CO_2 released from regenerator	771	

Lean-Rich Heat Exchanger Temperatures

	In	Out
Lean	245	129
Rich	121	224

Regenerator Data

Steam flow to reboiler, lb/hr	906
Steam pressure, psia	43.4
Steam temperature, ºF	275
Regenerator bottom temperature, ºF	247
Heat of regeneration, Btu/lb (measured)	1090
Heat of regeneration, Btu/lb (adjusted) (1)	1040

(1) Allowing for heat losses (estimated at 26,800 Btu/hr) and adjusting lean-rich approach temperature (lean out – rich in) from 8 to 6.5ºF.

Table A-5 - Balance Period 5: Three Absorber Beds

Start and end dates and times	09:00, 5th July 2012 to 11:40, 5th July 2012
Duration, hours and minutes	2:40

Absorber Gas Flows

	Inlet	Wash Tower Outlet	Closure, %
Nitrogen, lb/hr	3550	3520	0.85
Oxygen, lb/hr	311	315	1.28
CO_2, lb/hr	884	87.3	
Moisture, lb/hr	247	282	
TOTAL, lb/hr	4992	4204	
Temperature, ºF	110	117	

Absorber Liquid Flows

	Inlet	Outlet
Water + solvent, lb/hr	11,170	10,910
CO_2, lb/hr	345	1150
TOTAL, lb/hr	11,515	12,060
Temperature, ºF	105	123
Liquid/gas ratio, -	2.31	

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

	Inlet	Outlet	Closure, %
CO_2	1229	1237	0.65

CO_2 Flow Cross Checks

	Rates, lb/hr	Capture efficiency, %
CO_2 removed from flue gas	797	90.2
CO_2 absorbed by solvent	805	
CO_2 released from regenerator	758	

Lean-Rich Heat Exchanger Temperatures

	In	Out
Lean	243	132
Rich	123	226

Regenerator Data

Steam flow to reboiler, lb/hr	916
Steam pressure, psia	42.1
Steam temperature, ºF	273
Regenerator bottom temperature, ºF	245
Heat of regeneration, Btu/lb (measured)	1070
Heat of regeneration, Btu/lb (adjusted) (1)	1010

(1) Allowing for heat losses (estimated at 25,900 Btu/hr) and adjusting lean-rich approach temperature (lean out – rich in) from 9 to 6.5ºF

Table A-6 - Balance Period 6: Three Absorber Beds

Start and end dates and times	00:20, 6th July 2012 to 03:20, 6th July 2012
Duration, hours and minutes	3:00

Absorber Gas Flows

	Inlet	Wash Tower Outlet	Closure, %
Nitrogen, lb/hr	3590	3550	1.13
Oxygen, lb/hr	370	376	1.62
CO_2, lb/hr	814	113	
Moisture, lb/hr	221	257	
TOTAL, lb/hr	4995	4396	
Temperature, °F	106	113	

Absorber Liquid Flows

	Inlet	Outlet
Water + solvent, lb/hr	12,550	12,480
CO_2, lb/hr	487	1190
TOTAL, lb/hr	13,037	13,670
Temperature, °F	102	123
Liquid/gas ratio, -	2.61	

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

	Inlet	Outlet	Closure, %
CO_2	1301	1303	0.15

CO_2 Flow Cross Checks

	Rates, lb/hr	Capture efficiency, %
CO_2 removed from flue gas	701	86.1
CO_2 absorbed by solvent	703	
CO_2 released from regenerator	702	

Lean-Rich Heat Exchanger Temperatures

	In	Out
Lean	240	132
Rich	123	227

Regenerator Data

Steam flow to reboiler, lb/hr	892
Steam pressure, psia	40.5
Steam temperature, °F	271
Regenerator bottom temperature, °F	242
Heat of regeneration, Btu/lb (measured)	1180
Heat of regeneration, Btu/lb (adjusted) (1)	1100

(1) Allowing for heat losses (estimated at 29,000 Btu/hr) and adjusting lean-rich approach temperature (lean out – rich in) from 9 to 6.5°F.

Table A-7 - Balance Period 7: Two Absorber Beds

Start and end dates and times	16:00, 29th May 2012 to 00:00, 30th May 2012
Duration, hours and minutes	8:00

Absorber Gas Flows

	Inlet	Wash Tower Outlet	Closure, %
Nitrogen, lb/hr	3590	3590	0.00
Oxygen, lb/hr	380	383	0.79
CO_2, lb/hr	806	91.1	
Moisture, lb/hr	216	256	
TOTAL, lb/hr	4992	4320	
Temperature, ºF	105	113	

Absorber Liquid Flows

	Inlet	Outlet
Water + solvent, lb/hr	8770	8530
CO_2, lb/hr	229	947
TOTAL, lb/hr	8999	9477
Temperature, ºF	103	116
Liquid/gas ratio, -	1.80	

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

	Inlet	Outlet	Closure, %
CO_2	1035	1038	0.29

CO_2 Flow Cross Checks

	Rates, lb/hr	Capture efficiency, %
CO_2 removed from flue gas	715	88.7
CO_2 absorbed by solvent	718	
CO_2 released from regenerator	733	

Lean-Rich Heat Exchanger Temperatures

	In	Out
Lean	245	127
Rich	116	224

Regenerator Data

Steam flow to reboiler, lb/hr	886
Steam pressure, psia	46.0
Steam temperature, ºF	280
Regenerator bottom temperature, ºF	249
Heat of regeneration, Btu/lb (measured)	1150
Heat of regeneration, Btu/lb (adjusted) (1)	1080

(1) Allowing for heat losses (estimated at 27,100 Btu/hr) and adjusting lean-rich approach temperature (lean out – rich in) from 11 to 6.5ºF.

Table A-8 - Balance Period 8: One Absorber Bed

Start and end dates and times	15:45, 30th May 2012 to 00:15, 31st May 2012
Duration, hours and minutes	8:20

Absorber Gas Flows

	Inlet	Wash Tower Outlet	Closure, %
Nitrogen, lb/hr	3580	3590	0.28
Oxygen, lb/hr	335	332	0.90
CO_2, lb/hr	867	206	
Moisture, lb/hr	215	262	
TOTAL, lb/hr	4997	4390	
Temperature, ºF	105	113	

Absorber Liquid Flows

	Inlet	Outlet
Water + solvent, lb/hr	8820	8600
CO_2, lb/hr	176	844
TOTAL, lb/hr	8896	9444
Temperature, ºF	103	117
Liquid/gas ratio, -	1.78	

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

	Inlet	Outlet	Closure, %
CO_2	1043	1050	0.67

CO_2 Flow Cross Checks

	Rates, lb/hr	Capture efficiency, %
CO_2 removed from flue gas	661	76.2
CO_2 absorbed by solvent	668	
CO_2 released from regenerator	680	

Lean-Rich Heat Exchanger Temperatures

	In	Out
Lean	248	128
Rich	118	229

Regenerator Data

Steam flow to reboiler, lb/hr	884
Steam pressure, psia	45.6
Steam temperature, ºF	280
Regenerator bottom temperature, ºF	251
Heat of regeneration, Btu/lb (measured)	1240
Heat of regeneration, Btu/lb (adjusted) (1)	1150

(1) Allowing for heat losses (estimated at 28,100 Btu/hr) and adjusting lean-rich approach temperature (lean out – rich in) from 10 to 6.5ºF.
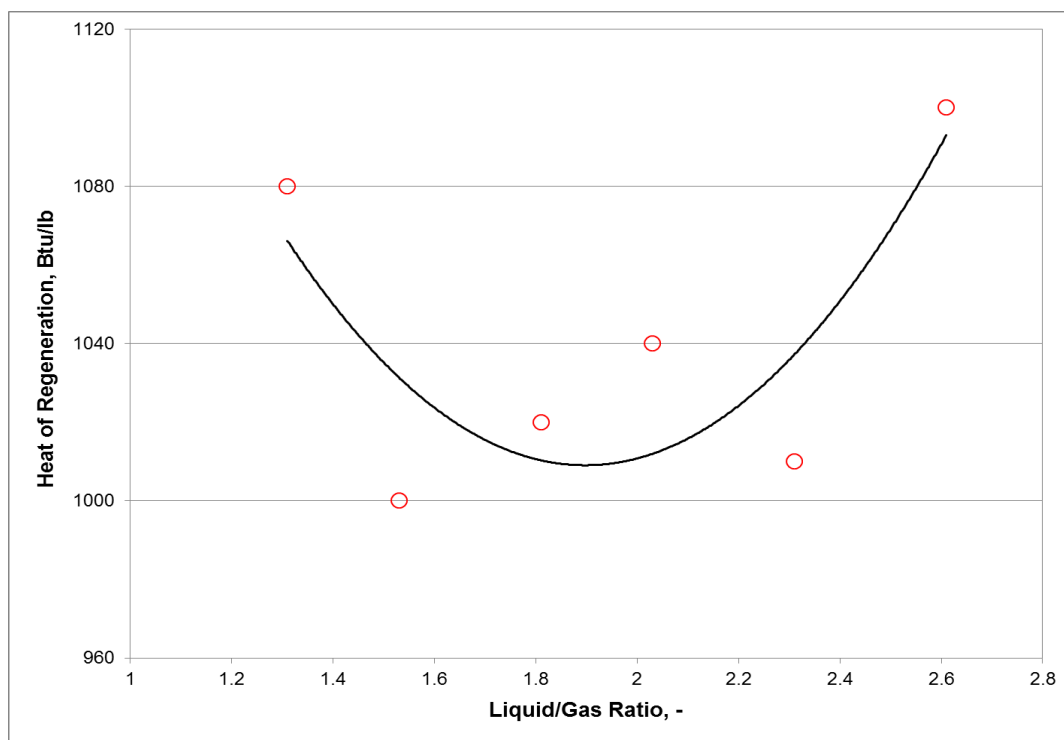
Figure A-1 - Variation of Heat of Regeneration with L/G Ratio for the Sample Mass Balance
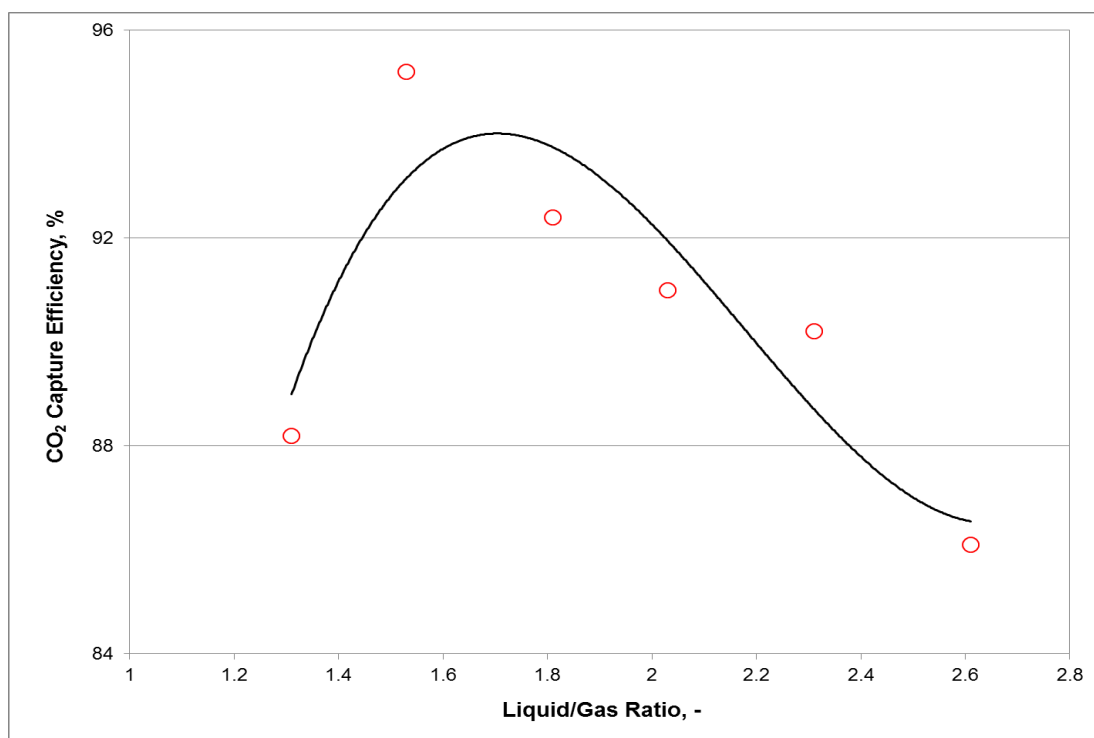Cases with Three Absorber Beds in Service

Figure A-2 - Variation of CO_2 Capture Efficiency with L/G Ratio for the Sample Mass Balance
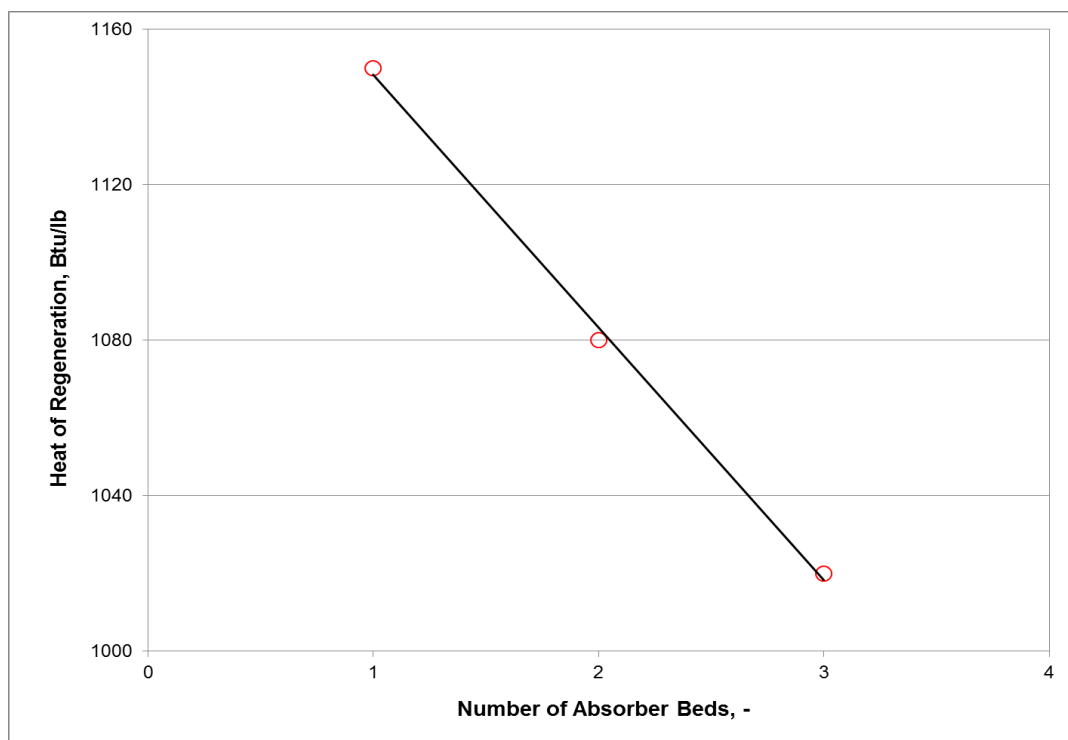Cases with Three Absorber Beds in Service

Figure A-3 - Variation of Heat of Regeneration with Absorber Beds for L/G Ratio of 1.8, for Sample Mass Balance Cases
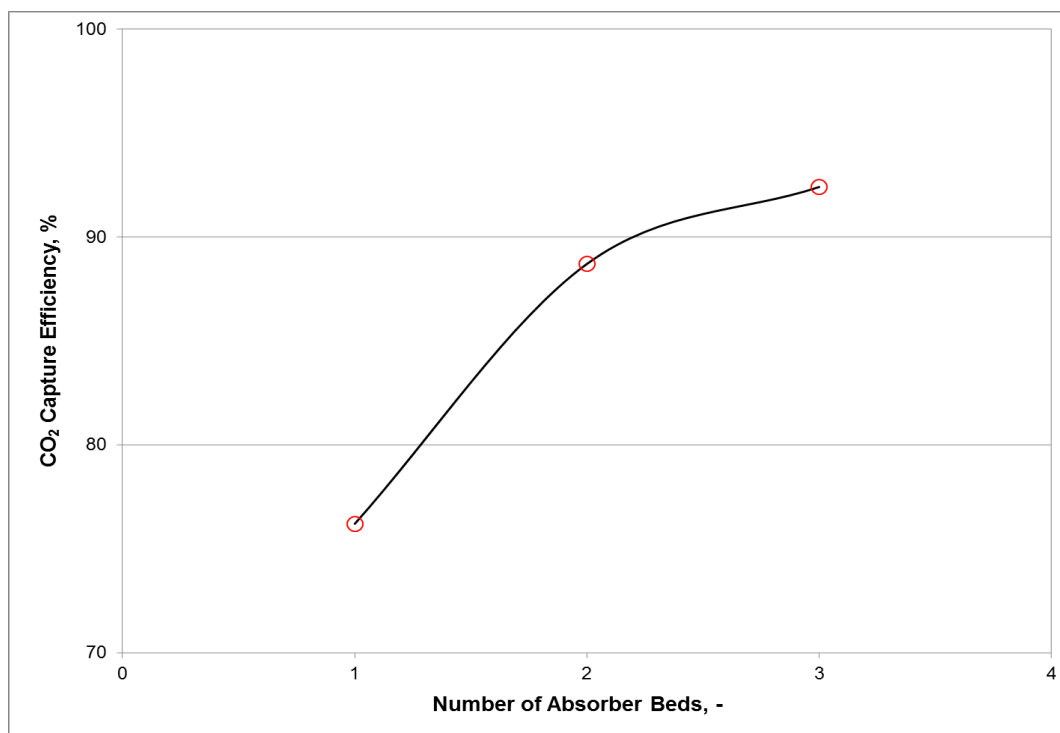

Figure A-4 - Variation of CO_2 Capture Efficiency with Absorber Beds for L/G Ratio of 1.8, for Sample Mass Balance Cases