Novel Solvent System for Post Combustion CO_2 Capture

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Final Technical / Scientific Report Novel Solvent System for Post Combustion CO_2 Capture

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Abstract

The purpose of this project was to evaluate the performance of ION's lead solvent and determine if ION's solvent candidate could potentially meet DOE's target of achieving 90% CO_2 Capture from a 550 MWe Pulverized Coal Plant without resulting in an increase in COE greater than 35%. In this project, ION's lead solvent demonstrated a 65% reduction in regeneration energy and a simultaneous 35% reduction in liquid to gas ratio (L/G) in comparison to aqMEA at 90% CO_2 capture using actual flue gas at 0.2 MWe. Results have clearly demonstrated that the ION technology is in line with DOE performance expectations and has the potential to meet DOE's performance targets in larger scale testing environments.

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Executive Summary

ION Engineering has been committed to developing coherent, economic solutions for post combustion CO_2 capture. A new class of concentrated-organic solvents was evaluated throughout this project and compared to a commercial benchmark using both theoretically driven performance simulations, and process simulations based on empirical data. Development of theoretical and empirical performance models, in addition to generating the required physical property, thermodynamic and process data to drive these simulations has largely comprised the activities of the project.

ION's solvents have been specifically designed to overcome the inherent thermodynamic inefficiencies of aqueous monoethanolamine (aqMEA) processes. Solvents currently in development at ION have demonstrated that new and existing fossil power plants can reduce CO_2 emissions with lowered impact on the cost of electricity (COE) compared to benchmarked carbon capture systems. The purpose of this project was to evaluate the performance of ION's lead solvent and determine if the solvent could potentially achieve DOE's target of 90% CO_2 capture from a 550 MWe pulverized coal plant with a resulting increase in COE less than 35%.

ION's lead solvent has demonstrated promising results towards achieving this goal set out by DOE. In this project, ION's lead solvent, using actual flue gas at 0.2 MWe and 90% CO_2 capture, showed a 65% reduction in regeneration energy and a simultaneous 35% reduction in L/G as compared to aqMEA. Results clearly demonstrate that the ION technology is in line with performance expectations and has the potential to meet the DOE target in larger scale testing demonstrations.

Introduction

Over the past decade, there has been a significant interest in exploring a new class of concentrated-organic solvents for post-combustion carbon capture. Early research efforts targeted the use of ionic liquids (ILs) and other novel organic solvents as alternative physical solvents for gas processing and CO_2 capture applications. The IL platform offered some unique opportunities with respect to controlling physical and chemical properties of the solvent. In addition, ILs have essentially zero vapor pressure and there is little risk of loss due to volatilization, which could theoretically eliminate the need for unit operations for solvent recovery.

Hundreds of different ILs have been explored in laboratory and small-scale tests for CO_2 capture, most with resulting apparent drawbacks. For the vast majority of ILs, physical solubility was the dominant mechanism of gas absorption. The inherent slow reaction rate and low CO_2 solubility renders the vast majority of ILs unsuitable for post-combustion CO_2 capture. Efforts had been made to develop amine-functionalized task-specific ionic liquids (TSILs) as a means of increasing CO_2 solubility for post-combustion applications. While TSILs were able to improve CO_2 uptake at low partial pressures, they suffered from high viscosities and prohibitively expensive synthetic procedures.

A more straightforward, cost-effective approach to improving CO_2 solubility in IL solvents was reported in 2008 (Camper, Bara, et al. *Ind. Eng. Chem. Res.* **2008**). This approach involved simply blending the IL with a commodity amine (e.g. MEA) to combine the benefits of IL non-volatility with the CO_2 capacity of traditional aqueous amine systems. This resulted in a low energy penalty solvent for post-combustion CO_2

capture by reducing the latent energy lost in the regeneration process without significantly increasing the liquid flow rates required. Incorporating an amine increased the CO_2 carrying capacity of the new organic, yet water tolerant solvent. Similar to ILs, imidazoles have been found to have desirable and tunable chemical and physical properties, including very low vapor pressures and viscosities comparable to water. Imidazole-amine blends have been demonstrated to provide a stable, low-aqueous platform with low volatility and high capacity for CO_2.

Project Definition

This project was intended to evaluate ION's carbon capture solvent technology to determine if it has the potential to meet or exceed DOE's economic criteria for post-combustion CO_2 capture technologies to remove 90% CO_2 from flue gas, with a $\leq$ 35% increase in Cost of Electricity (COE). The project included computer simulations to finalize process designs supported by laboratory evaluation, and the scale-up from the laboratory capture units to the bench scale process unit. In addition to bench-scale and simulation work, the project included testing against actual coal-fired flue gas and NGCC conditions. An economic analysis of the solvent performance was done according to DOE guidelines (Case 10) and used to estimate the COE.

Project Definition and Scope Statement

Phase 1: Solvent Development, Process Design and Construction of the Laboratory Test Unit included solvent performance analysis in the laboratory, process simulation modeling development using laboratory findings and solvent physical data, and testing of the solvent formulation in a laboratory scale continuous process test unit ("lab test unit"). During Phase I, a lab test unit (34 L/hr. liquid, 180 L/min gas) was designed, constructed and commissioned for solvent testing. The main objective of Phase I was to develop both the solvent and laboratory protocols to evaluate solvent/process performance during Phase II to advance the solvent to field pilot (4 – 12 LPM scale) ready status.

Phase 2: Economic Analysis of Solvent Performance at Scale included the development of an estimate for the COE metric for comparison to other technologies in use and under development. Experimental results from steady state operation of the lab test unit with ION's solvent were used to feed an equilibrium model of the capture process developed in ASPEN+^{TM}.

Scope of Work

A 22 month project was proposed to demonstrate the performance of ION Engineering's solvent in CO_2 capture using laboratory and lab test unit data and an ASPEN+ ^{TM} simulation model to estimate COE. Project scope included simulations to finalize process designs, supported by laboratory evaluation, and the scale-up to the lab test unit. Design, construction, installation, operation and monitoring of the lab test unit were included, as well as commercial and operational assessments of the ability to scale up following the project. Multiple organizations were involved, providing robust development, engineering and plant operations expertise to manage successful project design and execution. Such broad private sector involvement and support improved the technology's probability of ultimate commercial deployment and success.

Project Significance

The solvents under development by ION and the University of Alabama showed a significant reduction in energy penalty compared to the aqMEA baseline and other advanced amine solvents. High solvent carrying capacity for carbon dioxide and reduced regeneration energy requirement were key factors limiting the process impact on COE. The presence of water in the solvent resulted in technical and economic benefits, while the effective water management in the system minimized make-up water requirements.

Degradation of ionic liquid based solvents led to the development of second-generation imidazole-based system. The stability of the imidazole-based solvent slowed degradation and reduced the need for solvent replacement. This led to a greater understanding of the influence of the molecular structure on physical and chemical properties, and provided a rational approach for further improvements in solvent composition.

Project Goals and Objectives

The objectives of this project were to evaluate the ION solvent technology for coal-fired post-combustion carbon capture (PCCC) using process modeling simulation, laboratory experimentation, and bench scale testing in a ~0.57 LPM continuous process unit, and testing against actual coal-fired flue gas.

To ensure that project objectives were met, success criteria were established. Success criteria proposed and negotiated by phase were:

Phase I: Process Design

The success criteria for Phase I were that the solvent must regenerate to a maximum CO_2 loading of (1.1 mol/kg solvent) at 125-150°C, and the solvent must show no degradation when held at 120°C for the mean residence time for regeneration in the proposed 4 LPM process. Process modeling results with updated solvent parameters from laboratory testing should be consistent with previous projections for reduced energy requirements, and detailed engineering design should be completed with reasonable projections.

Phase II: Process Operation and Evaluation

Success criteria for Phase II included: (1) a continuous run of at least 72 hours at steady-state with 90% capture of CO_2 from actual flue gas; (2) a demonstration of minimal or no degradation of the solvent in presence of flue gas; (3) the data needed for evaluation is effectively captured by sampling activities and process analytics; (4) the evaluation of solvent and process maintenance requirements are profiled for scale-up; (5) engineering, economic and operational models confirming the potential of the ION solvent and process to significantly reduce capture costs when implemented at full scale (500 MWe); and (6) evidence in engineering and economic analysis that DOE targets of 90% CO_2 capture and a maximum increase in COE of 35% may be possible at full scale.

Major Changes to the Project:

In Scope Modification I:

Based on Phase I results, ION proposed an in-scope modification of the Phase II Scope of Work (SOW) in order to move forward with the identification of a commercially attractive solvent with a better stability profile (**Table 1**). The project management plan was amended to include solvent screening & selection tasks in Phase II (**Figure 1**) to focus on the identification of solvents demonstrating less degradation than the aqMEA benchmark.

Table 1: Comparison of original project to updated Phase II scope.

Original Phase 2		Updated Phase 2
	Added	**4. Selection of Solvent B** 4.1 Screen prospects 4.2 Rank and prioritize top candidates 4.3 Conduct detailed candidate characterization
4. Bench-scale Field Testing 4.1 Fabricate field test unit 4.2 Receive solvent for tests 4.3 Install/commission test unit 4.4 Analyze field test data 4.5 Summarize findings	Deferred beyond project timeline	
5. Assess performance 5.1 Model process at larger scale 5.2 Conduct commercial/operational analysis 5.3 Summarize findings	Modified	**5. Process Development** 5.1 Update/validate simulation model 5.2 Conduct test runs in lab pilot unit 5.3 Conduct process simulation studies **6. Technical and economic evaluation** 6.1 Develop reference unit design & COE metrics 6.2 Summarize findings and benefits analysis
Task 6. Decommission test unit	Deleted	

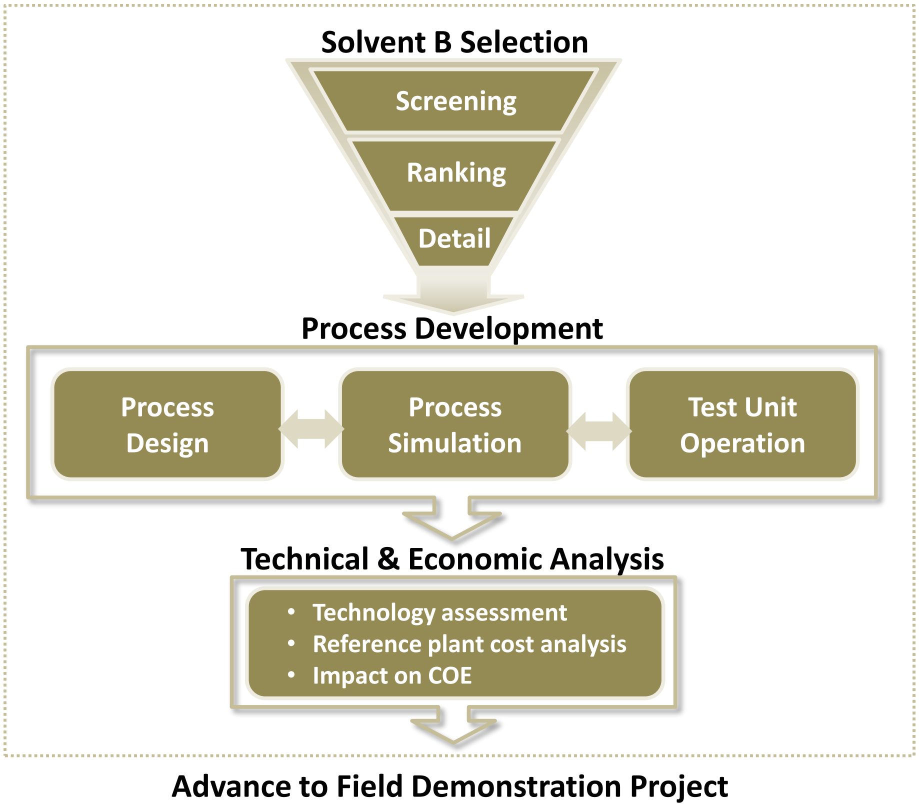


Figure 1: Flow diagram showing amended PMP including solvent screening and evaluation.

Phase II Continuation:

Based on the encouraging results for Solvent C, ION met with DOE NETL in November 2011 and proposed an in scope modification to the project that included additional testing of Solvent C at ION and testing with actual flue gas at EERC using their 0.2 MWe coal-fired pilot. These modifications were approved in March 2012 after a formal application had been submitted.

Phase II Continuation Objectives:

The objectives for the Phase II continuation were (1) to develop and test the predictability of ION's Process Simulations to facilitate the design of larger scale process equipment, (2) directly compare the performance of ION technology to an aqMEA CO_2 capture process, and (3) perform a techno-economic analysis of the ION solvent based on solvent performance at the EERC. To achieve objective (1) the goals were to improve agreement between ASPEN+ ^{TM} simulation and experimental data, to empirically determine solvent performance over an extended range of operational conditions, and to validate the regeneration energy requirements. Comparison of ION's advanced solvent with aqMEA for objective (2) involved data for aqMEA run on the process test unit at the EERC facility, and testing of aqMEA in the ION Test Unit.

Phase II Continuation Scope of Work:

A 12-month project continuation was approved to achieve the objectives outlined above. To achieve objective (1) improvements were made to the ION's Laboratory Test Unit and solvent performance was measured over an extended range of operational conditions. The experimental data were used to improve ASPEN+^{TM} software simulations. The project scope also included testing campaigns with real flue gas at the EERC facility to manage the water content, further test and optimize operational conditions and directly measure the net heat required for solvent regeneration.

Objective (2) was achieved by solvent testing and benchmarking of aqMEA and comparison to ION's Solvent C. This work was done at the ION's lab test unit using simulated flue gas and at the EERC facility with real flue gas.

An economic analysis of ION Solvent C performance was conducted by the EERC based on DOE Case 10, and compared to aqMEA for Case 10.

Results and discussion:

Phase I: Solvent Development, Process Design and Construction of Laboratory Test Unit.

Phase I Objective(s):

The main goal of Phase I was to develop tools and in-house capabilities to assess 1st generation ION technology for post-combustion CO_2 capture using the following success criteria: (1) solvent regeneration to a maximum CO_2 loading of (1.1 mol CO_2/kg solvent) at 125-150°C, (2) validation that the IL-amine solvent does not degrade while held at 120°C for the mean residence time for regeneration in the proposed 3.8 liter per minute (LPM) process, and (3) process modeling results with updated solvent parameters are consistent with previous projections for reduced energy requirements.

Phase I Technical Approach:

In order to achieve these objectives, ION developed its technical capabilities in three main areas: (1) analytical laboratory, (2) lab test unit, and (3) Process simulation (ASPEN+^{TM}). At ION, an analytical laboratory has been established to enable bench top solvent testing and analysis including equilibrium CO_2 loading, temperature dependent CO_2 solubility, isothermal and cycled solvent degradation (under controlled single and mixed gas atmospheres (N_2, CO_2, O_2 and SO_2)) and GC/MS analytical capabilities for gas and non-ionic liquid samples. A lab test unit (**Figure 2**) was designed, fabricated, and commissioned in order to allow steady state operation and testing of ION solvents with synthetic flue gas (N_2, CO_2 and H_2O).

Figure 2: Image of ION’s ~0.57 LPM continuous process lab test unit.

A process flow diagram of the lab test unit is shown in **Figure 3**, **Figure 4**, & **Figure 5**. ION's lab test unit provided critical information regarding solvent performance under steady state operation, which has been used to develop the ASPEN+ ^{TM} process simulation. A process simulation (ASPEN+^{TM}) has been constructed in collaboration with Bara's lab and used to develop a simulation model for ION solvents. Commercially available engineering performance simulation packages are not currently programed for the use of ION's proprietary solvents. Phase 1 work has developed specific modules for ASPEN+ ^{TM} for the characterization of ionic liquid and amine mixtures. Simulation of ION's solvents was done using the ENRTL-RK property method. The ENRTL-RK is identical to the ELECNRTL method if only one electrolyte is present, but is better equipped to handle mixed electrolytes and has a simplified framework for handling the thermodynamic properties calculations. Representation of ION's novel solvents was achieved using ASPEN+ ^{TM} features that enable the creation of a "user-defined" component. The parameters that are needed for property calculations can be supplied in two ways: (1) ASPEN+ ^{TM} includes a number of parameter estimation correlations that are based on the molecular structure of the compound, and (2) parameters can be correlated directly from experimental data supplied by the user for the compound.

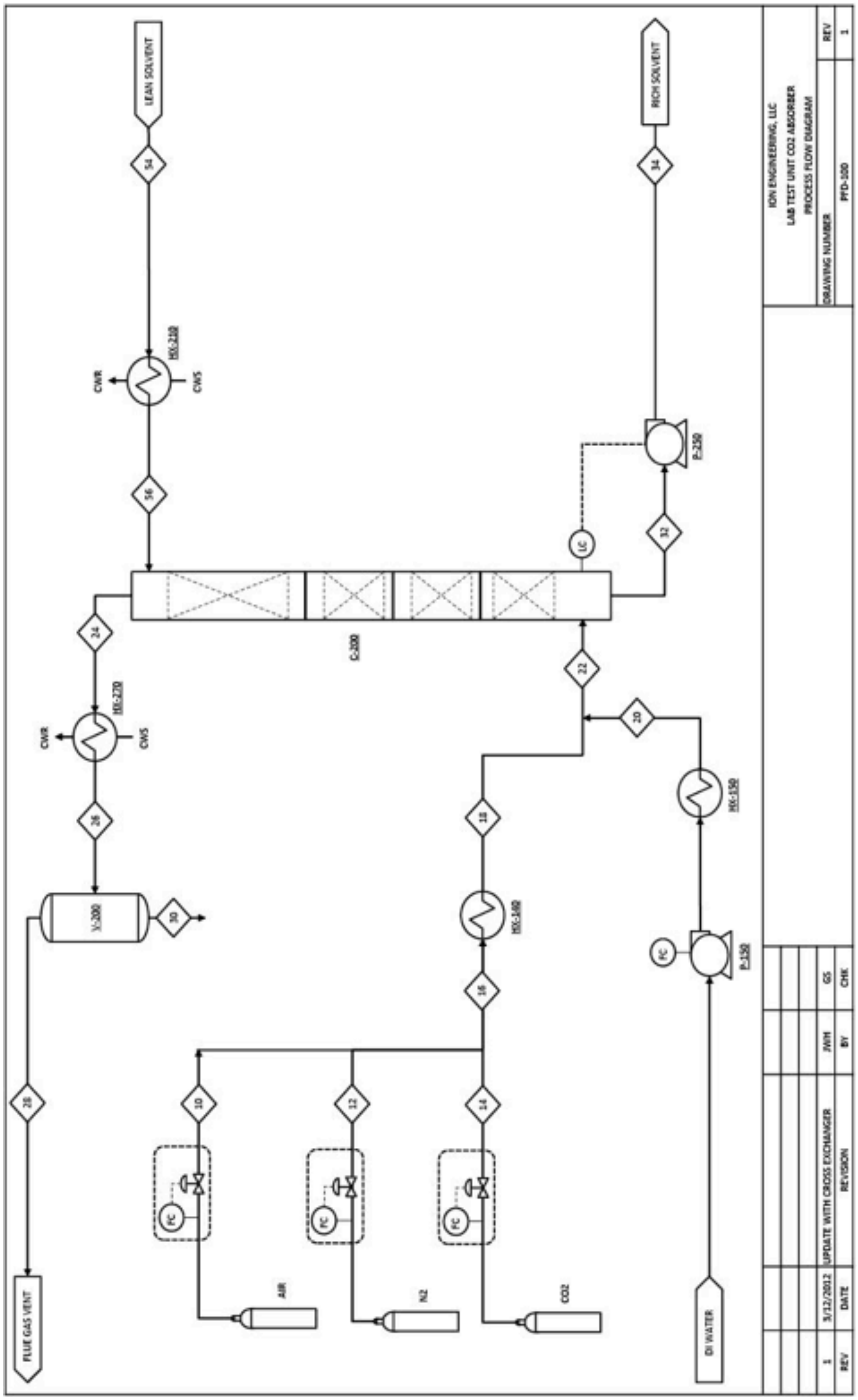


Figure 3: PFD of Laboratory Test Unit absorber section.

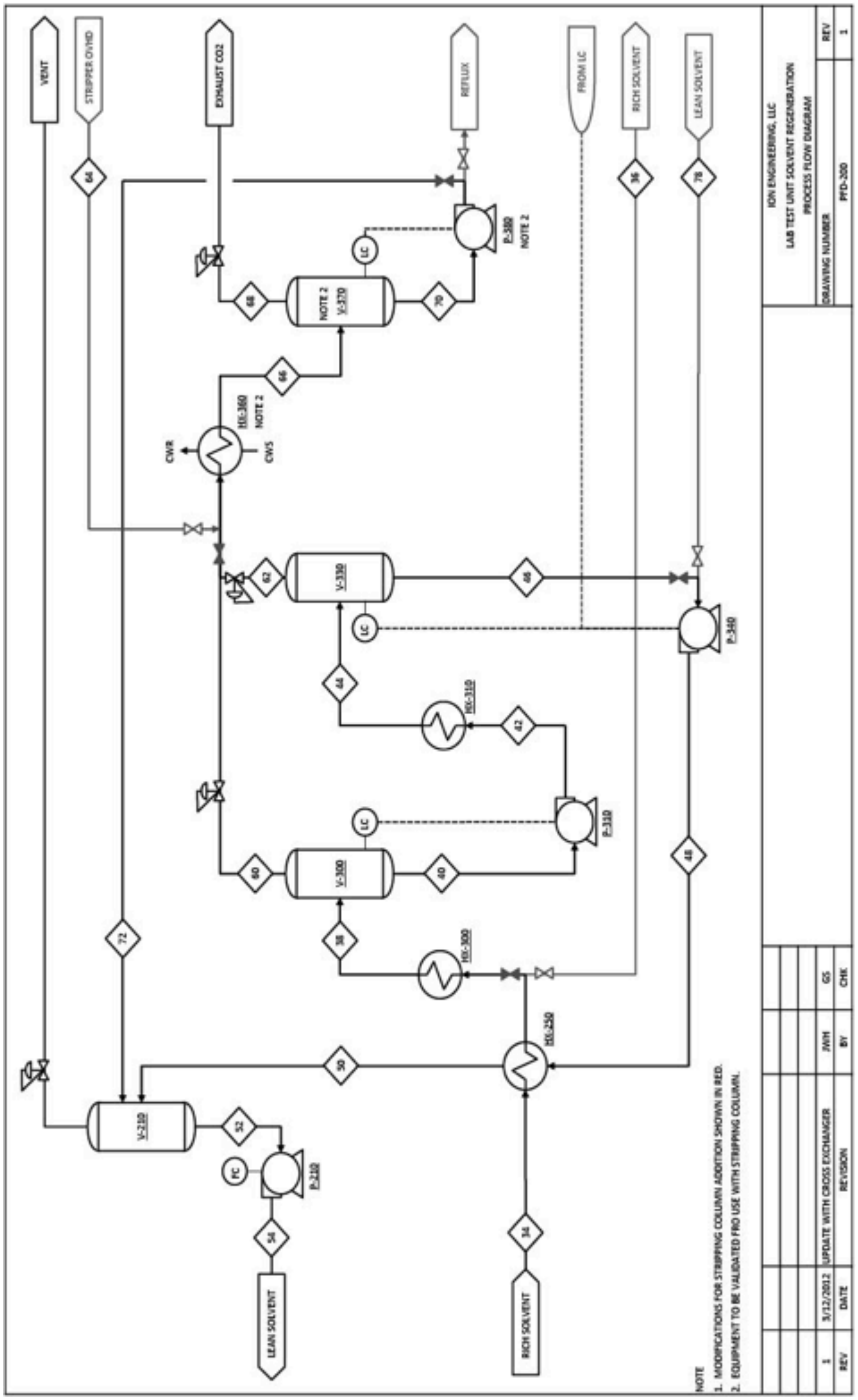


Figure 4: PFD of Laboratory Test Unit regeneration section.

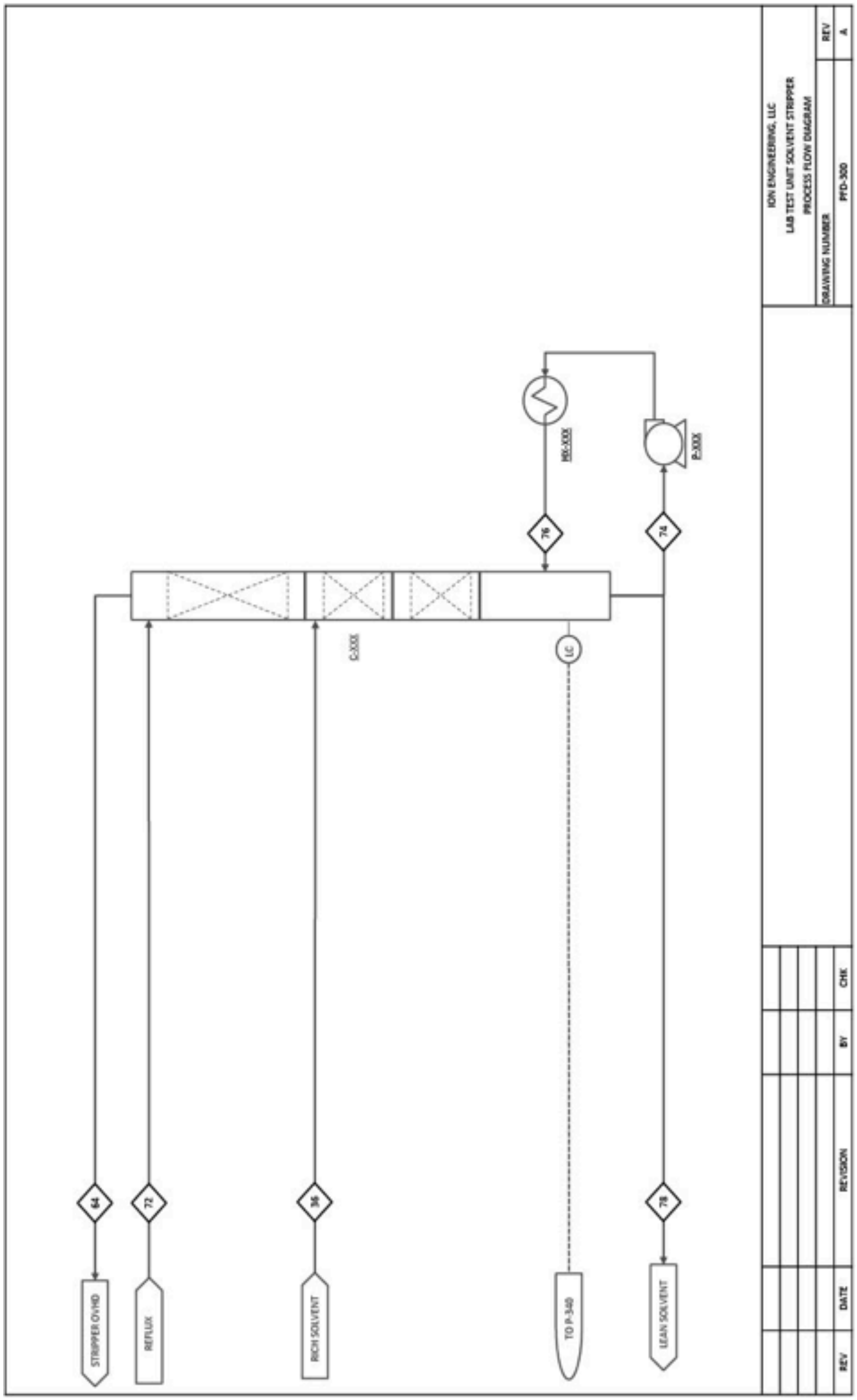


Figure 5: PFD of Laboratory Test Unit steam stripping column.

In Phase I, a simulation model was developed in ASPEN+ ^{TM} for Solvent A using physical property data measured in ION’s laboratory. Simulation of ION’s solvents was done using the ENRTL-RK property method with experimental solubility data incorporated into the model as shown in **Figure 6**. The approach to equilibrium in the absorber was estimated by using empirical data from the lab test unit for column temperatures and intermediate solvent loadings from process test samples. Using the process model, regeneration energy requirements were calculated for both Solvent A and for aqMEA, which had physical property data included in the ASPEN+ ^{TM} software package. The calculated regeneration energy results for Solvent A and for aqMEA are shown in **Figure 7** and normalized to 1.0 for aqMEA. A break down of simulation results for specific components of the process heat duty is given in **Table 2**, similarly with aqMEA results normalized to 1.0.

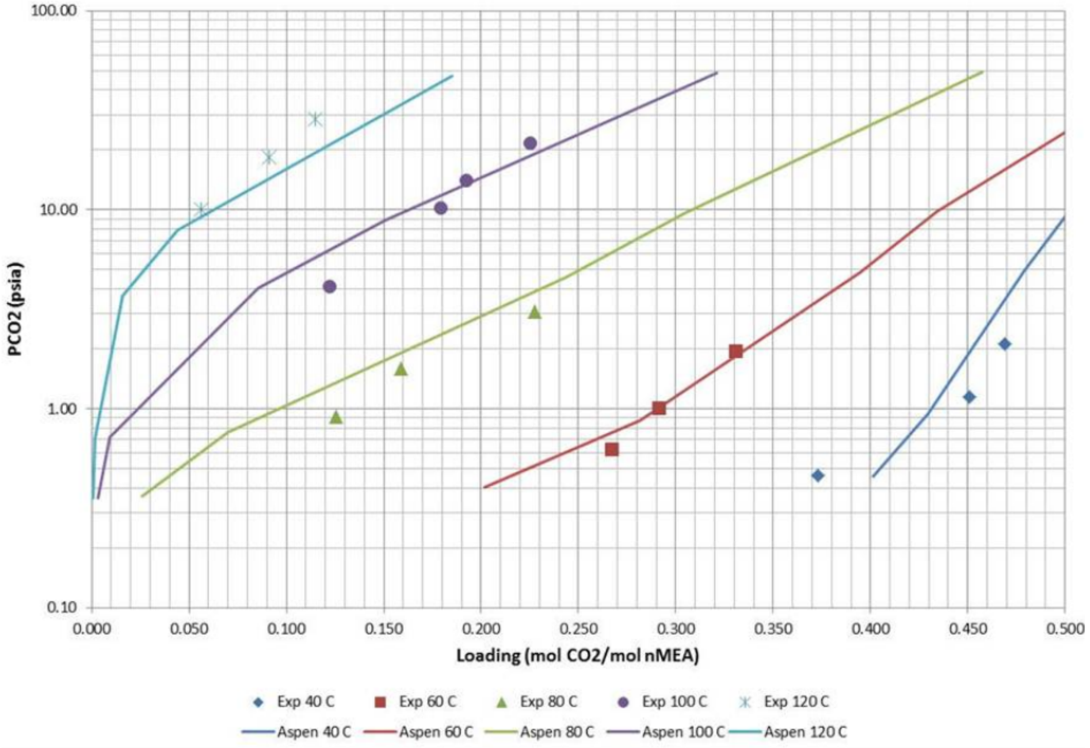


Figure 6: CO_2 solubility data for Solvent A with lines for ASPEN+ ^{TM} regression.

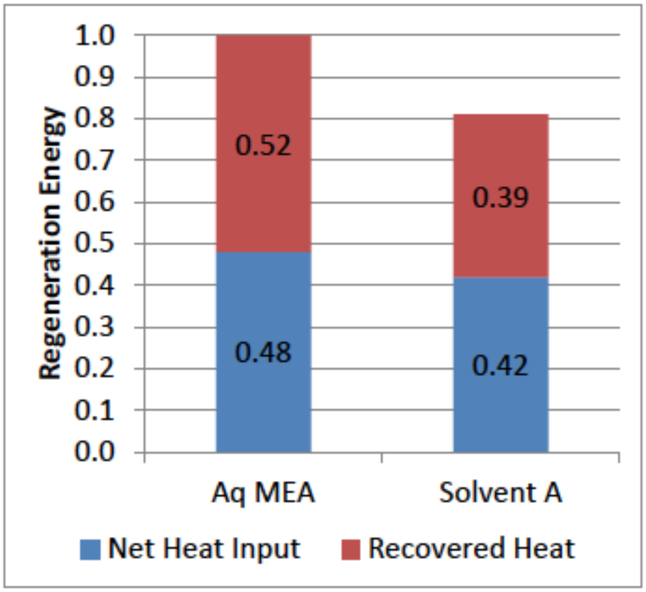


Figure 7: Comparison of regeneration energy as calculated by ASPEN+ ^{TM} process simulation for Solvent A and aqMEA (MEA normalized to 1.0).

Table 2: Comparison of process heat duty components from ASPEN+ ^{TM} process simulation between aqMEA (normalized to 1.0) and IL Solvent A.

Component of Heat Input	Aqueous Amine	Solvent A	Effect
Latent Heat Duty	1.0	0.4	+
Sensible Heat Duty	1.0	0.7	↔
ΔH Reaction/Absorption	1.0	1.3	?
Relative Total Energy	1.0	0.8	+

While conducting early test runs with Solvent A in ION's lab unit, two potential solvent issues were revealed. The first observation was made during anhydrous operation of the solvent, in that absorber pressure was observed to increase during the experimental run. Evaluation of the test unit revealed an unexpected formation of amine carbamate crystals in all absorber flue gas outlet piping, leading to increased resistance to flow (**Figure 8**). The entire absorber outgas section was subsequently cleaned and the experiment repeated. The repeated experiment showed reduced carbon capture and again resulted in increasing backpressure. Observation showed that the same build-up of carbamate crystals was the source of the increased backpressure. The solvent was then diluted to 5 wt.% water content and the experiment repeated.

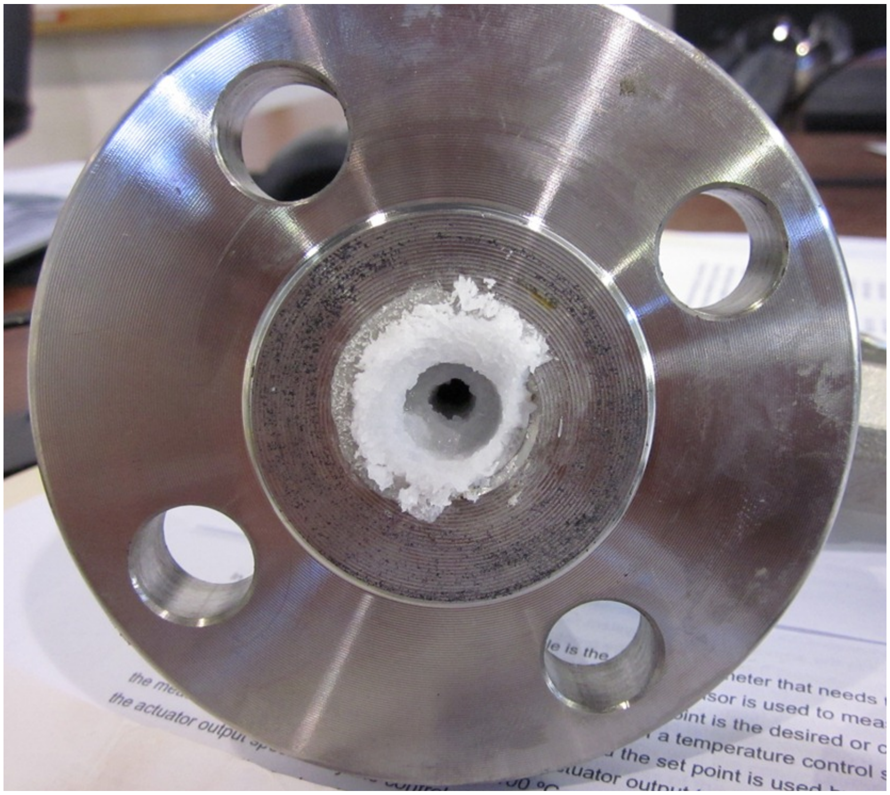


Figure 8: Image of test unit absorber outlet flange showing build-up of amine carbamate crystals during anhydrous operation with Solvent A.

Using Solvent A with 5% water content showed a large reduction in the amount of crystalized carbamate in the piping. Carbon capture performance was again observed to decrease upon repeat of the experiment, though not as significantly. With water content raised to 10 wt.%, the experiment was repeated, and no crystalline carbamate formation was observed in the piping. Repeating the experiment again showed reduced performance in the following experiment. The reduced performance observed for the different water content is shown in **Figure 9** as increased slip of CO_2 through the absorber.

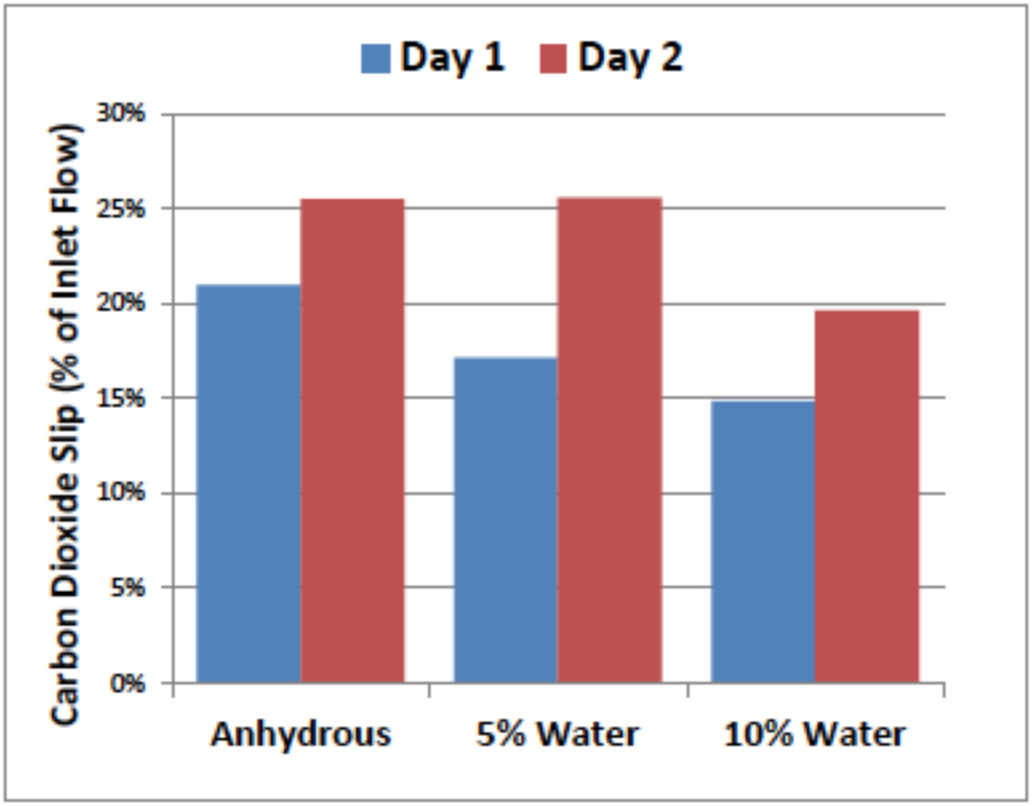


Figure 9: Carbon capture results for repeated experiments with Solvent A in test unit with 0%, 5%, 10% water content by weight (synthetic flue gas, 12 vol% CO_2).

This result led ION to revise its solvent stability performance metric to include more rigorous testing. Solvent samples containing CO_2 were subject to thermal cycling between 40°C and 120°C. The measured pressure after temperature cycling of Solvent A showed an increase in pressure at both temperatures (**Figure 10**) indicating a loss of CO_2 loading capacity at both temperatures due to decomposition of the solvent.

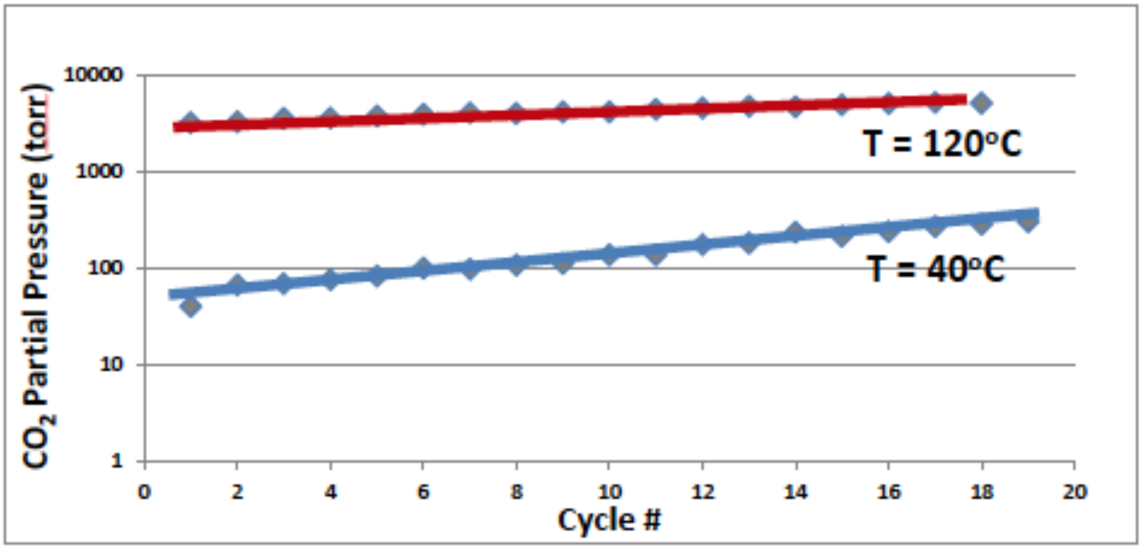


Figure 10: Results of the thermal cycling experiment with Solvent A showing increased pressure with repeated cycling.

An accelerated solvent thermal aging experiment was designed to quickly measure the ability of the solvent to carry CO_2 over time. A solvent sample was placed in a closed cell, evacuated, and loaded with CO_2 to 0.4 mol CO_2/mol amine. The cell was then brought to 120°C while stirring and the cell pressure was recorded. **Figure 11** shows accelerated aging results of Solvent A in comparision to aqMEA expressed as a fraction of initial amine capacity. This confirmed the previous finding from the temperature cycling experiment (**Figure 10**) that Solvent A containing CO_2 is significantly decomposing under the experimental conditions.

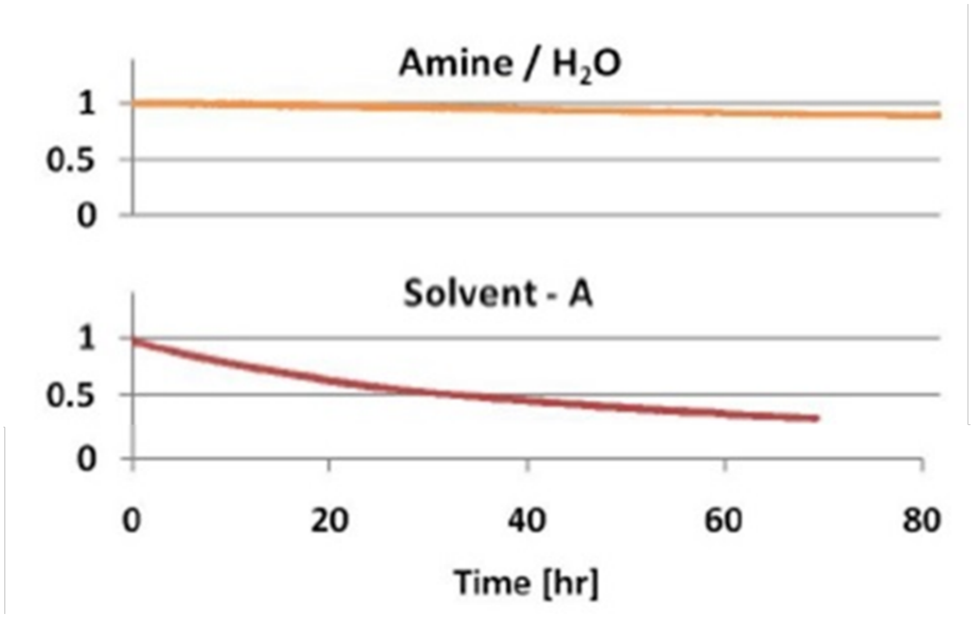


Figure 11: Results of accelerated thermal aging experiment at 120°C for 1st generation Solvent A and 30 wt.% aqMEA Amine/H_2O). Results are shown as the fraction of initial loading capacity.

Initial concerns regarding Solvent A degradation were later confirmed through extensive laboratory analysis and have been published [LaFrate, et al. *Energy & Fuels* 2012]. Therefore, even though Solvent A demonstrated good performance in the continuous CO_2 capture process and possessed low regeneration energy requirements in initial simulation studies, degradation of the specific anion in this solvent was observed at levels that obviated its commercial viability due to a cross alkylation reaction with the amine.

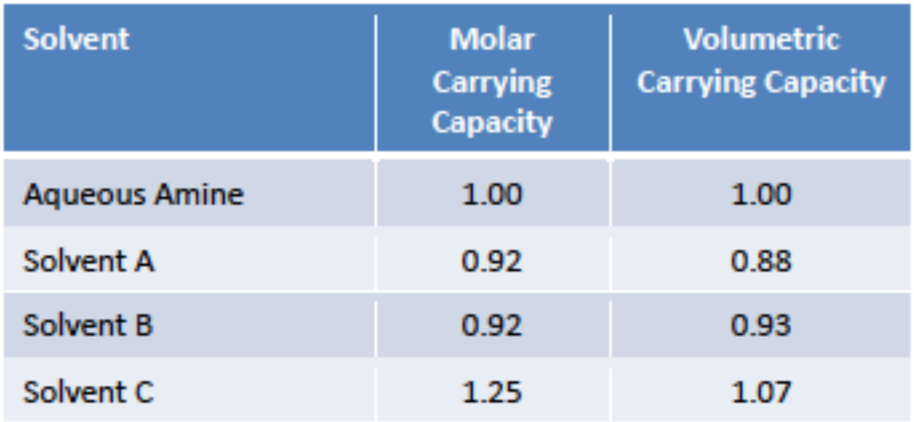
As a result of the unexpected degradation of Solvent A, ION created a series of test protocols to screen and evaluate base materials and identified a slate of potential replacements for the solvent base with a range of viscosity, reactivity, polarity and hydrophobicity. The slate of "prospects" was chosen to represent all reasonable alternative anions for the ionic liquid as well as non-ionic compounds such as imidazole-based solvent mixtures under investigation by Bara's group at University of Alabama.

Test protocols included initial screening based on physical properties such as viscosity and density, followed by more complete testing involving accelerated thermal aging and degradation studies of both loaded and unloaded solvent samples. Detailed data such as CO_2 solubility and solvent vapor pressure were acquired for only the most promising solvent candidates and used to populate the process simulation model. Simulation studies, test runs in the 34-liter per hour (LPH) lab pilot unit and economic analyses were conducted to assess the attractiveness of several solvent mixtures.

Phase I Results:

Results of Phase I showed that ION solvent carrying capacities (**Table 3**) were comparable or greater than aqueous MEA and sufficient to meet Phase 1 success criteria. Also, process simulations (**Figure 7**) were consistent with initial performance projections supporting that 1st generation ION solvent offers significant (~20%) energy savings over aqueous MEA systems. However, the first generation ION solvent, Solvent A, did not show thermal stability at 120°C sufficient to meet the success criteria.

Table 3: Equilibrium CO_2 carrying capacity for ION solvents normalized to aqueous MEA.



Solvent	Molar Carrying Capacity	Volumetric Carrying Capacity
Aqueous Amine	1.00	1.00
Solvent A	0.92	0.88
Solvent B	0.92	0.93
Solvent C	1.25	1.07

As a result of the thermal stability and degradation study results, ION proposed an in-scope modification of the Phase 2 SOW in order to move forward with the identification of a commercially attractive solvent with a better stability profile. The project management plan was then amended to include solvent screening & selection tasks in Phase 2 (**Figure 1**) to focus on the identification of solvents demonstrating less degradation than the aqMEA benchmark.

In addition to the work at ION, the collaboration with Dr. Bara at UA identified a potential solvent (Solvent C, an imidazole – amine mixture) from the broad class of molecules Dr. Bara was investigating [Shannon & Bara, *Ind. Eng. Chem. Res.* 2011].

Phase II: Economic Analysis of Solvent Performance at Scale.

As previously stated, because of the stability issues for Solvent A, the Phase II scope of work was revised to focus on further development of Solvents B & C and include a complete technical and economic evaluation.

Phase II Objective(s):

The goal of Phase II was redefined as the development of an estimate for the potential impact on the cost of electricity for using ION's technology in comparison to other alternatives being evaluated by NETL. The redefined objectives, as well as the original Phase II objectives are given in **Table 1**.

Phase II Technical Approach:

Phase II work started with laboratory work and simulation development for two solvent candidates identified in Phase I, Solvent B (IL/amine) and Solvent C (imidazole/amine). Accelerated thermal aging studies were accomplished on both candidates and showed substantial improvement over the 1st generation solvent (**Figure 12**).

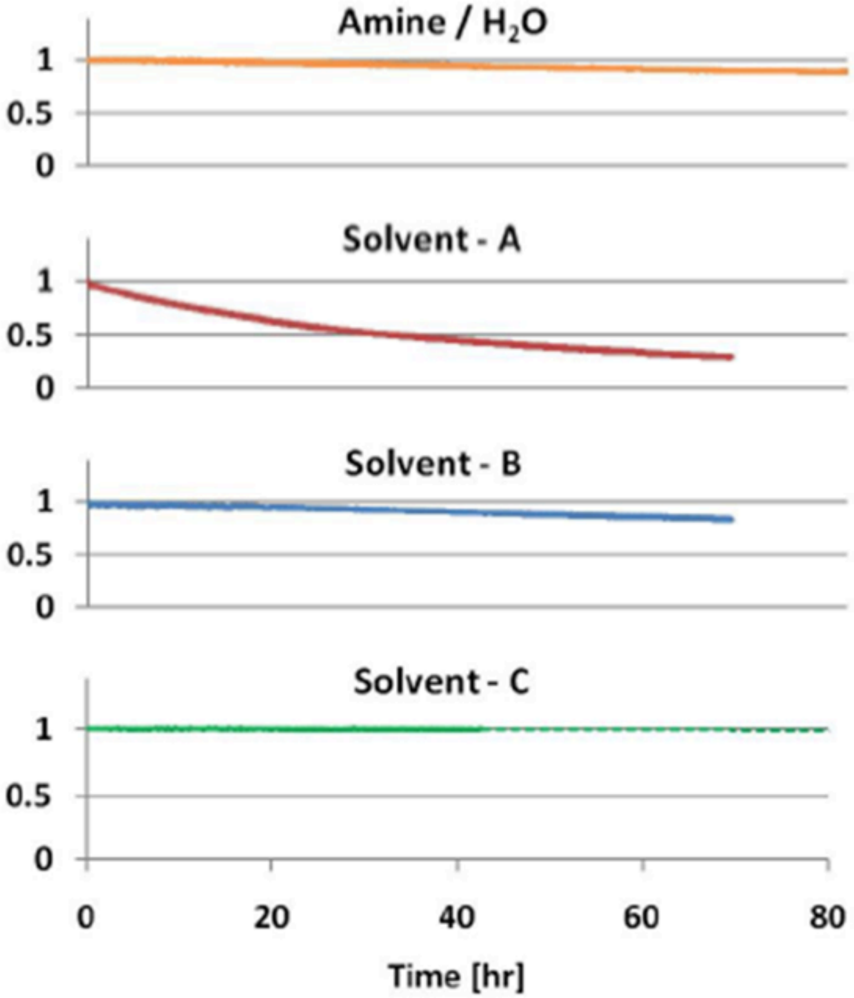


Figure 12: Results of accelerated thermal aging experiments at 120°C for 1st generation Solvent A, 2nd generation Solvents B, C and 30 wt% aqueous MEA. Results are shown as the fraction of initial loading capacity.

The accelerated aging experiment was done in a closed-cell experimental vessel with a total volume of 0.3 L. The vessel was equipped with a temperature control/monitoring device, a stirrer, and a pressure transducer. A solvent sample (50g) was placed into the vessel and evacuated to remove ambient atmosphere. Using a gas regulator, CO_2 gas was added to the cell and the weight monitored until the solution was loaded to approximately 0.4 mol CO_2/mol amine. The apparatus was then insulated and heated to 120°C and the temperature and pressure recorded. The increase in pressure over time was calculated as the percent loss of original carrying capacity vs. time (**Figure 12**). CO_2 solubility data was measured for both solvent systems and used as input into the ASPEN+ TM process simulation (**Figure 13**). Solvent loadings were calculated for typical absorber and regeneration process conditions from the solubility data to determine solvent carrying capacities and compared to aqMEA (**Table 3**).

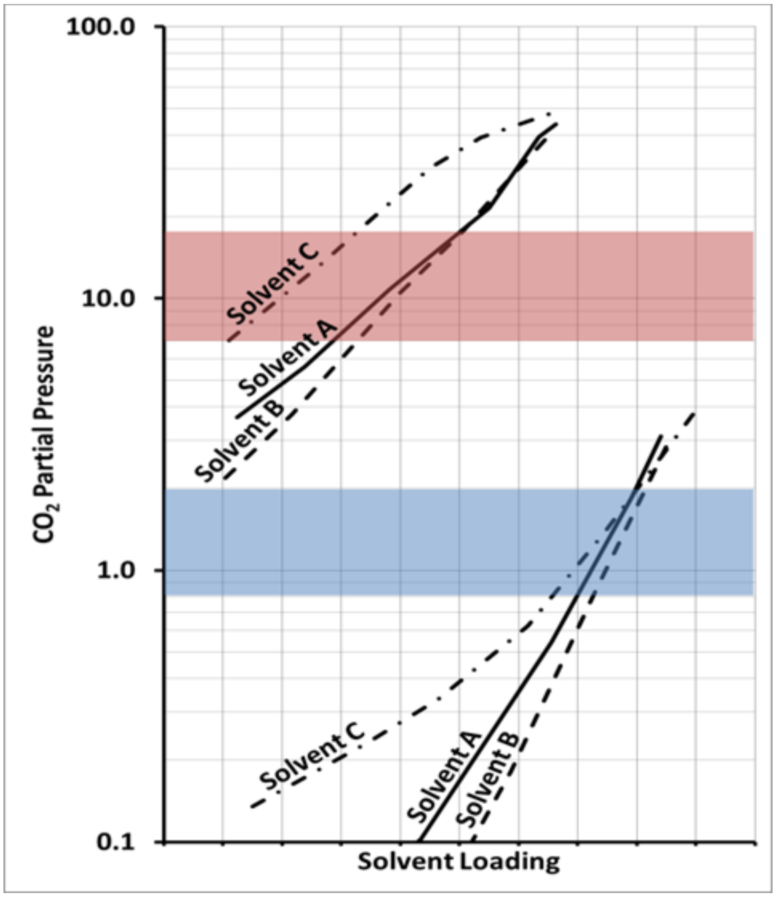


Figure 13: CO_2 solubility data for ION 1st (A) and 2nd (B&C) generation solvents showing solvent loading vs. equilibrium CO_2 partial pressure (PSIA). Process absorber (blue) and regeneration (red) P_{CO_2} ranges indicated. Solvent loading range shown from 0 to 0.5 mol CO_2/mol amine.

During Phase I, ION identified several upgrades and modifications that would improve the lab pilot unit for operation in Phase II. Replacement of metering pumps with positive displacement design pumps enabled better reproduction of absorber solvent feed rates independent of absorber process conditions. The addition of liquid volumetric flow transducers allowed monitoring of solvent flows into and out of the absorber and allowed feedback control of lean solvent feed rate. A gas chromatograph was added to evaluate the purity of the product CO_2 stream and confirm the rich and lean synthetic flue gas composition. A lean-rich solvent cross exchanger was installed for heat recovery integration and to improve the utility of the test unit data for the process simulation, which incorporated a cross exchanger. After completing the upgrades, the selected candidate solvents were evaluated in ION's test unit using a pure N_2/CO_2 mixture. The results from the lab test unit were used to calibrate and validate the ASPEN+ ^{TM} process simulation. Additional test runs were performed to profile a range of operating conditions for CO_2 removal efficiency.

The process simulation was calibrated with operational data from the lab test unit, and a new simulation case was developed for a reference plant (assumed to be a hypothetical 500 MW coal fired power plant). A process flow diagram and heat and material balance were produced for the reference plant to support economic evaluation (see Appendix_A_ION_Sections_of_PCO2C_Final_Report_Coal). Additionally, the components of regeneration energy for Solvents B & C were calculated and compared to similar values computed for a typical aqMEA solution (**Figure 14**). The process simulation results indicated a >20% reduction in net heat input for ION's 2nd generation solvents when compared to aqMEA (**Figure 15**). In each case, the energy demand was calculated for the CO_2 capture system at equilibrium conditions in both the absorber and the regeneration system. Because CO_2 absorbers do not operate at equilibrium conditions, these results should be considered to be hypothetical cases. Deviations from equilibrium in the absorber and regeneration system will tend to change the solvent circulation rate. However, a change in solvent flow rate does not necessarily have a large impact on the net heat input required for regeneration. Therefore, the equilibrium case is still useful to gauge the potential energy savings that can be obtained for a particular CO_2 solvent technology.

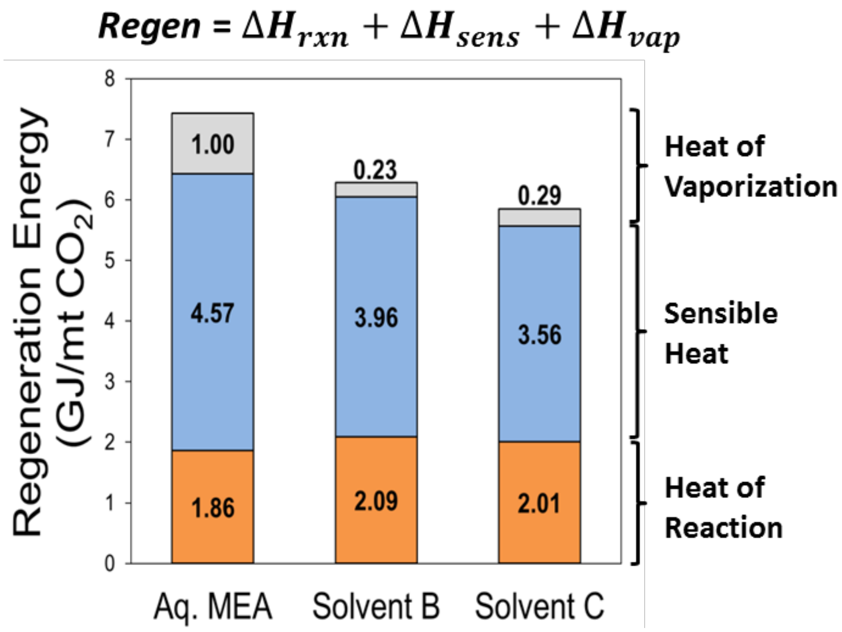


Figure 14: Comparison of thermal regeneration components for 2nd generation Solvents B & C, and aqueous MEA.

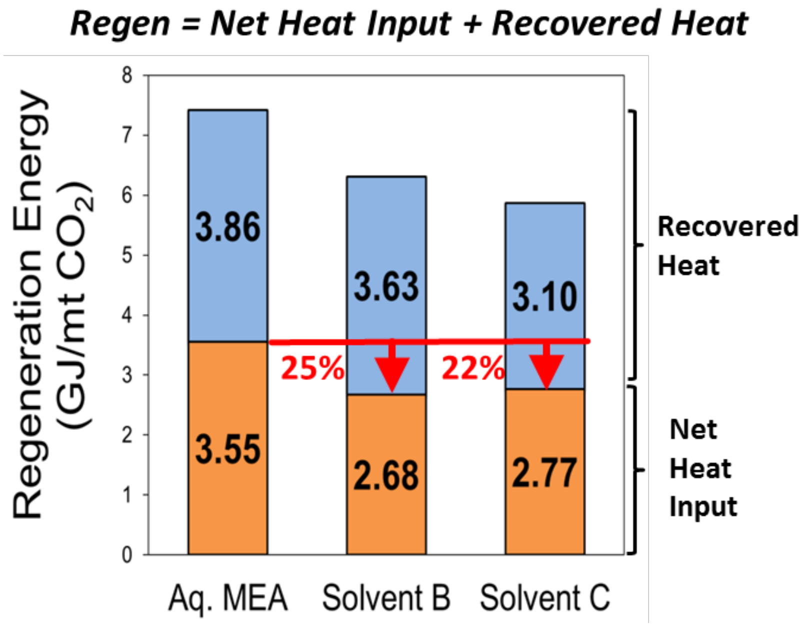


Figure 15: ASPEN+ TM comparison of thermal regeneration requirements for 2nd generation solvents and aqueous MEA showing >20% reduction in heat input (Topical rep. 4.3).

The regeneration energy demands for the two solvents were compared to the regeneration energy demand for an advanced aqMEA process. Typical operating conditions for the advanced aqMEA process were obtained from the literature, and used to construct a process simulation. These simulation results were used to calculate the total regeneration energy and the net heat input demand for the aqMEA process.

Other parasitic energy demands typical to CO_2 capture solvent processes were not within the scope of this analysis. Some examples of these other energy demands include: solvent cooling and condensation; CO_2 compression power; and liquid solvent pumping power. Additionally, many primary and secondary aqueous amines require reclaiming to purify the solvent of heat-stable salts. It is not known what, if any, percentage of the solvent will need to be reclaimed and that energy demand has also been excluded from the evaluation for Solvents B and C.

Based on the encouraging results for Solvent C, ION met with DOE NETL in November 2011 to propose an in scope modification to the Project that included additional testing of Solvent C at ION and testing at EERC using their 0.2 MWe coal fired pilot unit. These modifications were approved in March 2012 after a formal application had been submitted.

Prior to receiving approval for the proposed continuation to Phase 2, ION initiated preliminary design and costing studies for a hypothetical 500 MWe coal-fired power plant with post-combustion CO_2 capture using WorleyParsons (WP). ION's work with WP has resulted in a scalable costing model that can be further calibrated based on demonstrated solvent performance.

Phase II Result(s):

Solvent screening activities were successful and led to the identification of Solvent B (a more stable IL – amine mixture). While successful in stability and performance, the high cost of the IL in Solvent B would not have been economically viable. A second candidate was identified in collaboration with Dr. Bara and has been referred to as Solvent C. It replaces the IL with an imidazole, which belongs to a broad class of molecules Dr. Bara is investigating [Shannon & Bara, *Ind. Eng. Chem. Res.* 2011]. Solvents B & C demonstrated increased stability compared to Solvent A and aqMEA in accelerated aging tests (**Figure 12**). An economic analysis of the Solvent C technology was completed and shows results comparable to DOE Base Case 10 (**Figure 16**).

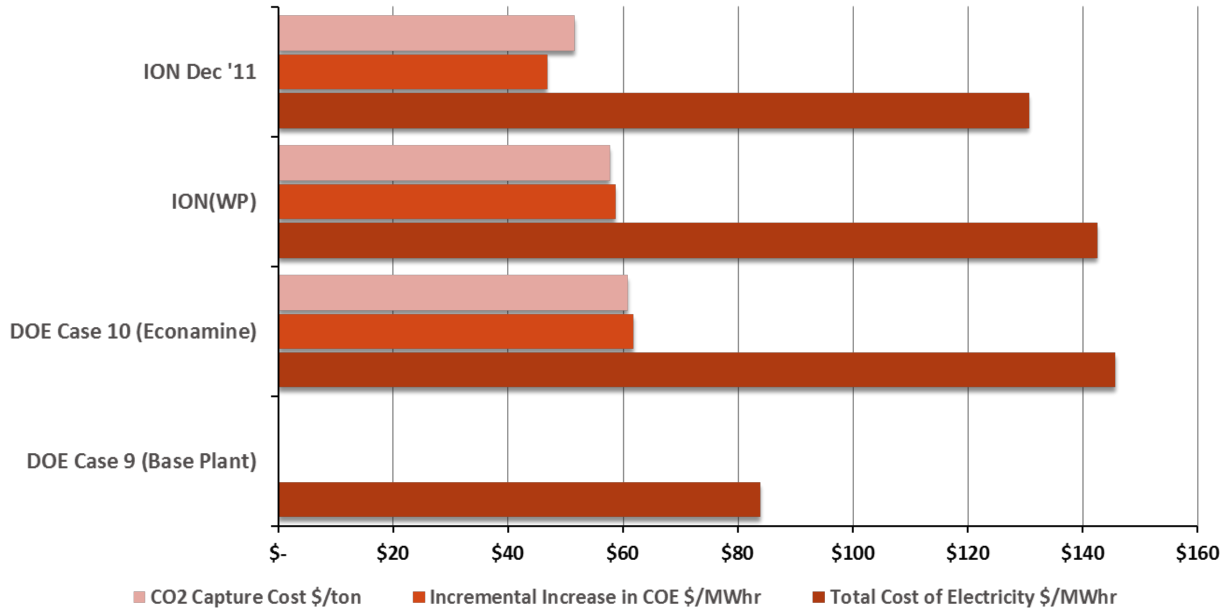


Figure 16: Techno-economic analysis of ION Solvent C.

Phase II Continuation (Phase IIc):

Phase IIc Objective(s):

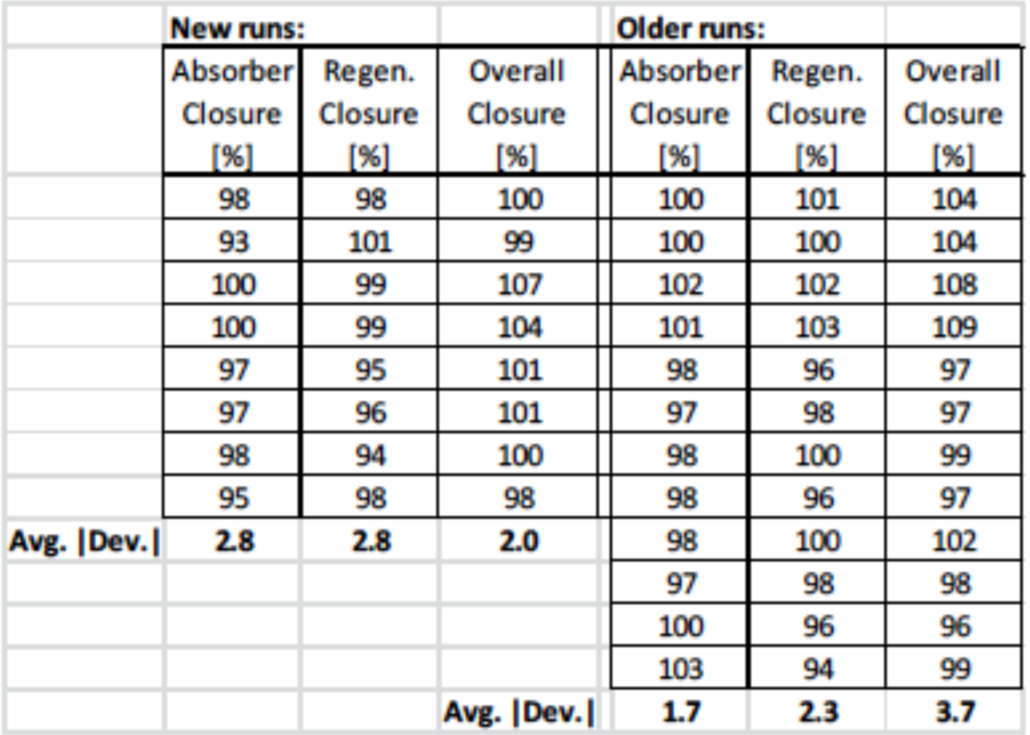
Project objectives for the continuation of Phase II involved two main goals. The first goal was to compare the ION solvent against aqueous MEA in continuous process conditions, both at the EERC facility and at ION's Laboratory Test Unit, and second, to use laboratory analysis to gather empirical thermo-physical property data and optimize the solvent composition. The process testing at ION involved the addition of a steam-stripping column for the Laboratory Test Unit to be able to evaluate the performance of ION's solvent against the traditional aqMEA on an equal basis. Since aqMEA had already been benchmarked at the EERC only testing of the ION solvent was necessary for comparison. At ION, the laboratory capability was expanded by the purchase of a calorimeter (TAM III, TA Instruments) equipped with a gas/liquid contact cell for measurement of the heat of reaction. Also, a controlled temperature setup was added to allow for temperature dependent density and viscosity measurements.

Phase IIc Technical Approach:

In order to accomplish the above objectives, ION further developed its technical infrastructure in order to conduct solvent performance characterizations beyond the level of initial assessment, and in parallel undertook a solvent testing campaign which included five one week steady state test runs using combusted flue gas at the EERC facilities in North Dakota.

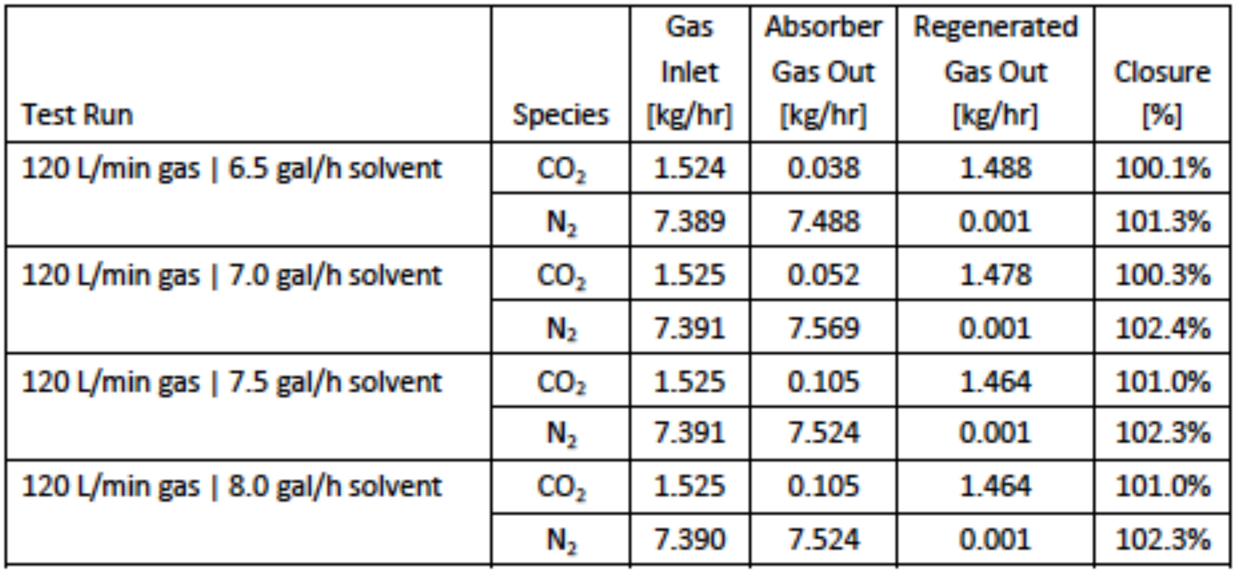
ION's lab unit was upgraded to enable improved gas stream analytics, including mass flow and composition. The upgrades included coriolis mass flow meters and a gas chromatograph to analyze process gas streams. With these upgrades, ION improved overall mass balance closures significantly (**Table 4**) and on-line GC analytics have allowed for identification of gas stream compositions, eliminating assumptions which were previously required for closure of individual species balances (**Table 5**).

Table 4: Mass balance closure for equilibrium test runs in laboratory test unit showing results with improved gas stream analytics (New) and without (Old).



	New runs:			Older runs:		
	Absorber Closure [%]	Regen. Closure [%]	Overall Closure [%]	Absorber Closure [%]	Regen. Closure [%]	Overall Closure [%]
	98	98	100	100	101	104
	93	101	99	100	100	104
	100	99	107	102	102	108
	100	99	104	101	103	109
	97	95	101	98	96	97
	97	96	101	97	98	97
	98	94	100	98	100	99
	95	98	98	98	96	97
Avg. |Dev.|	**2.8**	**2.8**	**2.0**	98	100	102
				97	98	98
				100	96	96
				103	94	99
			Avg. |Dev.|	**1.7**	**2.3**	**3.7**

Table 5: Gas mass balance closure for equilibrium test runs in laboratory test unit with improved gas analytics (Solvent C).



Test Run	Species	Gas Inlet [kg/hr]	Absorber Gas Out [kg/hr]	Regenerated Gas Out [kg/hr]	Closure [%]
120 L/min gas | 6.5 gal/h solvent	CO_2	1.524	0.038	1.488	100.1%
	N_2	7.389	7.488	0.001	101.3%
120 L/min gas | 7.0 gal/h solvent	CO_2	1.525	0.052	1.478	100.3%
	N_2	7.391	7.569	0.001	102.4%
120 L/min gas | 7.5 gal/h solvent	CO_2	1.525	0.105	1.464	101.0%
	N_2	7.391	7.524	0.001	102.3%
120 L/min gas | 8.0 gal/h solvent	CO_2	1.525	0.105	1.464	101.0%
	N_2	7.390	7.524	0.001	102.3%

The goal to evaluate our solvent against aqueous MEA in the test unit required the addition of a steam-stripping column because aqMEA does not achieve the needed lean loadings in a flash regeneration system. With the help of the EERC, the ION lab test unit was expanded to include a traditional steam-stripping column for solvent regeneration with the ability to switch between dual flash regeneration and the stripping column. A process flow diagram (PFD) of the test unit with both, the original dual flash and the added steam-stripping module is shown above in **Figure 3**, **Figure 4**, & **Figure 5**.

Thermo-physical property characterization of lead solvents was undertaken to provide experimentally derived values for heat of reaction and the density of multicomponent systems to drive ASPEN+ ^{TM} simulations, thus reducing dependence on theoretically-derived numbers (Task 6.2). To improve accuracy, ION's laboratory capabilities were extended to include a gas flow calorimeter and temperature controlled density analytics. In addition, solvent compositions were investigated over a range of concentrations in order to determine the optimal amine to imidazole ratio in addition to target operational water concentration.

To evaluate solvent compositions an equilibrium solvent evaluation apparatus was assembled. The configuration of the solvent evaluation apparatus is shown in **Figure 17**.

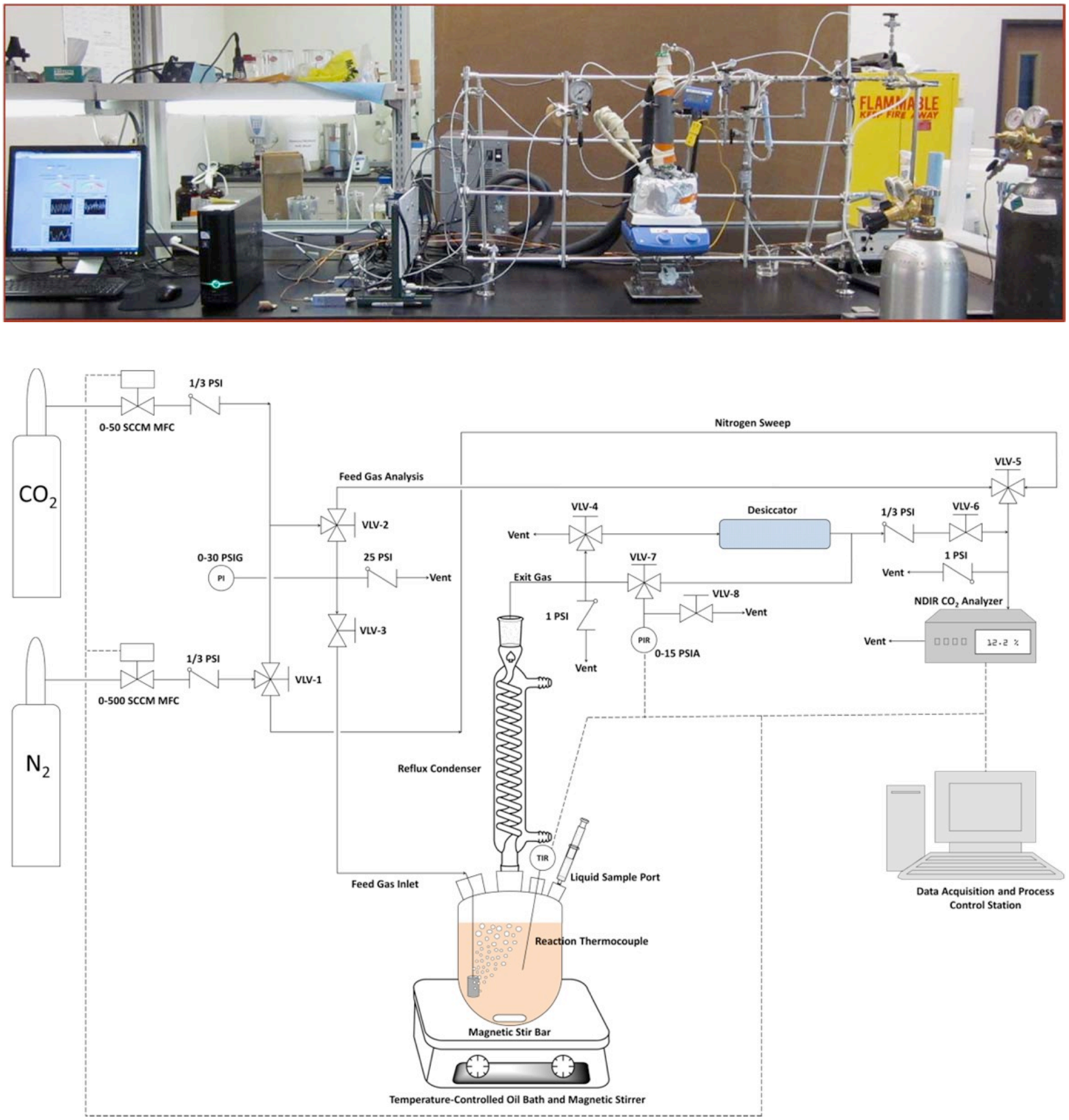


Figure 17: Photo and schematic of the solvent evaluation apparatus.

Gas flow to a 4-neck, 150 mL reaction vessel was controlled with 0-50 SCCM (CO_2) and 0-500 SCCM (N_2) Alicat Scientific mass flow controllers. Approximately 100 mL of solvent were added to the reaction vessel and the gas mixture was introduced into the solvent via an aeration stone. The solvent was stirred with a magnetic stir bar and heated by placing the reaction flask in a temperature-controlled oil bath. The reaction temperature was measured with a K-type thermocouple and the solution was sampled via a septa sample port using a syringe. The gas leaving the reaction vessel passed through a 53 cm Graham-style reflux condenser. The temperature in the condenser was controlled to 0.3 °C with a Polyscience LM-Series chiller. Product gas leaving the condenser was either vented into the room via a water bubbler or directed to a Quantek Instruments model 906 continuous CO_2 analyzer. Prior to entering the CO_2 analyzer the gas was dried by passing through a desiccant column (Indicating Drierite). A CO_2 analyzer with a measurement range of 0-20% (v/v) CO_2 and a linear output of 0-5 Vdc was used. The total pressure in the reaction vessel was measured with an Omega Instruments PX303 0-15 PSIA pressure transducer. Data acquisition (i.e., reaction temperature, CO_2 concentration, reaction pressure, and individual gas mass flows) and control (i.e., CO_2 and N_2 mass flow controller setpoints) were monitored using LabView software.

The apparatus shown in **Figure 17** was operated in two different modes depending on the reaction conditions. In either case the total reaction pressure was slightly above ambient atmospheric pressure (~13.6 psi). The reaction temperature was controlled to 60°C and a gas mixture of 12% CO_2 (balance N_2) was fed into the reaction vessel at a flow rate of 500 sccm for absorption conditions. The feed gas composition was controlled via mass flow controllers and the two gases were blended prior to entering the reaction vessel. The solvent was determined to have reached equilibrium CO_2 loading when the exit gas composition was the same as the feed composition (i.e., the solvent is no longer absorbing CO_2).

To study regeneration conditions the reaction temperature was set to 110°C and pure CO_2 was fed into the reaction vessel. Nitrogen gas was used to sweep (dilute) the product gas (CO_2) to the CO_2 analyzer when operating at this condition. The solvent was determined to contain equilibrium CO_2 loading when the final CO_2 composition was equal to the composition of the combined feed CO_2 and N_2 sweep gas (i.e., the flow rate of CO_2 entering the reaction vessel was equal to the CO_2 flow exiting when the solvent is at equilibrium).

A 1.2 mL liquid sample was removed via a syringe when the solvent had achieved equilibrium (at both conditions) for a sufficient amount of time (e.g., 50 minutes). The liquid sample was analyzed for wt.% CO_2 with a UIC Inc. model CM5015 CO_2 Coulometer which was confirmed by the CO_2 uptake as calculated from the feed CO_2 composition/flow rate and the final CO_2 composition of the outlet stream. The sample was also analyzed for water content with a Mettler-Toledo V30 Volumetric Karl-Fischer Titrator. Water content was measured to determine if significant water loss had occurred over the course of the experiment. Changes in water content were consistently less than 10% for all of the studies discussed here.

The carrying capacity of two modified Solvent C solutions was measured using the solvent evaluation apparatus to investigate the effect of water uptake on Solvent C performance. One solvent contained twice the nominal water content (ION C 2x Water), and the other solvent contained three times the nominal water content of Solvent C (ION C 3x Water). The target temperature for the CO_2-rich condition (i.e., absorption condition) for all solvents was 60°C. Likewise, the target temperature for the CO_2- lean condition (i.e., regeneration condition) for all solvents was 110°C. However, the high temperature target could not be reached in either solvent because the boiling points were below 110°C. For ION C 2x Water the boiling point was approximately 106°C, and for ION C 3x Water the boiling point was approximately 99°C. The carrying capacities for the studied solvents are presented in **Figure 18**. The carrying capacity on a mol CO_2/mol amine basis is shown in **Figure 18a**, whereas the carrying capacity on a mass basis is shown in **Figure 18b**.

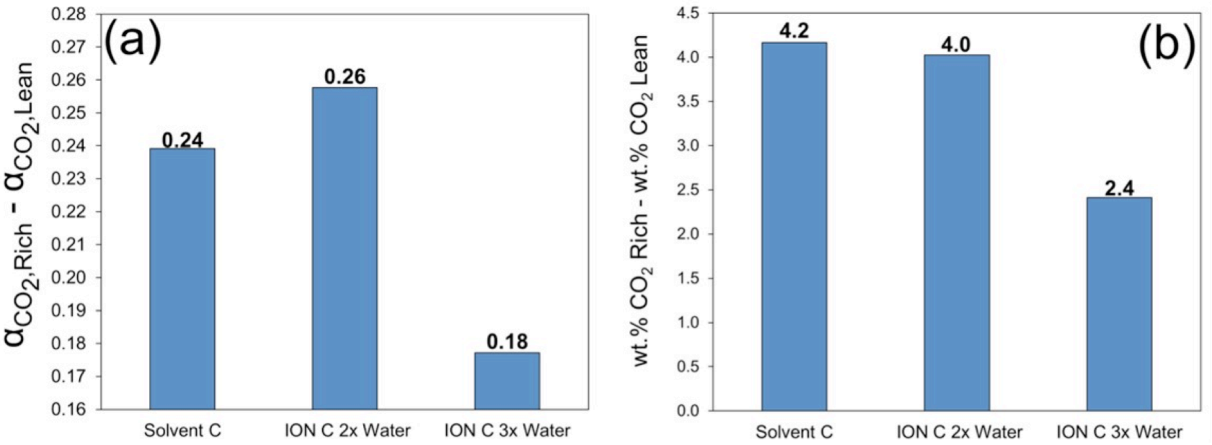


Figure 18: Carrying capacities of Solvent C, ION C 2x Water, and ION C 3x Water on (a) a mol CO_2 /mol amine basis and (b) on a wt. % CO_2 basis. Note that the lean loading temperatures for Solvent C, ION C 2x Water, and ION C 3x Water were 109°C, 106°C, and 99°C, respectively. The lean loading target temperature was 110°C, however the boiling points of ION C 2x Water and ION C 3x Water were found to be lower than the target temperature.

The most notable effect of increased water content was a significant reduction in solvent boiling point. The temperature at which Solvent C was studied (109°C) was not at the boiling point. However, doubling the amount of water in Solvent C resulted in a boiling point of approximately 106°C, and tripling the amount of water resulted in a boiling point of approximately 99°C. The stripper/flash pressure would likely need to be increased in order to achieve regeneration temperatures above 110°C with water contents above 20 wt.%.

On a mol CO_2/mol amine basis, ION C 2x Water appears to be slightly improved over Solvent C (**Figure 18a**). This measured improvement in amine efficiency is likely understated considering that the lean temperature of ION C 2x Water (106°C) was lower than Solvent C (109°C). ION C 2x Water was found to have a very slight reduction in carrying capacity performance on a mass basis (**Figure 18b**). Again, recall that the regeneration temperature was lower for ION C 2x Water. This slight reduction in capacity can very likely be compensated by marginally increasing the system pressure (i.e., increasing regeneration temperature). It was difficult to draw any conclusions about the performance of ION C 3x Water compared to Solvent C due to the difference in regeneration temperatures. Without increasing system pressure, and thus regeneration temperature, ION C 3x Water clearly would perform significantly worse than Solvent C. It seems reasonable, however, to expect that this shortcoming can also be overcome with an increase in system pressure based on the behavior of ION C 2x Water. The rich loadings (59°C) of ION C 2x Water and ION C 3x Water were reduced only by 8.4% and 14%, respectively, compared to Solvent C despite the significant dilution of the organics in these solvents. These data would suggest that Solvent C carrying capacity would not be drastically reduced if diluted with 2x-3x water since effect of increased water on regeneration energy could not be clearly elucidated by this experimental set-up. The energy penalty due to water vaporization would likely increase, but any estimate on the magnitude of this increase would be completely speculative. In a different vapor-liquid equilibrium experiment the effect of additional water on the CO_2 solubility was shown to increase both rich and lean solvent loadings, but had little effect on the effective carrying capacity of the solvent (**Figure 19**).

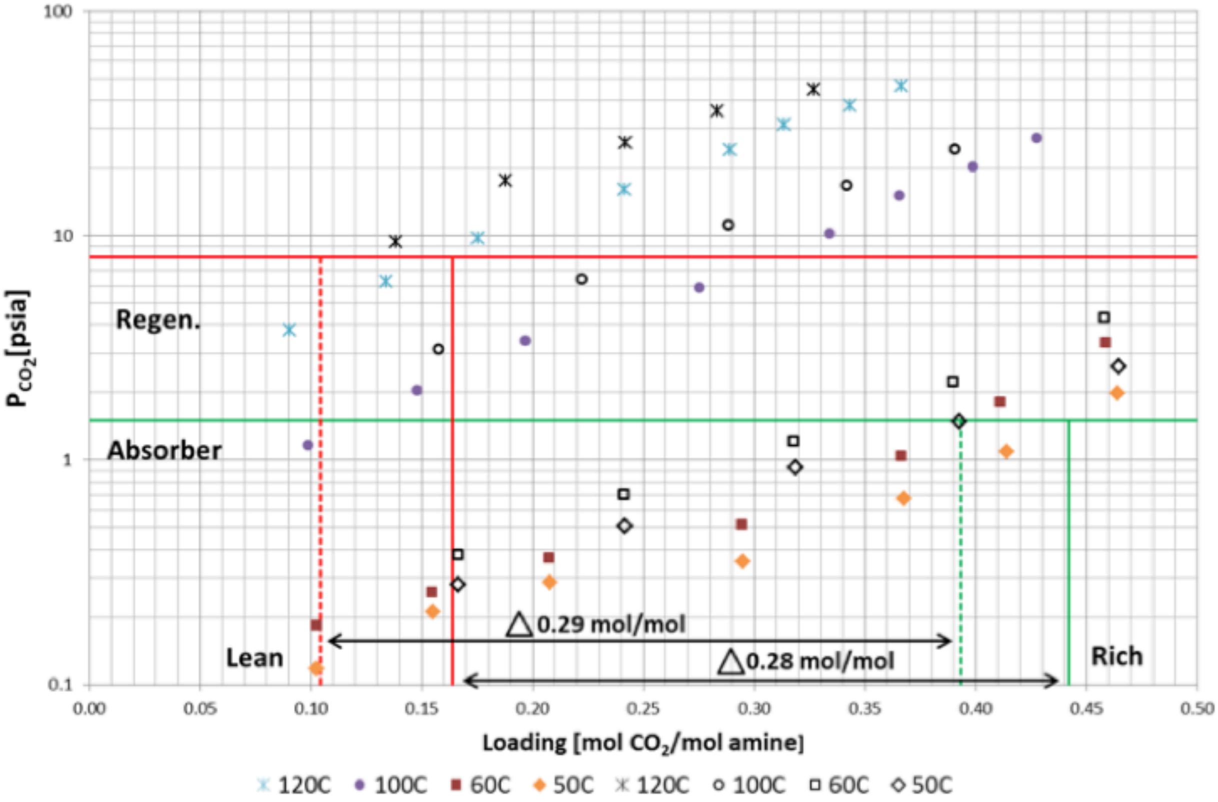


Figure 19: CO_2 solubility data for ION Solvent C (open) and Solvent C with additional water content (closed).

The effect of amine concentration on Solvent C performance was evaluated by measuring the lean and rich loading of two modified Solvent C compositions (Figure 20). One composition had approximately 20% more amine by weight (ION C High Am.), and the other had approximately 40% less amine by weight (ION C Low Am.). The loading of both solvents was measured at target temperatures of 60°C and 110°C. The gas feed compositions for these two temperature conditions were 12% (absorption) and 100% CO_2 (desorption), as mentioned previously. The total system pressure at both conditions was approximately 13.6 psia.

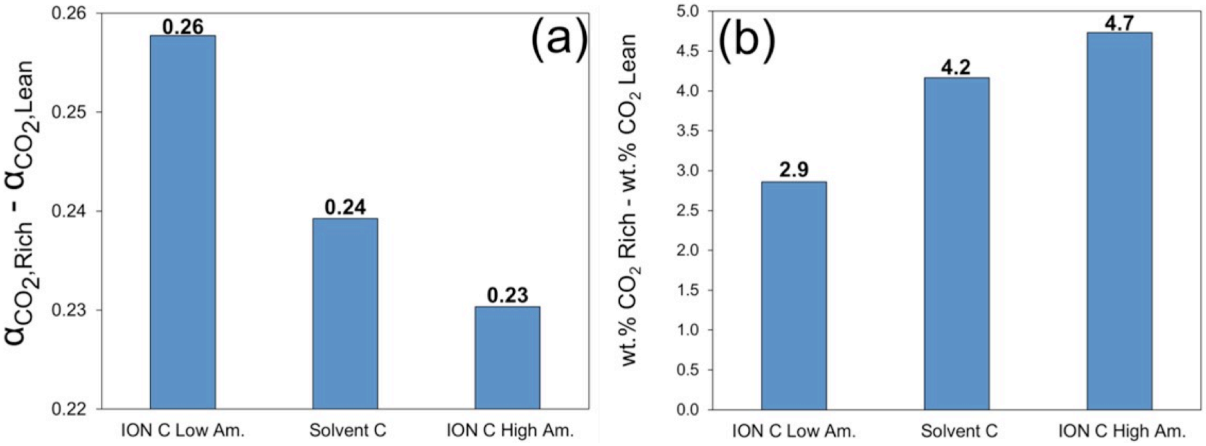


Figure 20: (a) Carrying capacity on a mol CO_2/mol amine basis for Solvent C, ION C Low Am., and ION C High Am.; (b) Carrying capacity on a wt. % CO_2 basis for Solvent C, ION C Low Am., and ION C High Am.

The calculated carrying capacities for solvents ION C High Am. and ION C Low Am. in comparison to regular Solvent C are shown in **Figure 20**. The carrying capacities on a mol CO_2/mol amine basis are shown in **Figure 20a**, whereas the carrying capacities on a wt. % CO_2 basis are shown in **Figure 20b**.

Solvent performance was also investigated in response to a range of liquid and gas flow rates using the laboratory test unit at the ION facility to confirm the process simulation predictions and explore operating conditions for optimal performance (**Figure 21**; Task 6.3 & 6.4). The laboratory test unit was operated in a continuous recirculation mode, with synthetic feed gas of 12 vol.% CO_2. Two gas feed rates were used in the runs, 120 slpm and 80 slpm.

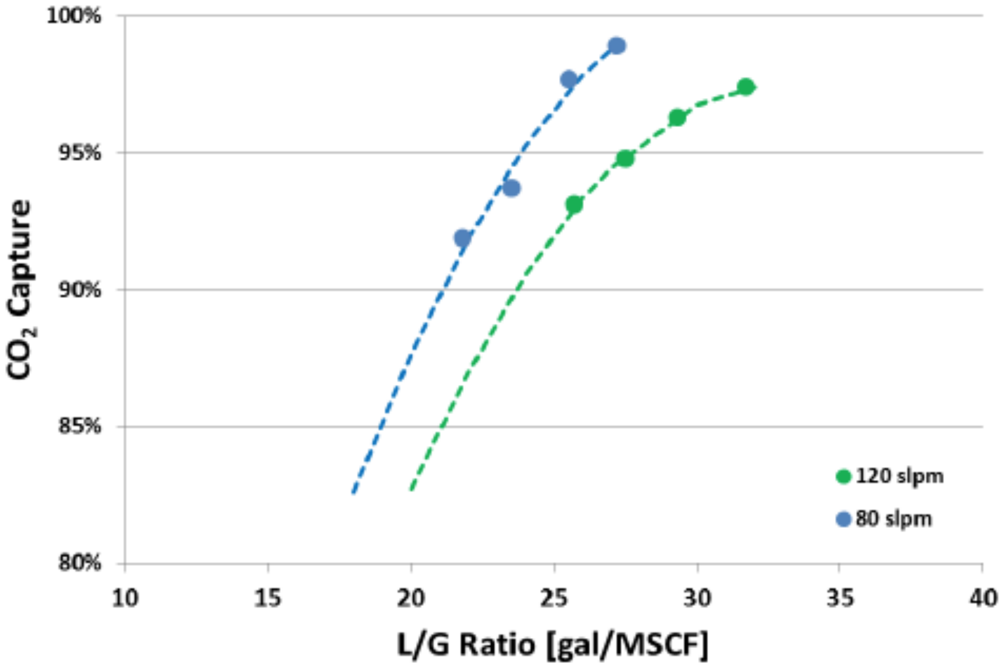


Figure 21: Capture % vs. L/G for Solvent C in ION's laboratory test unit using synthetic flue gas (12 vol.% CO_2, 40 °C) at 120 slpm and 80 slpm feed rates.

Initial solvent testing at EERC focused on first achieving steady 90% CO_2 capture and secondly on completing a series of parametric tests (**Figure 22**) in order to determine the operational window for optimal solvent performance, e.g., liquid/gas ratio in the absorber column and reboiler steam load (**Figure 23**, **Figure 24**)

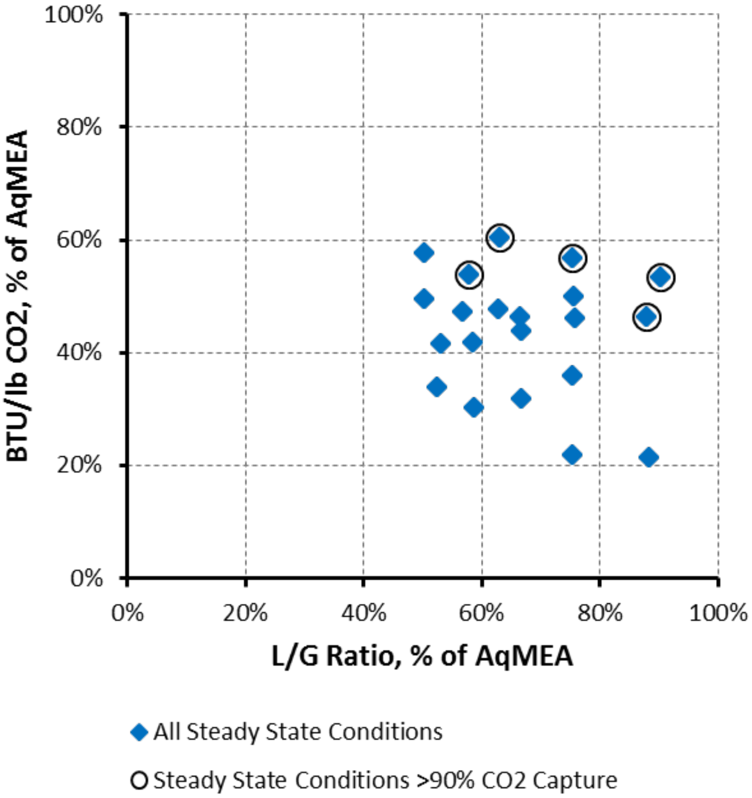


Figure 22: Results of parametric testing at EERC in the 0.2 MWe coal-fired pilot. Results are expressed as % in comparison to aqueous MEA on their pilot system.

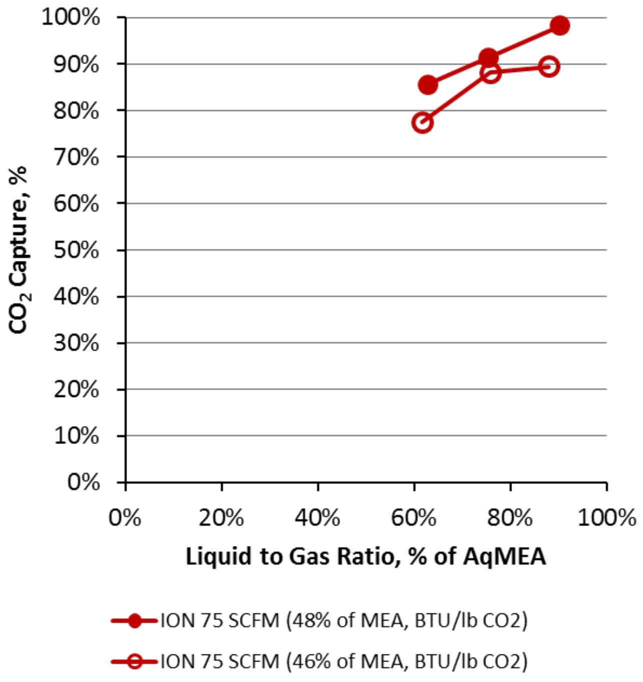


Figure 23: Capture % vs. L/G for ION solvent in EERC pilot process at two steam rates (46% and 50% relative to aqMEA).

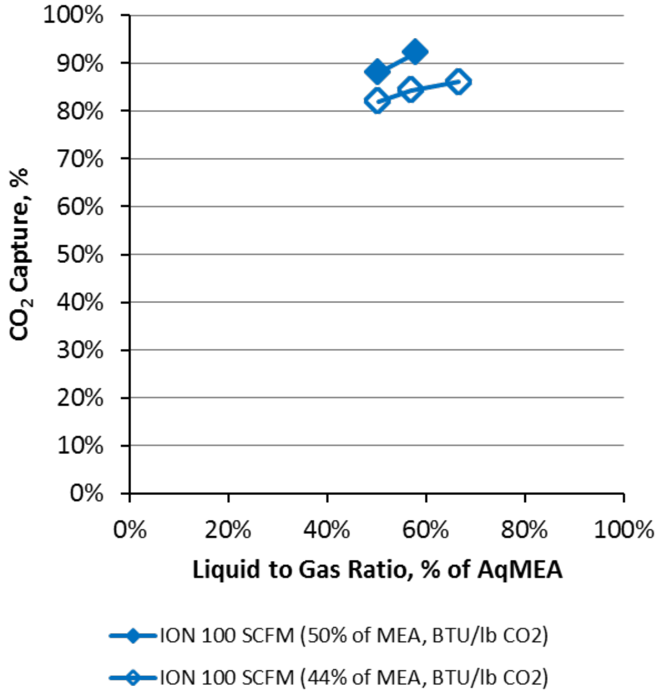


Figure 24: Capture % vs. L/G for ION solvent in EERC pilot process at two steam rates (44% and 50% relative to aqMEA).

Variables such as flue gas and column temperatures were controlled and systematically varied in order to determine the appropriate operating conditions required to preserve steady-state operation within the defined process operating window.

During the early testing, the water content of the solvent was observed to increase based on Karl Fischer testing at periodic intervals (**Figure 25**). Process variables such as absorber inlet (**Figure 26**) and outlet flue gas temperatures were adjusted which allowed effective control of solvent water content (**Figure 27**).

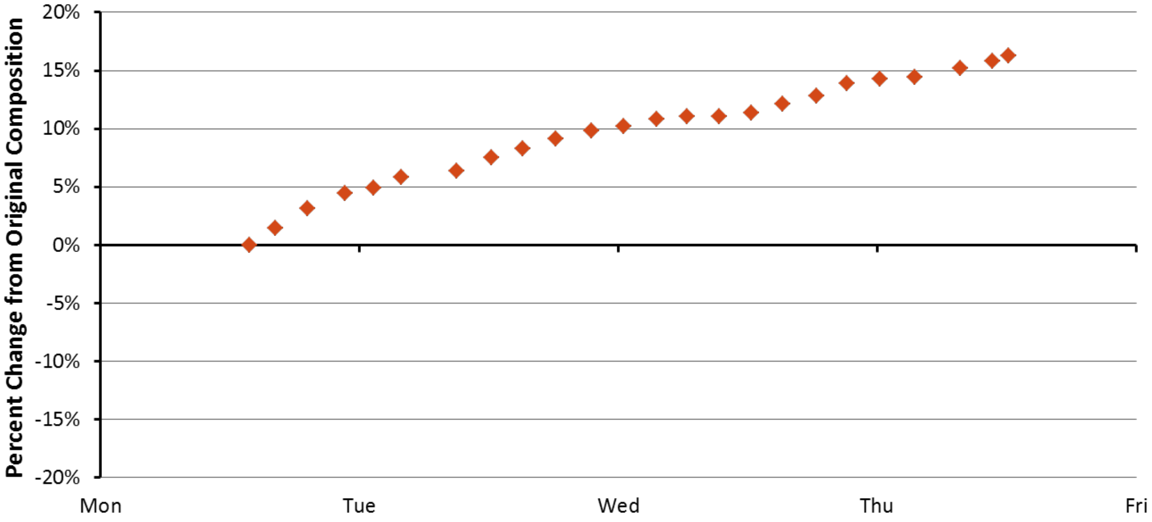


Figure 25: Change in solvent water content vs. time during early test run at EERC.

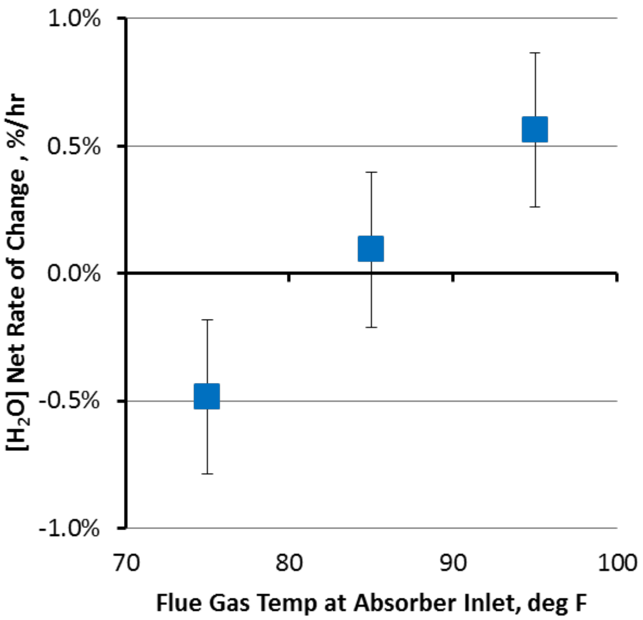


Figure 26: Change in solvent water content as a function of absorber inlet flue gas temperature.

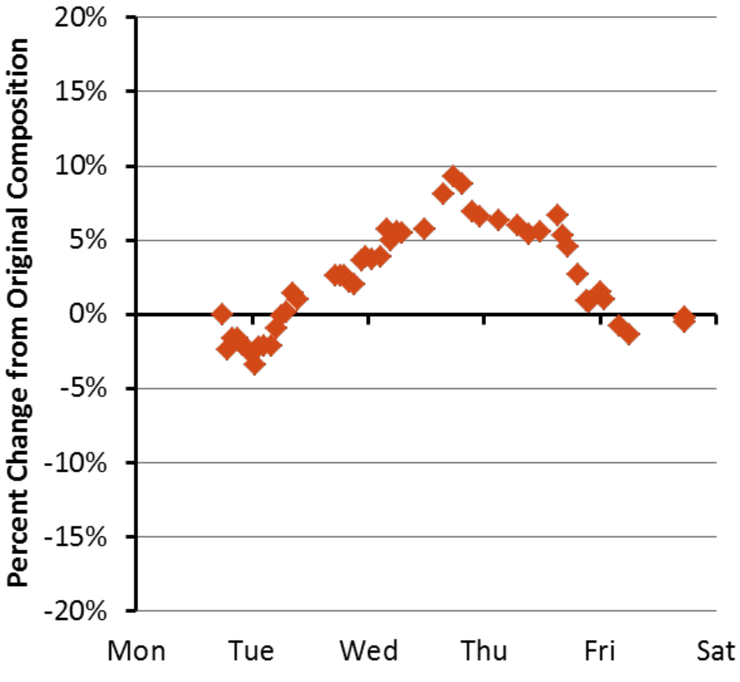


Figure 27: Solvent water content vs. time in EERC testing showing control of water content.

Additional steady state solvent performance evaluations were conducted at the EERC facility to determine solvent performance in comparison to aqMEA and in comparison to test runs in ION’s test unit which uses simulated flue gas (Task 6.4, 8.2). Performance was evaluated on a mass (L/G) and heat (BTU/lb CO_2) basis for ION’s Solvent C in the EERC test unit (**Figure 28**), and on a mass basis (L/G) in the ION’s laboratory test unit (**Figure 29**) which allowed for direct comparison to that of aqMEA which was benchmarked in both test units (Task 7.2, 7.3).

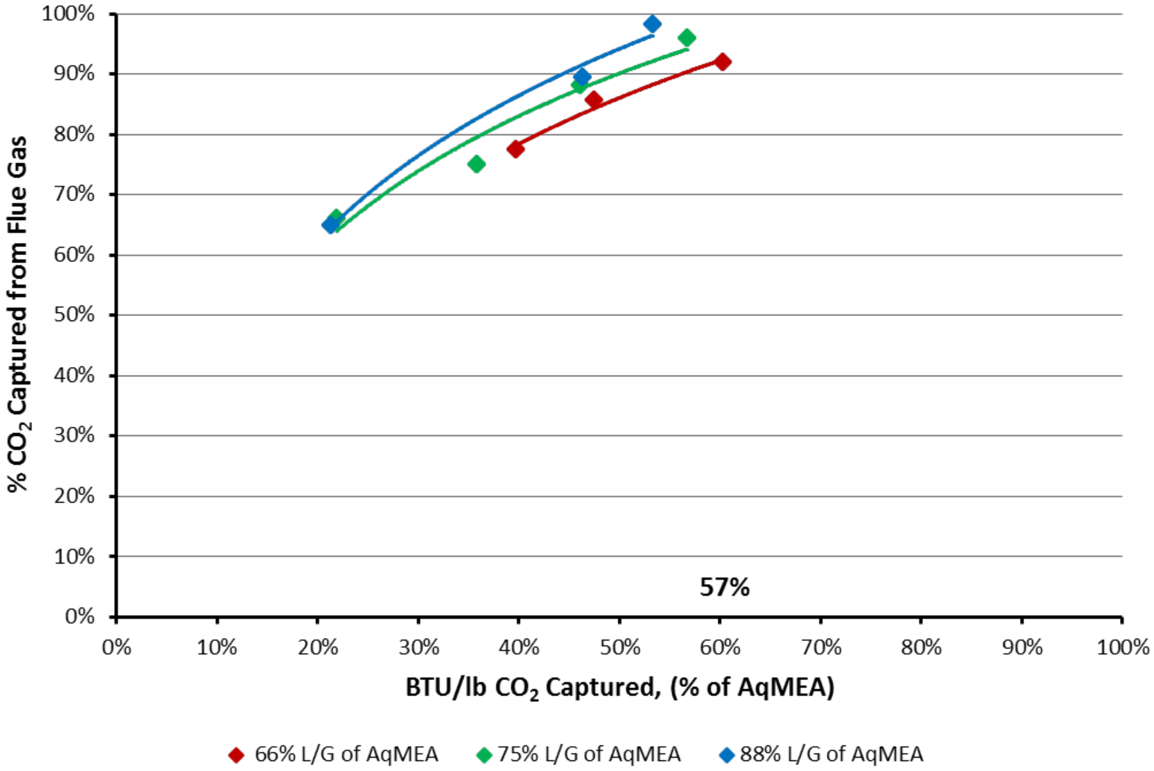


Figure 28: Capture % vs. energy requirement for ION solvent in EERC pilot process compared to aqueous MEA.

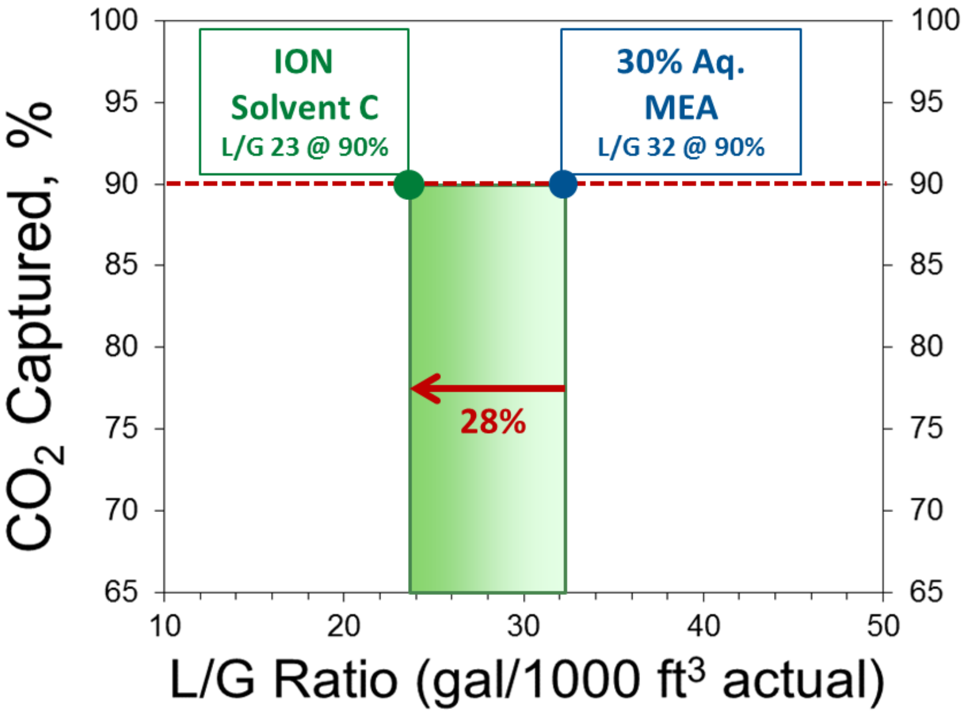


Figure 29: Comparison of L/G at 90% capture in ION's laboratory test unit between Solvent C and aqueous MEA. Test used synthetic flue gas (N_2/CO_2) at 120 slpm, 12 vol.% CO_2 feed.

Phase IIc Results:

ION Advanced Solvent Performance Results for Coal-Fired Post Combustion Capture at EERC

Based on EERC pilot studies, ION's advanced solvent required 75% of the liquid flow requirements and 57% of the regeneration energy requirements for 90% CO_2 capture relative to 30wt% aqMEA as demonstrated in EERC's test unit (Case 10 EERC). This information was used in an ASPEN+ TM process model to develop the mass and energy balance for ION's advanced solvent, and to further resize the CO_2

absorber, steam cycle and boiler models to account for the lower steam requirements for 90% CO_2 capture. These results were published in a report to DOE (Pavlish, B.M.; Kay, J.P.; Strege, J.R.; Fiala, N.J.; Stanislowski, J.J.; Snyder, A.C. *Subtask 2.5 – Partnership for CO_2 Capture – Phases I and II*; Final Report (Sept 1, 2010 – April 30, 2013) for U.S. Department of Energy National Energy Technology Laboratory Cooperative Agreement No. DE-FC26-08NT43291; EERC Publication 2013-EERC-04-12; Energy & Environmental Research Center: Grand Forks, ND, April 2013). Excerpt of full report including complete results for ION solvent in Post-Combustion Coal-Fired flue gas testing at the Energy & Environmental Research Center, Grand Forks, ND is attached to this report as: Appendix_A_ION_Sections_of_PCO2C_Final_Report_Coal.

Modeling results for ION's advanced solvent (Case 10 ION) demonstrated that a coal feed rate of 518,438 lb/hr with a reboiler steam usage requirement of 1,112,770 lb/hr were necessary to generate net power output of 550 MW, and yielded a total steam turbine output of 623.8 MW. By comparison, DOE's MEA Case 10 required a total steam output of 672.7 MW to generate net power output of 550 MW.

When compared to DOE's MEA Case 10, the overall plant efficiency for the ION advanced solvent increased by 4.8 percentage points, from 26.2% to 31.0%. By comparison, DOE's Case 9 (no capture) demonstrated an overall plant efficiency of 36.8%.

These studies demonstrate a 38% improvement in plant efficiency for ION's capture system vs. DOE's MEA Case 10 and savings of 49 MW of additional power generation in order to generate a net power output of 550 MW.

These studies also indicate coal consumption of 423,000 tons/year less and CO_2 emissions of 24,000 tons/year less than DOE's MEA Case 10.

ION Advanced Solvent Heat Stable Salt Analysis Performed at EERC

During a 72 hour steady state test run at EERC, lean solvent samples were analyzed for the presence of heat-stable salts (HSS) known to accumulate in aqueous systems and to contribute to solvent degradation. The heat stable salts were separated by HPLC using a Dionex IonPac AS11-HC hydroxide-selective anion-exchange column with a sodium hydroxide gradient. The analysis was achieved using a conductivity detector (private conversation with Dr. Nicholas Lentz, Associate Director of Energy Technology Applications, University of North Dakota).

For 48 hours prior to spiking the flue gas with increasing concentrations of NOx and SO_2, the ION advanced solvent was run at steady-state conditions with an in-line scrubber for NOx and a wet scrubber for SO_2 such that the flue gas was maintained at 2 ppm for NOx and 1 ppm for SO_2. The test involved spiking the scrubbed flue gas with 10, 20 and 50 ppm NOx and SO_2 for several hours followed by analysis of solvent samples at 4 hour intervals post spikes during the test runs. MEA results were obtained from similar test runs and analyses by EERC.

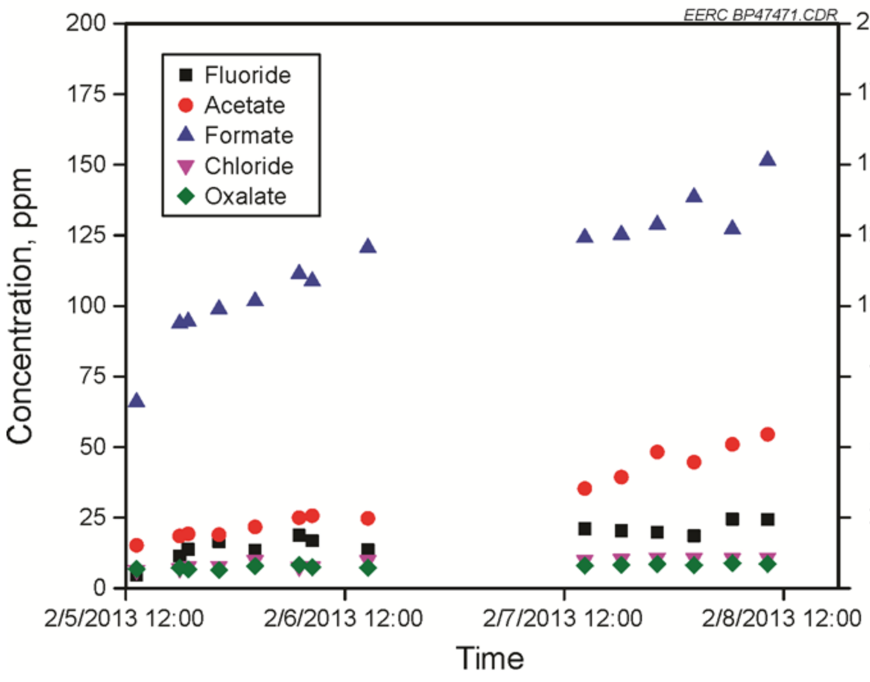


Figure 30: Concentration of HSS in lean ION samples.

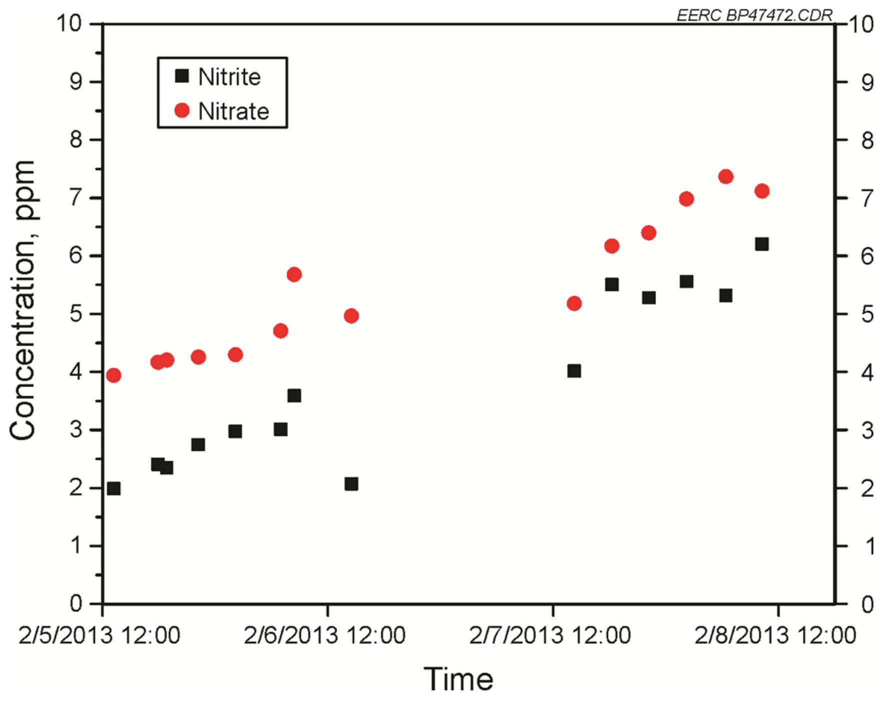


Figure 31: Concentration of nitrate and nitrite HSS ions in lean ION samples.

Among the organic HSS, formate was found at the highest concentrations rising from 50 to 150 ppm (**Figure 30**), which was not significantly different from MEA. Nitrate and nitrite HSS remained below 8 ppm for both the ION advanced solvent (**Figure 31**) and MEA (**Figure 32**).

There was a significant difference in chloride content between the ION advanced solvent and MEA. Chloride is typically present at 20 ppm in Antelope PBR subbituminous coal. ION's advanced solvent showed chloride levels below 11 ppm (**Figure 30**) whereas the MEA solvent showed levels between 100 – 220 ppm (**Figure 32**).

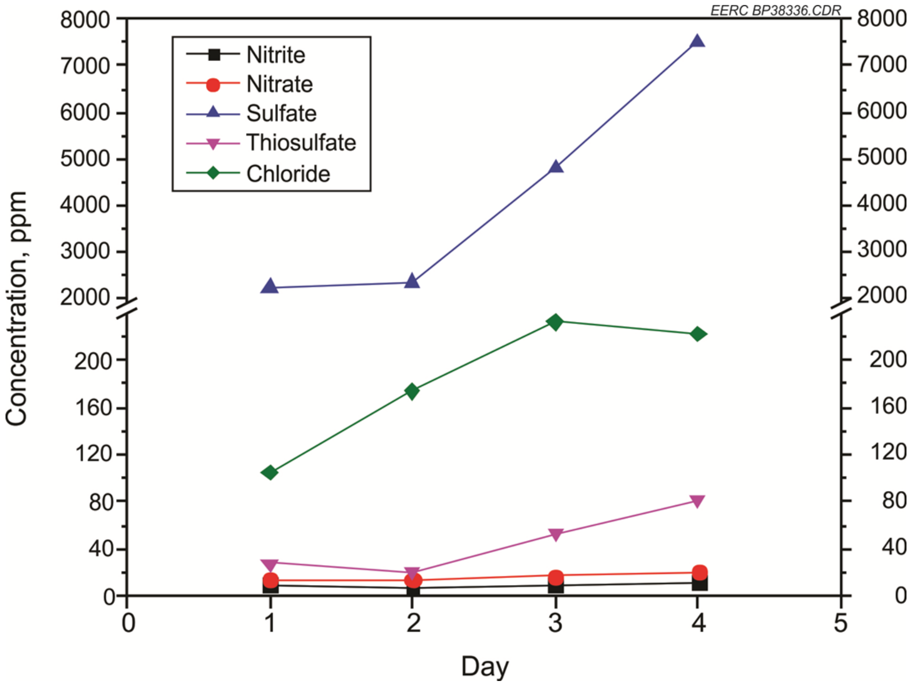


Figure 32: Concentration of inorganic anions in lean MEA solvent.

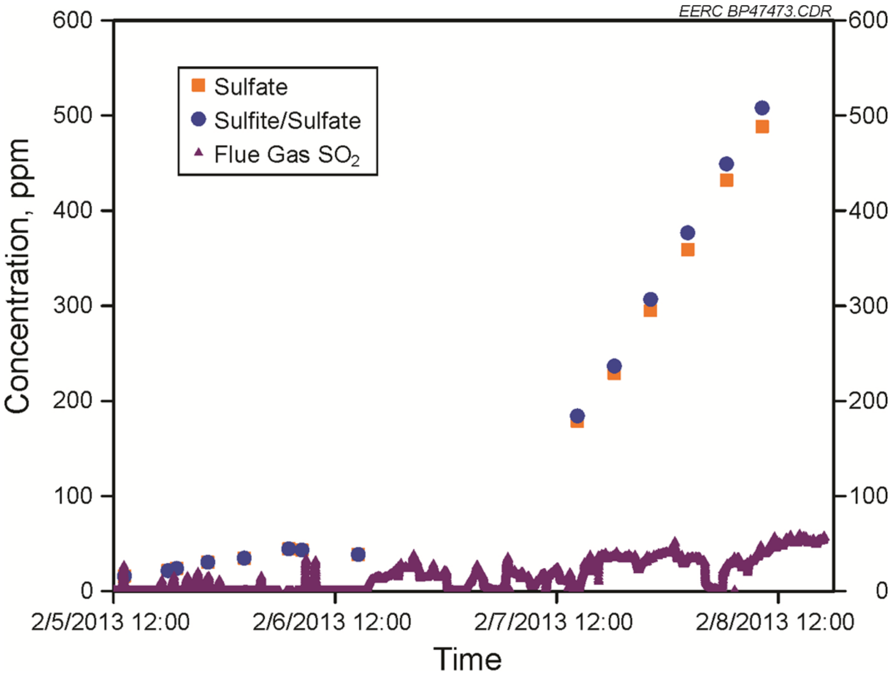


Figure 33: Concentration of sulfate and sulfite HSS ions in ION samples.

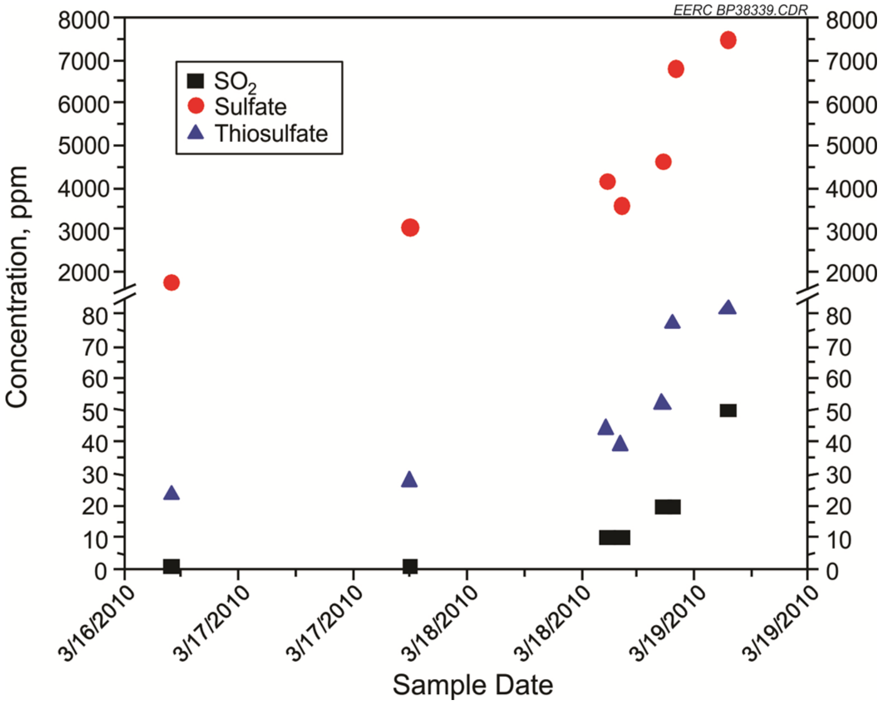


Figure 34: Concentration of sulfate and thiosulfate HSS ion in MEA samples.

SOx HSS ions, sulfate and sulfite, also showed significant differences between the ION advanced solvent and aqMEA. Sulfate concentrations for aqMEA were 10 – 15 times higher than for the ION's advanced solvent (**Figure 33** & **Figure 34**).

Given the appreciation that these studies are parametric in nature and will be conducted over longer test runs in future work, these tests indicate that the ION's advanced solvent was resistant to chlorine build-up, and demonstrated less sulfate HSS formation by a factor of greater than 10 when compared to MEA solvent. At the same time, ION's advanced solvent maintained low reactivity to NOx species.

These results indicate that ION's advanced solvent has the potential to require less makeup demand, thereby reducing annual solvent costs, reducing potential corrosion of the capture system and decreasing maintenance needs.

ION Advanced Solvent Economic Evaluation Results Performed by EERC

Total plant capital costs, fixed and variable operating costs, and fuel costs were computed by the EERC in a manner consistent with DOE's Cost and Performance Baseline for Fossil Energy Plants. DOE's Case 10 was used as the baseline for comparisons to the performance of 30 wt% aqMEA at EERC (Case 10 EERC) and ION's advanced solvent (Case 10 ION). Case 10 EERC performed better than DOE Case 10 due to inter-column cooling and advanced structured packing which were also used for ION Case 10. Case 10 ION advanced solvent resulted in a 37% increase in cost of electricity (COE) relative to a 73% increase in COE for DOE Case 10 and a 57% increase in COE for EERC Case 10 (**Table 6**).

Table 6: Techno-economic analysis of ION Solvent C from EERC performance data.

	Base Plant Case 9	Case 10	MEA EERC	ION
TOC	1,331,192	2,440,898	2,131,187	1,886,451
OCFIX	44,884	76,066	71,795	59,115
OCVAR	38,458	67,389	63,427	51,662
Fuel	131,491	184,909	177,593	155,870
COE, US$/MWh	82	142	130	112
ICOE[1], %	N/A[2]	73%	57%	37%
US$/ton CO2 Captured	N/A	57	46	34

[1] Increase in cost of electricity

[2] Not applicable

Correspondingly, Case 10 ION's advanced solvent resulted in $34/ton CO_2 captured in comparison to $57/ton CO_2 captured for DOE Case 10 and $46/ton CO_2 captured cost for EERC Case 10. These results demonstrate exceptionally strong performance and economic savings using the ION's advanced solvent as compared to DOE's MEA Case 10. These results also demonstrate that ION's advanced solvent is on track to meet or exceed DOE's performance objective of 90% CO_2 capture for less than $40/ton of CO_2 captured for commercial implementation at conventional PC coal-fired power plants by 2025.

Project Deliverables and Conclusions

Phase I Deliverables:

Topical Report 3.4: Use of ION's Test Unit to Validate Data & Process Design (Appendix T1, this document)

Objective(s):

The objectives for this Topical Report were to validate property data and process designs using laboratory property measurement and operation of the laboratory test unit, and to convey the rationale, approach, criteria, initial findings and lessons learned in the "three way" integration of data between a continuous processing laboratory test unit, laboratory chemical tests, and a process simulation to support a more detailed process design.

Conclusion(s):

The testing program demonstrated that Solvent A can absorb CO_2 and be regenerated in a continuous process. During testing, Solvent A reacted more slowly in the absorber unit than a 30 wt.% aqueous MEA solution. Whether this is due to increased viscosity limiting mass transfer or slower reaction rates for the secondary amine is unclear. This indicates that the absorber design will either need to be higher or have more efficient packing than a conventional aqueous MEA absorber. Testing showed that the two-stage flash design can be used to regenerate Solvent A to a reasonable lean loading (0.15 mol CO_2/mol amine). Additional engineering work is needed to determine the optimal regeneration conditions and to determine if the flash design is more cost-effective than a traditional steam-stripper for solvent regeneration. This is especially true for solvent formulations containing some added water.

The reaction between anhydrous Solvent A and CO_2 in the vapor phase produces solid carbamate crystals in the vapor space exiting the absorber. Operational difficulties posed by the solids accumulation rule out the use of anhydrous amine solvents in conventional packed bed absorber technology.

Solvent A performance declined significantly over time in limited experimental runs due to the alkylating nature of the ethyl sulfate anion in the ionic liquid component. This led to rapid conversion of the amine component from secondary to tertiary, limiting the solvent carrying capacity [LaFrate, et al. *Energy & Fuels* 2012].

Topical Report 3.5: Process Simulation with a Non-Traditional Solvent (Appendix T2, this document)

Objective(s):

The objective of this report was to describe the issues faced in process simulation with non-traditional solvents (ionic liquids), and considerations in the selection, development and validation of a simulation tool to use as a basis for predicting performance and supporting detailed design.

Conclusion(s):

A modified ASPEN+^{TM} model can be used to predict the performance of ION's novel solvents in CO_2 capture applications. Comparison of literature and experimental data with predictions from the ASPEN+^{TM} simulation shows that sufficient property estimation parameters are available or can be regressed from the empirical data to allow a good prediction of physical and thermodynamic properties for the IL, amine, and IL/amine mixtures that are the basis of ION Engineering's proposed technology.

Phase II Deliverables:

Topical Report 5.3: Thermal Regeneration Energy Analysis (Appendix T3, this document)

Objective(s):

The objective of this deliverable was to conduct a hypothetical, size-independent comparison of solvent systems based on operation at equilibrium conditions in both the absorber and regeneration system; and to compare the heat of reaction, the sensible heat, and the latent heat of vaporization for both ION solvents and an optimized aqMEA process.

Conclusion(s):

The results of the study were that ION solvents B and C showed total regeneration energies that were 15% and 21% lower, respectively, than an optimized aqMEA process. Also, both ION solvents showed a net heat input reduction of more than 20% compared to aqMEA. The simulation suggested that with two simple process optimization strategies, Solvent C approached a net heat input of 2.5 GJ/tonne CO_2. Considering the net heat input, the heat of reaction between CO_2 and the amine component of ION's Solvent C is the largest component. By further optimization of the amine component, it may be possible to further reduce the net heat required to below 2.5 GJ/tonne CO_2.

Tasks 5 & 8.3: Techno Economic Evaluations of ION Solvent Technology & Demonstrated Performance

Objective(s):

The techno-economic evaluation involved a simulation of the parasitic load of the ION capture process at 500 MW scale (net energy) according to DOE guidelines and an estimation of the increased cost of electricity (COE) to the consumer using the ION process. The evaluation was to give a breakdown of the COE estimates to determine if ION technology can meet DOE goals with additional technical and/or business development. Finally, the evaluation was to compare the ION's solvent performance to the benchmark aqMEA process and other competing solvent technologies.

ION Advanced Solvent Economic Evaluation Results Performed by EERC (Appendix_A_ION_Sections_of_PCO2C_Final_Report_Coal)

The Case 10 Solvent simulation demonstrated exceptionally strong performance and economic savings for the ION advanced solvent as compared to DOE's MEA case 10. The results also demonstrate that ION's advanced solvent is on track to meet or exceed DOE's performance objective of 90% CO_2 capture for less than $40/ton of CO_2 captured for commercial implementation at conventional PC coal-fired power plants by 2025.

Project Implications

ION has completed a similar post-combustion CO_2 capture study using natural gas-fired flue gas at EERC with equally positive results as those reported here for coal-fired flue gas. In addition to carbon capture solvents, ION and UA are examining the use of imidazoles in membranes for post-combustion CO_2 capture and have been awarded a Phase I STTR from DOE. As a result of this work, the National Carbon Capture Center (NCCC) has expressed interest in multiple aspects of this work and has obtained baseline data for imidazole-based solvents under pre-combustion CO_2 capture conditions.

Prof. Bara at the University of Alabama has engaged collaborators in academia with this project to undertake additional physical property studies and molecular simulations of imidazole-based solvents already resulting in several peer-reviewed publications. Through this fundamental science work, a more thorough understanding of the synthesis, properties and applications of imidazoles can open new opportunities in fields even unrelated to CO_2 capture including pharmaceuticals, biomaterials and stimuli-responsive polymers. With Professor Bara’s work, this funding is supporting one Ph.D. student and has provided research opportunities for a number of undergraduate students.

Future Development Areas

Based on results to date and the advanced solvent testing planned over the coming six months, ION anticipates that initiation of slipstream testing could begin as early as the second half of 2014. Test campaigns at the slipstream level are anticipated to run for 1,000 to 1,500 hours and the total duration of testing is typically in the range of 12 to 15 months. Subsequent CO_2 capture demonstration projects have historically been at the 10 - 50 MWe slipstream scale, require a minimum of 2,000 hour campaigns and take up to 4 years to complete – assuming the construction of a new capture pilot unit. Design and construction of commercial units would be expected to follow slipstream and demonstration campaigns and could occur as early as 2020.

List of Abbreviations

R & D	Research and Development
ION	Ion Engineering, LLC
MEA	monoethanolamine
UA	University of Alabama
EERC	University of North Dakota Energy & Environmental Research Center
NCCC	National Carbon Capture Center
aqMEA	aqueous monoethanolamine
DOE	Department of Energy
HSS	Heat stable salts

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ION Engineering
Bold Science for Clean Energy

Appendix T1: Topical Report for Task 3.4
Solvent and Process Analysis Using Lab Pilot Unit

DOE Award: DE-FE0005799
ION Engineering
Project Title: Novel Solvent CO_2 Capture
Date Report Issued: 05/06/2011

Principal Investigator: Claude Corkadel
Co-Authors: Alfred Brown, PhD
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Reporting Period Start Date: 10/01/2010
Reporting Period End Date: 05/31/2011

Abstract

A lab-scale continuous processing CO_2 capture unit was developed and used to investigate operations with ION's novel solvents comprised of a mixture of ionic liquids (IL) and amines. The design incorporated a number of features to provide a broad range of operational flexibility. Instrumentation was integrated in the system to capture real-time data and sampling ports included to capture liquid samples. After a rigorous commissioning process identified component upgrades and some re-engineering requirements before operations could begin, the unit was completed and used for baseline runs with an aqueous MEA solvent and a series of test runs with ION's Solvent A. These runs demonstrated that the novel Solvent A can absorb CO_2 and be regenerated in a continuous process. Lab pilot operations are producing high-quality data and overall material balance closures typically ranging from 90% to 110%. Data from the lab pilot unit has also been used to calibrate the Aspen Plus process simulation model. In addition, the operations of the pilot unit have been instrumental in identifying conditions that were not expected or predicted in prior laboratory analysis of the solvents.

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Executive Summary

ION Engineering is developing technology for carbon dioxide (CO_2) capture using novel solvents comprised of mixtures of ionic liquids (IL) and amines. A critical task in ION's DOE supported project regarding this technology is the use of a continuous processing laboratory-scale pilot unit to generate operational data using simulated flue gases to better understand process operations. Data from the lab pilot unit also is a key input to validating the Aspen Plus process simulation model.

In the first phase of work, a 35 liter/hour (9 gallon/hour) unit was designed, fabricated, commissioned and operated in a series of baseline and test runs. Despite a two-month delay in the delivery and completion, the unit is now operating well and has delivered important information and operating insights in early experimental runs. In addition to the quality and importance of test data to calibrate the Aspen model, conditions were observed that were not expected nor predicted in prior laboratory analysis of the solvents.

ION 35 lph Lab Pilot Unit

Lab Pilot Unit Design

The overall process design for the lab pilot unit is based on established amine gas separation processes currently in use in the natural gas processing and chemical industries. As a pilot unit, a number of features were incorporated to provide a broad range of operational flexibility and data capture. The most significant deviation from conventional design is the use of a two-stage flash for regeneration. Preliminary engineering analysis identified this as a lower cost option taking advantage of properties of the IL-solvent that eliminate the need for stripping steam.

Aqueous Amine Reference Case

To test the lab pilot unit and generate data for the process simulation model, an aqueous monoethanolamine (MEA) solution was processed through the absorber section only, in a "once through" mode. The tests were conducted in this manner since the MEA solvent could not be effectively regenerated in the two-stage flash. Data was collected to support multiple approaches to calculating a material balance for the absorber column. Overall material balance closures ranged from 95% to 101%.

CO_2 Capture with ION Solvent A

A series of test runs using the ionic liquid-amine Solvent A were successfully conducted. Steady state operations were achieved and the successful absorption and desorption demonstrated in a continuous process. CO_2 capture ranged from 75 to 95% in the runs, with the use of an intercooler improving absorption in the solvents by about 12%. The two-stage flash design was successful in regenerating Solvent A to reasonable (0.15 mole/mole) lean solvent loadings.

During unit operations, problems were observed with increasing back-pressures in the absorber column that led to the discovery of a serious plugging problem in the overhead vapor line and several other components. Although not observed in prior lab work, it was determined that the Solvent A and CO_2 produced solid carbamate crystals at a rate that will create operational difficulties when operated in an anhydrous condition.

However, in a typical power plant operation moisture will be brought in with the flue gas so additional runs were made with 5% water added to Solvent A. No evidence of solids formation was observed in these runs. Further work is required to determine optimal levels of water in the solvent and how best to manage the moisture in the system.

Subsequent to solving the precipitation issue with anhydrous conditions, some additional loss of performance was observed when using Solvent A. This is now being investigated further by the project technical team.

1. Report

A lab scale continuous processing CO_2 capture unit was developed and used to investigate operations with the novel solvent as well as generate data for the Aspen Plus process model validation.

The 35 liters/hour (9 gallons/hour) lab pilot unit was designed, fabricated and commissioned over a six month period. Initial experimental runs were made with an aqueous monoethanolamine (MEA) solvent to establish a baseline and calibrate the absorber column to the Aspen simulation model. A series of test runs with ION's Solvent A were then made. Data and samples collected during these test runs were used to calculate a material balance around the absorber column, the regeneration section and the overall lab unit.

The use of the lab pilot unit has been instrumental in early assessments of both solvent and process performance. In addition to the importance of test data for to strengthen and validate process simulation, conditions were observed in experimental runs that were not expected or predicted in prior laboratory analysis of the solvents.

This report highlights key considerations in the development and commissioning of the lab pilot unit, followed by discussion of the data collected, results and conclusions drawn in the experimental runs.

1.1 Lab Pilot Unit Development and Commissioning

The design and fabrication of the lab unit was collaboration between ION and several partner and third party organizations. ION provided solvent characteristics and an initial process design for the design of pumps, heat exchangers, vessels and other process equipment. Eltron Research & Development (Eltron) and their affiliate Continental Technologies (ConTech) provided experience in gas process engineering and small pilot plant design and construction. Norwood S&S provided experience with packings for mass transfer applications as well as the detailed design for the absorber and fabrication of the absorber internals.

ConTech fabricated the unit at their Oklahoma plant and delivered it to ION, spending several more weeks onsite to complete the unit. ION's technical team commissioned the unit, supported by personnel from ConTech and Eltron.

1.1.1 Designing the Lab Pilot Unit

The lab pilot unit incorporates a number of features to provide a broad range of operational flexibility during this early stage of ION's testing, including the following:

- **Continuous Operation with Flash Regeneration**. The overall process design is derived from established processes currently in use in the natural gas processing and chemical industries. The solvent absorbs CO_2 from the gas in a continuous, counter-current flow packed absorber column. The solvent is regenerated by heating and flashing off the absorbed CO_2 in a series of flash vessels. The ability to regenerate the solvent in the unit allows the solvent to be continuously circulated, similar to operation of a commercial scale process.
- **Operational Flexibility**.
    - The unit features a supply gas manifold with independent flow controllers to allow for a variable incoming gas composition as well as varied inlet gas rates.
    - A steam generator allows for the incoming gas stream to be saturated with water.
    - A flue gas heater allows for the inlet gas temperature to be controlled and varied.
    - The absorber column contains multiple bed zones with multiple solvent feed nozzles to allow for variable bed height testing.

  - The absorber is also designed to be packed with at least two different types of packing.
  - Typical solvent operating variables such as flow rate, regeneration temperature and contacting temperature are all controlled.
  - The regeneration flash tanks can be operated with different liquid levels to investigate the effect of residence time on solvent regeneration.
  - The unit can be operated in a "once-through" configuration through the absorber in order to isolate the absorber and decouple the study of the absorber performance from the solvent regeneration process
  - Finally, the lab unit is well equipped with instrumentation and data recording to characterize the process conditions.
- **Appropriate Scale**. The 35 liters/hour scale represents a 10X to 20X scale up factor to the proposed demonstration unit for Phase 2 of this Project. With a 3" diameter absorber column, the lab scale unit is appropriately sized to investigate the operating parameters, yet small enough to be housed in ION's research facility.
- **Instrumentation and Data Collection**. The LabView software is used to control the system and capture real-time data during system operations. A detailed view of the LabVIEW control panel showing temperature, pressure and process control indicators is attached (Appendix A). Instrumentation was integrated in the system to capture gas and liquid flows, level indication in the absorber column and flash drums, and CO_2 composition of inlet and outlet gas. Sampling ports enable collection of liquid samples from four locations on the absorber column, the absorber and flash overhead condensate pots and at the outlet of the regeneration section.

1.1.2 Commissioning the Lab Pilot Unit

After delivery and completion of the unit on site by Contech, a thorough commissioning process was undertaken to assure the system was functioning properly before beginning the solvent test campaigns. This included testing of individual components (pumps, heat exchangers, instrumentation, etc.), lines and fittings, instrument communication and the LabVIEW control and recording software configuration. Flow tests were conducted with water and nitrogen prior to solvent and CO_2 tests. In the shakedown process, a number of problems were identified that took longer to address than hoped. Actions required included:

- Some re-engineering of the unit design to change certain indicators and regulators to provide greater sensitivity at low pressures
- Re-calibration of several meters delivering erratic or inaccurate readings under run conditions (high circulation rates, high temperatures)
- Re-location of thermocouples to provide accurate process temperature readings
- Installation of sight glasses for flash tanks to verify level readings
- Replacement of a mal-functioning pump to address failure to prime
- Repair of leaks around sample port flanges and tubing connections
- Installation of a knock-out pot to mitigate problems with condensation affecting the lean gas flow rate measurement
- Re-configuration of LabView software to correct mapping, tune controls and improve management of shutdown
- Replacement of the control computer and reprogramming of LabView to address random communications or processing glitches that created instability in the control system

Figure 1. Completed Lab Pilot Unit

1.1.3 Process Flow and Data Collection

The process flow and key data collection points for the lab pilot unit are illustrated in Figure 2. Unlike most conventional amine systems, a two stage flash is used for solvent regeneration. The unit also includes the option of using an intercooler with the absorber column.

The lab test unit regeneration system consists of two heaters and two flash drums. The equipment is arranged in stages such that the rich solvent from the column is first heated and flashed in the low temperature flash drum. The liquid is then further heated and flashed in the high temperature flash drum. The lean solvent is then cooled and pumped back to the absorber column. The vapor and gas from the flash tanks is collected and cooled to condense any solvent vapors that escaped from the flash tanks. Collected liquid is returned to the solvent surge drum while the cooled gas is exhausted from the unit. A key milestone in the development of this technology is validating the efficacy of this non-conventional amine regeneration process.

The LabView control system collects a large amount of real-time data during each test run. Data and samples used in the evaluation of the test runs and for the calculation of the material balance include the gas and liquid flow rates and composition at different points in the system. The methods used for each and point of collection are described below.

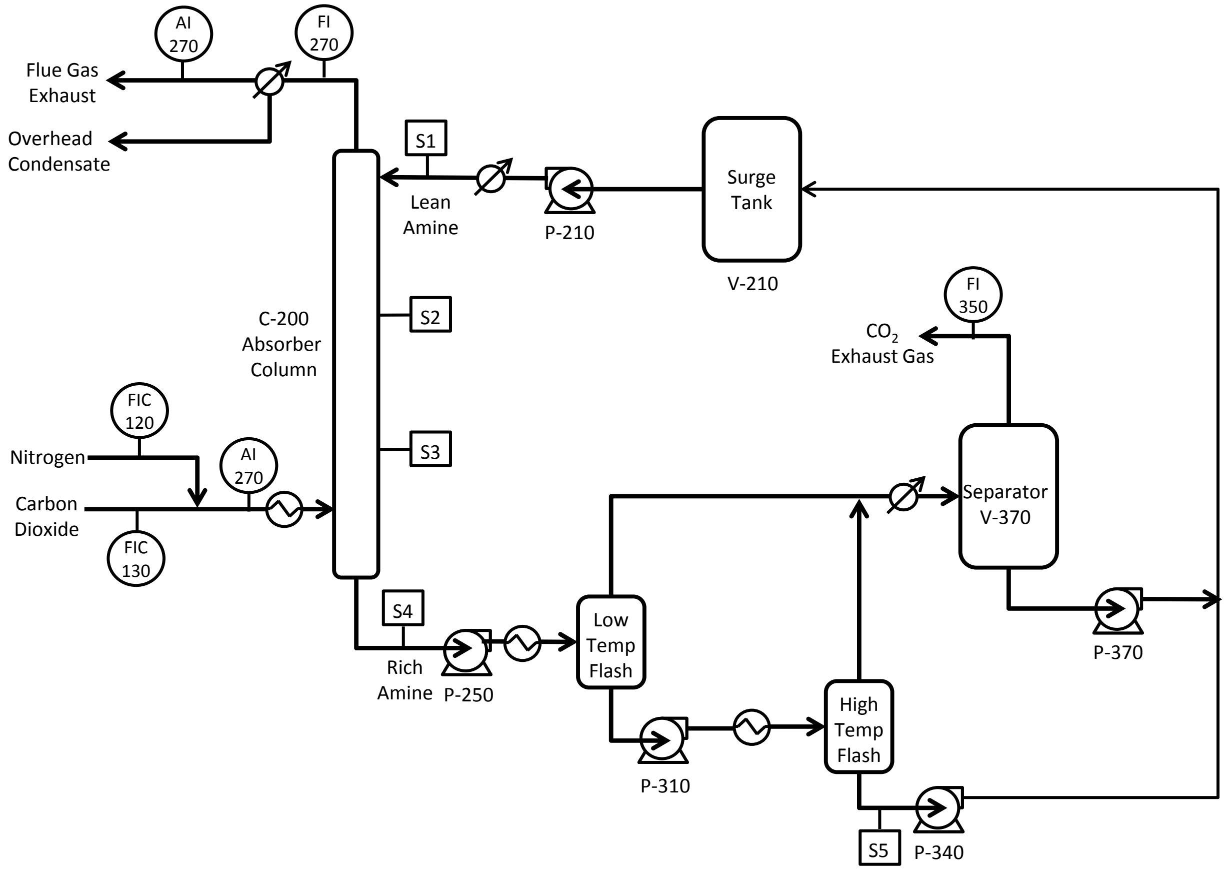


Figure 2. ION Lab Pilot Unit Process Flow

Gas Flow Rate

Inlet nitrogen and CO_2 flow rates are measured and controlled by Sierra Smart-Trak controllers. The nitrogen flow rate is controlled by FIC-120 and the CO_2 flow rate is controlled by FIC-130. The outlet gas flow rate is measured downstream of the overhead cooler by a Sierra flow meter, FI-270. The CO_2 exhaust gas flow rate is measured downstream of the flash gas separator by a Sierra flow meter, FI-350.

Gas Composition

A Horiba CO_2 analyzer, AI-270, is used to measure the CO_2 concentration of the inlet gas at a point just downstream of the mixing point. The analyzer also measures the CO_2 concentration of the exhaust flue gas downstream of the absorber overhead cooler after any condensed liquid has been removed from the exhaust stream. In initial test runs, gas samples were also analyzed by GC/MS to confirm the accuracy of the CO_2 analyzer measurements.

Liquid Flow Rate

The rich amine flow rate is measured by the rate of level accumulation in the bottom of the absorber column. The column is pumped dry by overspeeding the bottoms pump, P-250, relative to the feed pump, P-210. Then P-250 is shut off and the rate of level accumulation and the known internal cross-sectional area of the absorber column are used to calculate the rich amine volumetric flow rate. The density of the solvent at the outlet conditions is then used to calculate a mass flow rate of the outlet liquid.

Liquid Composition

Liquid samples are collected from four locations on the absorber column and one location in the regeneration section. The lean inlet liquid (S1) is collected before being injected into the column. Two intermediate sample points are located within the column. The first (S2) is below the top 4 feet of packing. The second (S3) is below the top 8 feet of packing. Finally, rich solvent (S4) is collected at the bottom of the column as the liquid flows to the bottoms pump. Lean solvent (S5) is collected at the outlet of the high-temperature flash drum, V-330, before being mixed with the solvent inventory in the surge drum, V-210.

Liquid samples are analyzed by titration to determine both the amount of CO_2 captured in the liquid and the total concentration of amine in the solvent.

1.2 Material Balance Calculation

Carbon Dioxide Removed from Inlet Gas

The rate of CO_2 removal from the inlet gas can be calculated using various combinations of measured inlet and outlet gas flow rates and CO_2 concentrations (Appendix B). In these experiments the calculated CO_2 removal rates varied by less than 2% between the three most dependable calculation methodologies. For clarity, only the average CO_2 removal rate is reported.

Carbon Dioxide Absorbed in the Solvent

The liquid samples from the inlet to the absorber column and from the bottom of the absorber column are titrated to determine a weight fraction of CO_2 in the lean and rich solvent. Using the liquid mass flow rate as determined above, the amount of CO_2 absorbed in the column is calculated from the difference in CO_2 measured in the rich and lean liquid. This calculation method assumes that the liquid flow rate calculation and the liquid sample analyses are all accurate.

Carbon Dioxide Removed from the Solvent

The liquid samples from the bottom of the absorber column and from the high-temperature flash drum are titrated to determine a weight fraction of CO_2 in the rich and lean solvent. Using the liquid mass flow rate as determined above, the amount of CO_2 released in the regeneration section is calculated from the difference in CO_2 measured in the rich and lean liquid. This calculation method assumes that the liquid flow rate calculation and the liquid sample analyses are all accurate.

Carbon Dioxide in the Flash Gas

The rate of CO_2 desorbed from the solvent in the regeneration section is calculated from the measurement of CO_2 exhaust gas flow rate from the flash gas separator at FI-350. The flash gas composition is assumed to be entirely CO_2. This calculation also assumes that the gas flow rate measurement at FI-350 is accurate.

1.3 Aqueous Amine Baseline

To test the lab pilot unit and to establish a reference case for comparison to the ION solvent, several "once-through" runs through the absorber using a 15% aqueous monoethanolamine (MEA) solution were conducted. Material balance calculations were completed using various combinations of the data collected during these runs. The resulting material balance demonstrates that sufficient data can be collected from the lab pilot unit to help validate the process simulation model.

Approach: ION Engineering's lab pilot unit for CO_2 capture was operated on aqueous MEA solvent at various run conditions to generate test data for process simulation validation and subsequent comparison to ION solvents. These tests were conducted using the absorber only since the MEA solvent could not be effectively regenerated using the two-stage flash approach. The unit was operated in a "once-through" fashion with fresh solvent entering the top of the column. Spent solvent exiting the bottom of the column was sent to waste. Data and samples were collected during the test runs to allow for the calculation of a material balance around the absorber column. The material balance envelope around the absorber is shown in Appendix C.

An aqueous composition of 15% MEA was chosen because initial calculations with a 30% MEA solution showed that absorber efficiency would be too high and the CO_2 would be totally absorbed in the column. Calibrating the simulation model absorber characteristics requires a run with incomplete CO_2 capture. The lab test unit would not be able to meet the desired absorber operating conditions with a typical 30% aqueous MEA solution. Based on typical flue gas compositions of 10%-11% CO_2, the lab pilot unit gas flows could not be set high enough to saturate a 30% aqueous MEA solution. Conversely, operation of the absorber at very low liquid flow would result in insufficient wetting of the column packing materials and less than optimum modeling.

The gas-basis material balance around the absorber can be calculated by using different combinations of measured variables such as inlet and outlet gas flow rates and inlet and outlet CO_2 concentrations. Table 1 shows the combinations of variables used for each of four material balance calculations. Comparing the results from different calculation methods can be helpful in identifying sources of inaccuracy in the data collection. The gas-basis material balance calculations can then be combined with the liquid-basis material balance to produce a material balance around the absorber as shown in Table 2. Also shown in Table 2 are the results of the material balance calculations using data from the GC/MS analyses instead of the CO_2 analyzer.

Table 1. Comparison of data used in different formulas to calculate material balance

Data Used	Location	Material Balance Calculation			
		(1)	(2)	(3)	(4)
Nitrogen inlet flow rate	FIC 120	■	■		■
CO_2 inlet flow rate	FIC 130	■	■	■	
CO_2 analyzer (inlet gas)	AI 270$^{(I)}$			■	■
Outlet gas flow rate	FE 270	■			
CO_2 analyzer (outlet gas)	AI 270 $^{(O)}$	■	■	■	■

Results: The results of the different calculations and overall material balance closure (outlet flow/inlet flow*100%) are summarized in Table 2.

Table 2. Overall Material Balance Results

	Calculation Method	CO_2 In (gmol/hr)			CO_2 Out (gmol/hr)			Closure
		Liquid	Gas	Total	Liquid	Gas	Total	
(1)	Gas Flows	0.9	34.6	35.5	30.5	35.7	66.2	186%
AI-270 (Analyzer)								
(2)	Outlet Gas Composition	0.9	34.6	35.5	30.5	3.3	33.8	95.2%
(3)	Gas Compositions / CO_2 Flow	0.9	34.6	35.5	30.5	3.4	33.9	95.5%
(4)	Gas Compositions / N_2 Flow	0.9	34.0	34.9	30.5	3.3	33.9	96.8%
GC/MS								
(2)	Outlet Gas Composition	0.9	34.6	35.5	30.5	3.8	34.3	96.6%
(3)	Gas Compositions / CO_2 Flow	0.9	34.6	35.5	30.5	4.0	34.5	97.2%
(4)	Gas Compositions / N_2 Flow	0.9	33.1	34.0	30.5	3.8	34.3	101%

With the exception of the calculation based on gas flow rates alone (1), the material balance closure was good. The installation location of the outlet gas flow meter, FE-270, resulted in the meter giving erroneously high gas flow rate measurements which resulted in the poor material balance closure. Since this test was completed, the meter has been moved to a new location which should provide more accurate data going forward. All of the other gas side calculations yielded overall material balance closures ranging from 95% to 101%. Disparity between the gas-basis and liquid-basis material balances range between 4% and 6% of the calculated CO_2 absorption. The GC/MS data yielded slightly better material balance closure than the CO_2 analyzer data, but both methods are in good agreement and yield acceptable quality results.

Conclusions: The lab pilot unit can be operated to obtain reliable material balance data around the absorber column. The once-through run with aqueous MEA provides a useful baseline for absorber efficiency comparisons to ION's CO_2 capture solvents.

1.4 ION Solvent A Tests and Analysis

Experimental runs with ION Solvent A and Solvent A with 5 wt% water added were completed in lab pilot unit. Water added to the solvent was a first step in evaluating the effects of moisture brought in with flue gas. The unit was operated in a continuous mode with lean solvent entering the top of the column. Rich solvent exiting the bottom of the column was sent to the regeneration equipment. After regeneration, the lean solvent was cooled and circulated back to the absorber column. Table 3 summarizes the runs discussed in this report.

In addition to testing the solvent in the unit, data was also collected to evaluate the impact of using an intercooler in the absorber column. The intercooler is a pump around heat exchanger that is used to cool the liquid flow from one stage in the absorber before it is returned to the next lower stage. A cooler liquid in the column is expected to be able to absorb additional CO_2.

Table 3. Solvent A Test Runs

Run ID	Description
1	Solvent: 15% Aqueous MEA at 6 gph Gas: 11.7% CO_2 at 120 slpm
2A	Solvent: Solvent A at 6 gph Gas: 11.7% CO_2 at 120 slpm
2B	Repeat Run using solvent from 2A
2C	Repeat Run 2A with intercooler in operation
3A	Solvent: 32% Solvent A/5% water at 6 gph Gas: 11.7% CO_2 at 120 slpm
3B	Repeat Run using solvent from 3A
3C	Repeat Run 3A with intercooler in operation

Data and samples were collected during the test runs to allow for the calculation of a material balance around the absorber column, the regeneration section, and the overall lab test unit (Appendix C). In the discussion that follows, the validity of the data is first addressed. This is followed by the results and discussion.

1.4.1 Absorption Results and Material Balance

Table 4 shows the results from the absorber for the Solvent A test runs as well as the aqueous amine test baseline run. With the exception of Run 2A, the agreement between CO_2 removed from the gas and the CO_2 absorbed in the liquid is good. The disparity between the gas-basis and liquid-basis calculations for the other runs ranges from 1.7% to 9.7% of the average CO_2 absorption rate.

Table 4. CO_2 Absorption Results

Calculation of CO_2 Absorbed Out of Gas Phase

Run No.	Description	Inlet Gas N_2 Flow (gmol/hr)	Inlet Gas CO_2 Flow (gmol/hr)	Outlet Gas CO_2 Flow (gmol/hr)	CO_2 Absorbed (gmol/hr)	CO_2 Capture %
1	Aqueous Amine, 15% MEA	264.7	34.4	3.3	31.1	90.4
2A	Solvent A, Anhydrous	265.7	34.3	7.2	27.1	79.0
2B	Solvent A, Anhydrous (repeat 2A)	263.7	34.5	8.8	25.7	74.4
2C	Solvent A, Anhydrous w/Intercooler	263.5	34.5	6.0	28.5	82.6
3A	Solvent A, 5% Water	264.1	34.4	5.9	28.5	82.8
3B	Solvent A, 5% Water w/Intercooler	264.2	34.4	4.9	29.5	85.7
3C	Solvent A, 5% Water (repeat 3A)	264.4	34.4	8.8	25.6	74.4

Calculation of CO_2 Absorbed Into the Liquid Phase

Run No.	Description	Liquid CO_2 Flow In (gmol/hr)	Liquid CO_2 Flow Out (gmol/hr)	Inlet Gas CO_2 Flow (gmol/hr)	CO_2 Absorbed (gmol/hr)	CO_2 Capture %
1	Aqueous Amine, 15% MEA	0.9	30.5	34.4	29.6	86.0
2A	Solvent A, Anhydrous	18.3	54.2	34.3	35.9	105
2B	Solvent A, Anhydrous (repeat 2A)	18.0	42.4	34.5	24.4	70.7
2C	Solvent A, Anhydrous w/Intercooler	17.0	46.2	34.5	29.2	84.6
3A	Solvent A, 5% Water	14.7	43.7	34.4	29.0	84.3
3B	Solvent A, 5% Water w/Intercooler	15.4	47.9	34.4	32.5	94.5
3C	Solvent A, 5% Water (repeat 3A)	16.5	44.4	34.4	27.9	81.1

The gas material balance around the absorber is believed to be the more accurate due to the method of measurement used for the liquid flow calculation. The liquid flow measurement is obtained by using the rate of level change in the bottom of the absorber column at steady state. Column feed pump flows are dependent on viscosity and system backpressure, so offline flow measurements are not representative. The column cross section is known and the column level is measured by a differential pressure sensor to measure fluid depth. The gas flows, on the other hand, are measured by online gas flow meters which were calibrated in place using mass flow controllers for gas flow. Gas CO_2 composition is also measured online with infrared absorption analysis calibrated to gas standard.

At first glance, the CO_2 capture looks more efficient in the aqueous amine solution than in the Solvent A solution. This is to be expected, since the aqueous amine was run once through the column and the inlet gas was always contacted by unloaded solvent. In contrast, Solvent A was circulated through the unit and regenerated. As can be seen in Table 4, the CO_2 loading in the lean Solvent A was appreciably greater than in the fresh aqueous amine solvent.

As expected, the intercooler improved the CO_2 absorption in the solvents by about 12% with improvements ranging from 3.5% to 20% depending on the run and the basis of calculation for the absorption.

From these results it appears that Solvent A may be losing efficacy over time. A comparison between Run 2A and Run 2B (gas basis) shows that the anhydrous solvent absorbed about 5% less CO_2 in Run 2B as compared to Run 2A. The 5% water solution absorbed about 10% less CO_2 in run 3C as compared to Run 3A.

Table 5 shows the absorber material balance closure. With the exception of Run 2A, the material balance around the absorber is very good with closures (outlet CO_2 flow / inlet CO_2 flow) ranging from 97.5% to 106% of the inlet CO_2 flow rate.

Table 5. Absorber Material Balance Results

Run ID	Description	CO_2 In (gmol/hr)			CO_2 Out (gmol/hr)			Closure
		Liquid	Gas	Total	Liquid	Gas	Total	
1	Aqueous Amine, 15% MEA	0.9	34.4	35.3	30.5	3.3	33.8	95.8%
2A	Solvent A, Anhydrous	18.3	34.3	52.6	54.2	7.2	61.4	117%
2B	Solvent A, Anhydrous	18.0	34.5	52.5	42.4	8.8	51.2	97.5%
2C	Anhydrous w/Intercooler	17.0	34.5	51.5	46.2	6.0	52.2	101%
3A	Solvent A, 5% Water	14.7	34.4	49.1	43.7	5.9	49.6	101%
3B	5% Water w/Intercooler	15.4	34.4	49.8	47.9	4.9	52.8	106%
3C	Solvent A, 5% Water	16.5	34.4	50.9	44.4	8.8	53.2	105%

1.4.2 Regeneration Material Balance

Table 6 shows the results from the regeneration section for the Solvent A test runs. In this case, there is no comparison to the aqueous MEA solution since the lab test unit was not designed to regenerate an aqueous solution. The material balance around the regeneration section is not as good as the absorber with closures ranging from 74% to 92%. These results indicate a systemic bias in the regeneration data, most likely inaccurate gas flow rate measurements at FI-350. This flow meter has been identified as needing more rigorous calibration.

Table 6. Regeneration Material Balance Results

Run ID	Description	CO_2 In (gmol/hr)			CO_2 Out (gmol/hr)			Closure
		Liquid	Gas	Total	Liquid	Gas	Total	
1	Aqueous Amine, 15% MEA	N/A	N/A	N/A	N/A	N/A	N/A	N/A
2A	Solvent A, Anhydrous	54.2	0.0	54.2	16.9	23.0	39.9	73.6%
2B	Solvent A, Anhydrous	42.4	0.0	42.4	17.2	21.8	39.0	92.0%
2C	Anhydrous w/Intercooler	46.2	0.0	46.2	16.6	25.1	41.7	90.3%
3A	Solvent A, 5% Water	43.7	0.0	43.7	13.4	25.0	38.4	87.9%
3B	5% Water w/Intercooler	47.9	0.0	47.9	14.6	25.0	39.6	82.7%
3C	Solvent A, 5% Water	44.4	0.0	44.4	15.4	21.9	37.3	84.0%

1.4.3 Overall Lab Pilot Unit Material Balance

Finally, Table 7A shows the overall material balance results for the entire lab test unit. With closures of about 90%, the data indicate the same systemic bias seen in the regeneration material balance. Again the most likely source of the inaccuracy is the flash gas flow rate measurement at FI-350. If the calculated CO_2 release rate from the liquid is considered instead of the measured flash gas rate, the overall material balance closures range from 99% to 111% with the exception of Run 2A as shown in Table 7B.

The quality of the material balance indicates that the results from the lab test unit can be used to reliably evaluate the performance of Solvent A and the proposed process for CO_2 capture. The key parameters to be evaluated are: absorber efficiency as compared to aqueous amine solvents, regeneration system efficiency, and the durability of Solvent A.

Table 7A. Overall Material Balance Results (CO_2 Exhaust Gas)

Run ID	Description	CO_2 In (gmol/hr)	CO_2 Out (gmol/hr)			Closure
		Inlet	Exhaust	Flash	Total	
1	Aqueous Amine, 15% MEA	N/A	N/A	N/A	N/A	N/A
2A	Solvent A, Anhydrous	34.3	7.2	23.0	30.2	88.0%
2B	Solvent A, Anhydrous	34.5	8.8	21.8	30.6	88.7%
2C	Anhydrous w/Intercooler	34.5	6.0	25.1	31.1	90.1%
3A	Solvent A, 5% Water	34.4	5.9	25.0	30.9	89.8%
3B	5% Water w/Intercooler	34.4	4.9	25.0	29.9	86.9%
3C	Solvent A, 5% Water	34.4	8.8	21.9	30.7	89.2%

Table 7B. Overall Material Balance Results (Liquid Desorption)

Run ID	Description	CO_2 In (gmol/hr)	CO_2 Out (gmol/hr)			Closure
		Inlet	Exhaust	Liquid	Total	
1	Aqueous Amine, 15% MEA	N/A	N/A	N/A	N/A	N/A
2A	Solvent A, Anhydrous	34.3	7.2	37.3	44.5	130%
2B	Solvent A, Anhydrous	34.5	8.8	25.2	34.0	98.6%
2C	Anhydrous with Intercooler	34.5	6.0	29.6	35.6	103%
3A	Solvent A, 5% Water	34.4	5.9	30.3	36.2	105%
3B	Solvent A, 5% Water	34.4	4.9	33.3	38.2	111%
3C	5% water with Intercooler	34.4	8.8	29.0	37.8	110%

1.4.4 Absorber Efficiency Comparison

A key measure of CO_2 capture process performance is the absorber efficiency. The amount of CO_2 that can be absorbed into a given volume of solvent determines the required circulation rate to effect the desired CO_2 removal.

The performance data from the once-through runs with 15% aqueous MEA were used to characterize the lab test unit absorber in an Aspen Plus process simulation. The process simulation was then exercised for a more typical aqueous amine formulation of 30 wt% MEA in water. Additionally, a CO_2 loading in the lean solvent more representative of a regenerated solvent was added to the simulation to more accurately reflect a typical practice. In this case, a lean solvent loading of 0.242 mole CO_2 per mole MEA was chosen to represent reported performance for commercial aqueous amine operation.[i]

Carrying Capacity

Table 8 shows the calculated carrying capacity for each experimental run and compares that with the carrying capacity predicted for the 30% MEA solution. These results are calculated from the loadings observed in the lab unit absorber and predicted by the absorber simulation.

In general, it appears that the Solvent A volumetric carrying capacity is less than that of 30% MEA. However, there seem to be circumstances, i.e. absorber intercooling , where the volumetric carrying capacity of the Solvent A solvent approaches that of the 30% MEA solution.

Table 8. Carrying Capacity Comparison

Run ID	Solvent Description	Loading (mole CO_2/mole amine)			Amine Conc.	Volumetric Capacity
		Inlet	Outlet	Pickup	mole/L	mole CO_2/L
1	30% MEA	0.242	0.514	0.272	4.67	1.27
2B	Solvent A, Anhydrous	0.155	0.365	0.210	4.87	1.02
2C	Anhydrous w/Intercooler	0.145	0.394	0.249	4.85	1.21
3A	Solvent A, 5% Water	0.133	0.394	0.261	4.57	1.19
3B	5% Water w/Intercooler	0.139	0.431	0.292	4.59	1.34
3C	Solvent A, 5% Water	0.149	0.401	0.252	4.57	1.15

Packing Height

Another measure of absorber efficiency is the height of packing required to provide the necessary time and surface area for mass transfer. Figure 3 shows the solvent loading as a function of position in the absorber column. This comparison shows that the aqueous MEA solvent approaches its ultimate loading more rapidly than the Solvent A test runs. After passing through the first four feet of packing, the aqueous amine solvents are already at 80% of ultimate loading. By contrast, most of the Solvent A test runs are at about 45% of ultimate loading. The aqueous amine solutions reached equilibrium in the column at some point in the top four feet of packing. Below that, the amine solution slowly cooled which is why the loading continues to increase in the bottom six feet. The rate of CO_2 absorption in the lower beds was so slow that the exothermic heat of reaction failed to balance the heat losses to the gas and the surroundings.

In contrast, the Solvent A test runs did not reach 80% of ultimate loading until about seven feet below the top of the packing. These results indicate that the Solvent A does not reach equilibrium until somewhere in the bottom two feet of packing, if at all, in the absorber. This is further supported by the observed temperature profile in the absorber column which tended to be more flat for Solvent A, suggesting that the exothermic absorption reaction was occurring throughout the height of the column.

These data do not illuminate the cause of the reduced efficiency. Solvent A is more viscous than typical amine solutions which will retard mass transfer between the gas and liquid phases. The rate of reaction between a secondary amine as used in Solvent A is reasonably expected to be lower than that of a primary amine such as MEA. Most likely it is some combination of both of these factors that is reducing the absorber column efficiency.

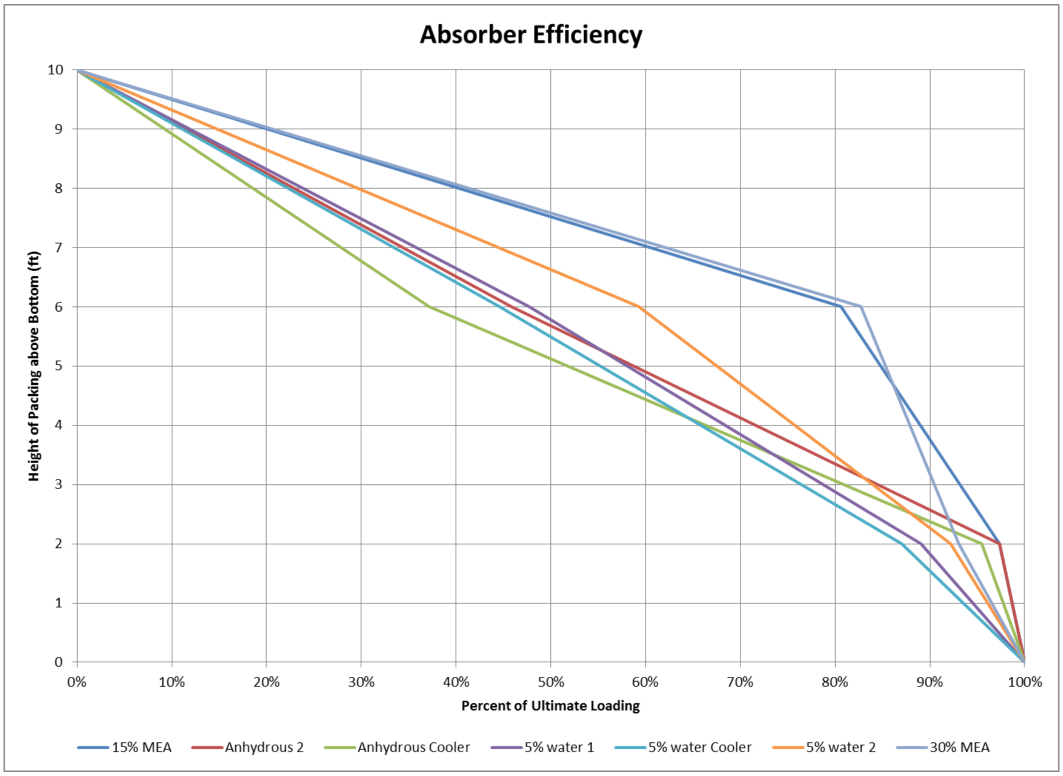


Figure 3. Absorber Efficiency Results

1.4.5 Regeneration System Efficiency

Figure 4 shows the results of liquid sample data collected from the regeneration system. Over the range of regeneration temperatures studied (100° C to 120° C), the lean solvent behaves like a liquid that is at an equilibrium temperature about 10° C lower than the actual regeneration temperature. The results in Table 5 suggest that with a maximum loading of around 0.4 moles CO_2 per mole of amine, Solvent A needs to be regenerated to a loading of about 0.1 moles CO_2 per mole of amine to have a carrying capacity per unit volume similar to that of aqueous amine solutions. The results of the regeneration study indicate that an actual temperature of about 130° C should meet that target. Unfortunately, the lab test unit is currently incapable of producing regeneration temperatures much above 120° C at the liquid flow rates needed to sufficiently wet the absorber packing.

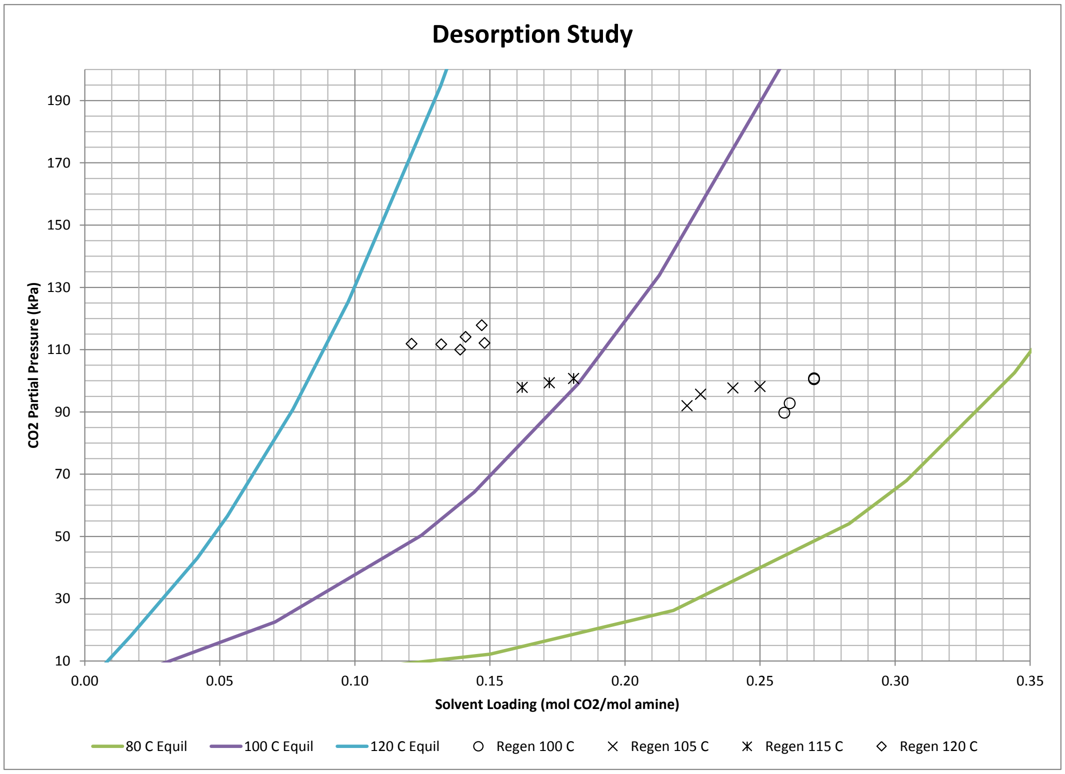


Figure 4. Regeneration System Results

Ultimately, the regeneration temperature will be selected to minimize the total energy required to regenerate the solvent. As with any amine system, there is a point at which regenerating the solvent to a lower loading requires more energy to obtain the higher temperature than what is required for a higher solvent circulation rate at a lower temperature. That balance, along with the thermal degradation of the amine will establish the optimal operating temperature in the regeneration system.

1.4.6 Solvent Durability

In the operation of the lab pilot unit, several issues were observed that were not predicted in prior laboratory analysis of Solvent A.

While operating the absorber with anhydrous Solvent A, the unit had significant plugging problems. The column mist eliminator, the overhead vapor line and the overhead cooler repeatedly plugged, causing high column operating pressures and high column pressure drops. When the unit was inspected, the mist eliminator and lines were found to be coated and plugged with solid carbamate crystals. Fortunately, the carbamate was relatively easy to dissolve in hot water and wash out of the system. Unfortunately, the rate of solid formation was so fast that it caused noticeable problems within a few hours of running after a thorough cleaning. The operational difficulties posed by the solid formation made it clear that using an anhydrous amine solvent for CO_2 capture is not feasible in conventional absorber technology. Subsequent runs with as little as 5% water in the solvent showed no evidence of solid formation. Further work will be required to identify the minimum amount of water in the solvent that is necessary to disrupt the solid carbamate deposition in the absorber.

Although the data collected in each experimental run are of good quality as evidenced by the material balance results presented in Tables 3 through 5, the observations from ‘A’ runs (early) to ‘B’ runs (later) indicate a decrease in solvent performance over time. The formation of solid carbamate crystals may help explain that trend in the anhydrous solvent, but that does not explain the observation for the 5 wt% water solvent. Obviously, there are not enough experimental runs to even know if this trend continues and far too few to draw meaningful conclusions. The question of solvent durability is being evaluated in further experimental work.

1.5 Conclusions

1. The test program successfully demonstrated that the ionic liquid-amine Solvent A can absorb CO_2 and be regenerated in a continuous process.
2. In these tests, Solvent A reacted more slowly in the absorber than an aqueous MEA solution. Whether this is due to increased solvent viscosity limiting mass transfer or slower reaction rates for the secondary amine is unclear. This indicates that the absorber column will either need to be higher or have a more efficient packing than a conventional aqueous MEA absorber.
3. The use of an intercooler in the absorber column appears to have beneficial impacts on the efficiency of the system, but further work is needed to better characterize this.
4. The two stage flash design can be used to regenerate the Solvent A to reasonable (0.15 mole/mole) lean solvent loadings. Additional engineering work is needed to determine the optimal regeneration conditions and to determine if the flash design is more cost-effective than a traditional stripper for solvent regeneration. This is especially true for solvent formulations containing some added water.
5. The reaction between an anhydrous Solvent A and CO_2 produces solid carbamate crystals. In addition to the ongoing loss of amine as carbamate, the operational difficulties posed by the solid formation rule out the use of anhydrous amine solvents for CO_2 capture in conventional packed bed absorber technology.
6. Solvent A performance appeared to decline over time in limited experimental runs. This potentially has a serious impact on the utility of Solvent A and needs further investigation.

2. References

1) Mohammad R.M. Abu-Zahra, Le´on H.J. Schneiders, John P.M. Niederer, Paul H.M. Feron, Geert F. Versteeg, International Journal of Greenhouse Gas Control 1 (2007) 37 – 46

3. Appendices

Appendix A: Lab Pilot Unit Control Panel

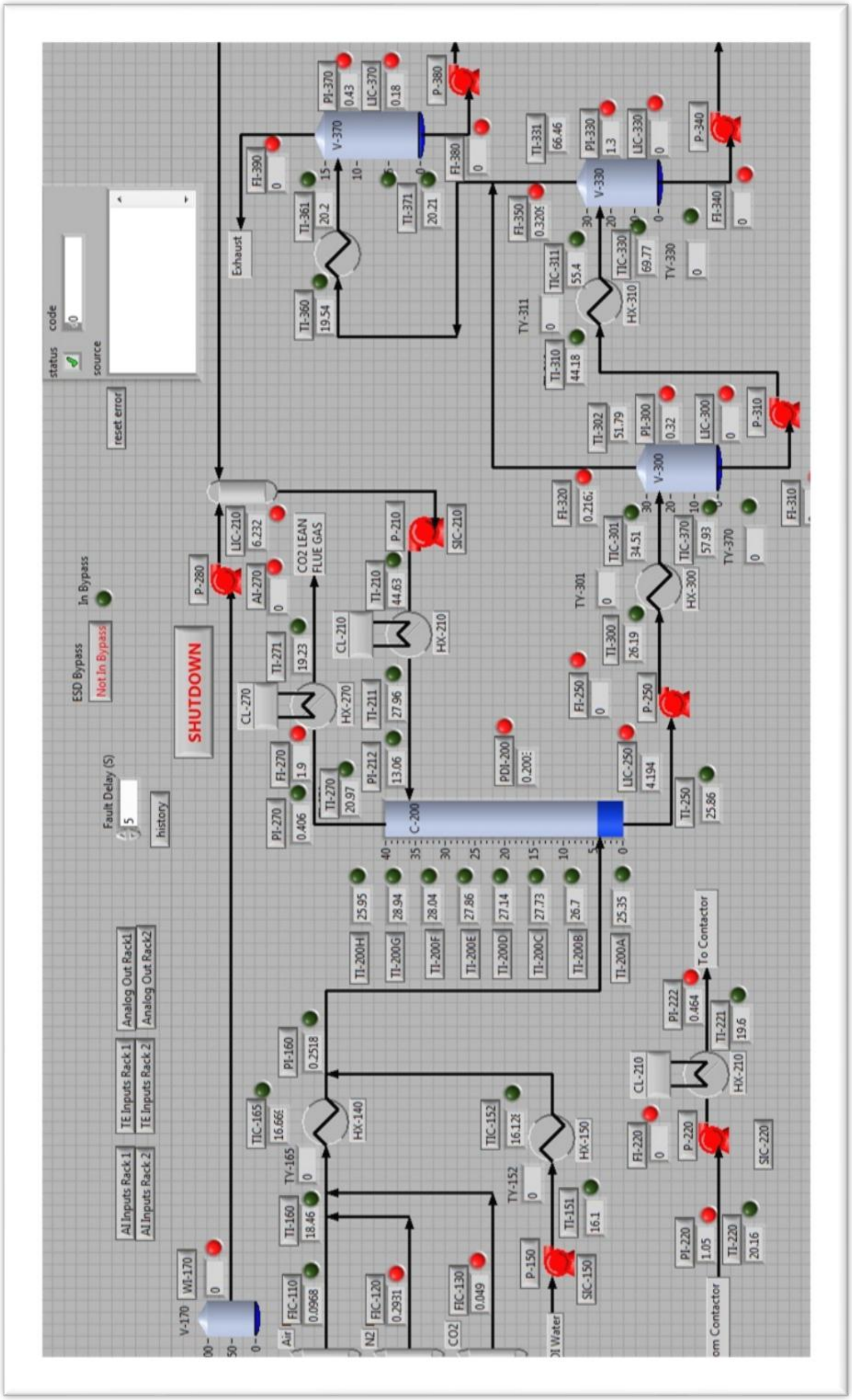


Figure A.1 LabView Master Control Panel

Appendix B: Material Balance Calculation Methods

The different methods for calculation of the material balance and nomenclature used in the equations are summarized below. Refer to Appendix C for locations of data collection points.

(1) Inlet and Outlet Gas Flow Rates

The rate of flue gas exhaust flow is measured at FI-270. The water vapor fraction of that flow can be calculated by knowing the vapor pressure of water at the outlet gas condition. The nitrogen flow rate is assumed to be the same as the inlet flow rate measured at FIC-120. The carbon dioxide flow rate can then be calculated by difference and compared to the inlet flow rate measured at FIC-130 to calculate CO_2 absorbed by the solvent.

This calculation method assumes that the flow rates measured at FIC-120, FIC-130, and FE-270 are all correct. The calculation ignores the inlet and outlet concentrations measured by the CO_2 analyzer, AI-270.

(2) Inlet Gas Flow Rates and Exhaust Gas Composition

The rate of flue gas exhaust flow is calculated by assuming that all the inlet nitrogen flow as measured by FIC-120 passes through the absorber column. The fraction of water vapor in the exhaust gas is estimated from the water vapor pressure at the overhead cooler outlet conditions. The fraction of CO_2 in the exhaust gas is measured at AI-270. The fraction of nitrogen in the gas is calculated by difference and used to calculate the total exhaust gas flow rate. Once the total gas flow rate is known, the outlet carbon dioxide flow rate can be calculated according to the measured CO_2 concentration and compared to inlet flow measured at FIC-130 to calculate CO_2 absorbed by the solvent.

This calculation method assumes that the flow rates measured at FIC-120 and FIC-130 and the exhaust CO_2 composition are all correct. The calculation ignores the outlet gas flow rate measured at FI-270 and the inlet gas composition.

(3) Inlet and Exhaust Gas Composition and Inlet CO_2 Flow Rate

The rate of exhaust gas flow is calculated by assuming that all the inlet nitrogen flow passes through the absorber column. The total inlet gas flow rate is calculated from the CO_2 flow rate measured at FIC-130 and the inlet CO_2 concentration measured at AI-270. The inlet nitrogen flow rate is then assumed to be the difference between the calculated total inlet gas flow rate and the measured inlet CO_2 flow rate. The water vapor concentration in the exhaust gas is estimated from the water vapor pressure at the overhead cooler outlet conditions. The fraction of CO_2 in the exhaust gas is measured at AI-270. The concentration of nitrogen in the exhaust gas is calculated by difference and along with the calculated inlet nitrogen rate, used to calculate the total exhaust gas flow rate. Once the total gas flow rate is known, the outlet carbon dioxide flow rate can be calculated according to the measured CO_2 concentration and compared to inlet flow measured at FIC-130 to calculate CO_2 absorbed by the solvent.

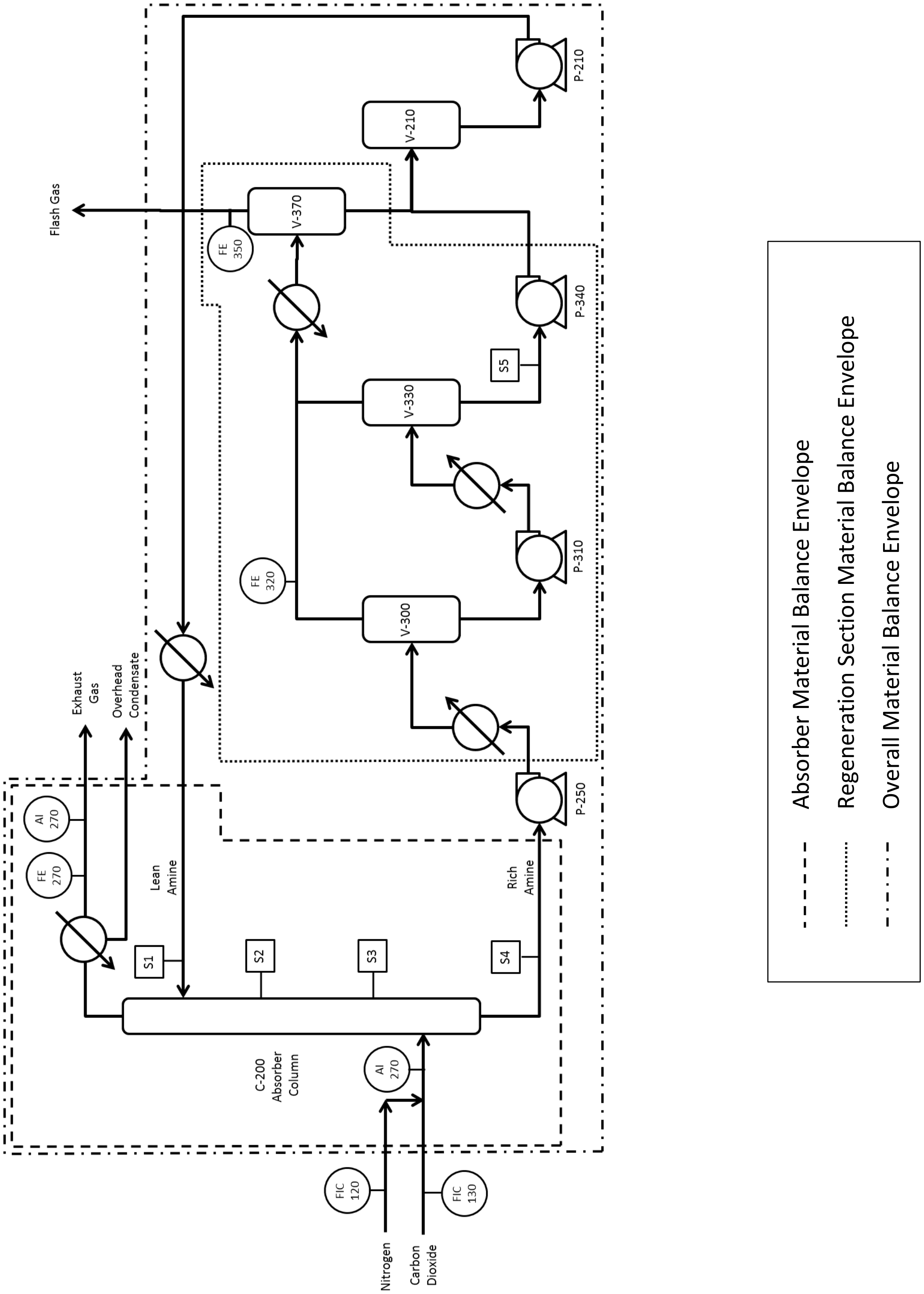
This calculation method assumes that the flow rate measured at FIC-130 and the inlet and outlet gas CO_2 concentrations are all correct. The calculation assumes that the flow rate at FIC-120 is erroneous. The calculation ignores the outlet gas flow rate measured at FI-270.

(4) Inlet and Exhaust Gas Composition and Inlet Nitrogen Flow Rate

The rate of exhaust gas flow is calculated by assuming that all the inlet nitrogen flow passes through the absorber column. The total inlet gas flow rate is calculated from the nitrogen flow rate measured at FIC-120 and the inlet CO_2 concentration measured at AI-270. The inlet CO_2 flow rate is then assumed to be the difference between the calculated total inlet gas flow rate and the measured inlet nitrogen flow rate. The water vapor concentration in the exhaust gas is estimated from the water vapor pressure at the overhead cooler outlet conditions. The fraction of CO_2 in the exhaust gas is measured at AI-270. The concentration of nitrogen in the exhaust gas is calculated by difference and used to calculate the total exhaust gas flow rate. Once the total gas flow rate is known, the outlet carbon dioxide flow rate can be calculated according to the measured CO_2 concentration and compared to calculated inlet CO_2 flow rate to calculate the CO_2 absorbed by the solvent.

This calculation method assumes that the flow rate measured at FIC-120 and the inlet and outlet gas CO_2 concentrations are all correct. The calculation assumes that the flow rate at FIC-130 is erroneous. The calculation ignores the outlet gas flow rate measured at FI-270.

Appendix C: Lab Pilot Unit Material Balance Envelopes



ION Engineering
Bold Science for Clean Energy

Appendix T2: Topical Report for Task 3.5 Process Simulation for Novel Solvent

DOE Award: DE-FE0005799

ION Engineering

Project Title: Novel Solvent CO_2 Capture
Date Report Issued: 05/06/2011

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Reporting Period End Date: 05/31/2011

Abstract

ION Engineering is developing technology for carbon dioxide (CO_2) capture using a novel solvent comprised of a mixture of ionic liquids (IL) and amines. One of the primary goals of the technology development program is to develop a process simulation that can be used for technology optimization, engineering design and process development. Existing commercial models do not typically include ionic liquids in available datasets and rely on existing internal calculations based on the behavior of aqueous amine solutions.

The Aspen Plus® process simulation software was selected for flexibility and the ability for the user to define components and to supply the parameters needed for thermodynamic and physical property calculations. Parameters were developed through regressions of experimental and published data in combination with parameter estimations provided by Aspen based on the molecular structure of the compounds used. To calibrate the model, data generated by Aspen was compared to published physical data and to experimental runs using a lab-scale pilot CO_2 capture unit.

The comparison of literature and experimental data with predictions from the Aspen Plus simulation demonstrates reasonable prediction of physical and thermodynamic properties for the IL, amine, and IL/amine mixtures that are the basis for this novel solvent.

As a result of this effort, ION Engineering now feels confident that the Aspen simulation model can be modified to effectively represent operating parameters for its proposed CO_2 capture technology.

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Executive Summary

ION Engineering is developing technology for carbon dioxide (CO_2) capture using a novel solvent comprised of a mixture of ionic liquids (IL) and amines. One of the primary goals of the technology development program is to develop a process simulation that can be used for technology optimization, engineering design and process development. Existing commercial models do not typically include ionic liquids in datasets and rely on proprietary algorithms to model aqueous amine solutions.

The Aspen Plus® process simulation software was selected for flexibility and the ability for the user to define components and to supply the parameters needed for thermodynamic and physical property calculations. These parameters were developed to characterize the properties of the pure ionic liquid and the mixture of ionic liquid and amine selected for initial testing. In addition, the properties of the specific amine selected and the carbamate ions that form upon reaction with CO_2 needed to be characterized as they were not part of the Aspen dataset.

Parameters were developed through regressions of experimental and published data in combination with parameter estimations provided by Aspen based on the molecular structure of the compounds used. Data generated by Aspen was then compared to known physical data and to experimental data from ION and University of Alabama to validate the model calculations.

ION's continuous process lab pilot unit was used to generate data to calibrate the absorber column performance in the Aspen model, using a baseline aqueous monoethalamine (MEA). The column can be characterized through the use of stage efficiencies and an approach to reaction equilibrium temperature. Using process flows corresponding to the lab pilot unit, simulations were run for a range of theoretical stages and design specifications adjusted to match observed temperature profiles, heat loss and liquid loadings.

Material balances calculated for the experimental data were in good agreement with the process simulation's overall material balance. The simulation resulted in 89.4% capture of the CO_2 feed to the column and the experiemental results showed between 87% and 91% of the CO_2 absorbed in the aqueous MEA solution.

The comparison of literature and experimental data with predictions from the Aspen Plus simulation shows that sufficient property estimation parameters are available or can be regressed from the data to allow a good prediction of physical and thermodynamic properties for the IL, amine, and IL/amine mixtures that are the basis of ION Engineering's proposed CO_2 capture technology.

However, challenges were encountered when the simulation studies began with ION's IL/amine solvent. Calculation errors were discovered in the preferred property method and referred to AspenTech for resolution by their technical support team. Within the past few days, an althernative property method has been identified that appears to be achieving good results in the model. This will be validated and additional experimental results from the lab pilot unit used to refine the simulation model for ION's novel solvents.

As a result of this recent effort, ION Engineering now feels confident that the Aspen simulation model can be modified to effectively represent operating parameters for its proposed CO_2 capture technology.

Report

1. Introduction

Process simulation software is an important tool in the engineering of carbon capture processes and evaluation of potential performance at larger scale. ION's technology, although based on conventional amine processes commonly used for natural gas processing, virtually eliminates water in the solvent and includes ionic liquids in the solvent mixtures. This presents a challenge for most commercially available software packages which are designed to predict aqueous amine solution behavior. In addition, commercially available software packages do not include ionic liquid (IL) components in their property parameter databases. Aspen Plus® (Aspen) was selected because of the software's flexibility and ability to customize IL components.

Developing a reliable and accurate Aspen simulation model for the novel solvent required a series of steps and iterations to compare projected data to data available from literature, laboratory analysis and ultimately test runs in a continuous processing lab pilot system. Different property methods were explored to achieve accurate results. Problems were encountered with internal Aspen model calculations that needed to be referred to the Aspen Tech code developers for resolution. Although ION now believes the model to be working well, the time required to achieve this has limited time available for extensive process simulations in the first phase of work.

The approach taken to develop and calibrate the model is summarized in this report:

1) Characterize solvent physical properties in Aspen database
    a) Properties of the pure IL
    b) Properties of the pure amine and the carbamate ions that form upon reaction with CO_2
    c) Properties of the IL-amine mixture
2) Validate initial model predictions (with these new data elements)
3) Configure process flows to represent lab pilot unit
4) Calibrate model predictions for column performance

2. Building a model to characterize ION solvents

The Aspen Plus process simulation software includes databases with parameters that enable the simulation software to calculate the thermodynamic and physical properties for an exhaustive number of compounds that are included in the software as "conventional" components. However, the databases do not include data for the compounds that comprise the IL solvent at the heart of ION Engineering's technology.

Representation of ION's novel solvents was achieved using Aspen Plus features that enable creation of a "user-defined" component. The parameters that are needed for property calculations can be supplied in two ways.

1) Aspen Plus includes a number of parameter estimation correlations that are based on the molecular structure of the compound.
2) Parameters can be correlated directly from experimental data supplied by the user for the compound.

Aspen Plus can then be used to generate tables of thermodynamic and physical properties so that the accuracy of the correlations can be confirmed against available experimental data.

Typical amines that can be used in the solvent mixture are included in the Aspen Plus databases. However, it is good practice to compare the default data generated from the Aspen Plus databases with known physical property data. If needed, the default parameters for a “conventional” component can be modified to better fit the reported physical properties. Additionally, the carbamate ions that are formed as products of the reaction between Amine A (ION’s current preferred amine component) and CO_2 are not included in the software databases. Those ions will also be created as “user-defined” components and supplied with available physical property data.

Simulation output is then compared with known physical properties of the IL-amine mixture. If needed, additional interaction parameters can be regressed for mixtures of binary pairs to more accurately reflect the physical properties of the mixed solvent.

2.1. Physical property characterization in Aspen Plus

Aspen Plus has a number of available property methods including equations of state and activity coefficient models that may be used to calculate the needed thermodynamic and physical properties. In general, Aspen recommends that amine processes such as CO_2 absorption be modeled with either the AMINES property method or an ELECNRTL method. The AMINES method is based on the Kent-Eisenberg model which has been developed for aqueous amines. Since the ION technology excludes an aqueous solvent mixture, this property method is not appropriate.

The Electrolyte Non-Random Two-Liquid (ELECNRTL) property method is a versatile electrolyte property method that can handle aqueous and mixed solvent systems. The base NRTL activity coefficient model is coupled with Redlich-Kwong (RK) equation of state for calculation of all vapor properties. The ELECNRTL property method depends on the Aspen database of molecular interaction parameters and chemical reaction equilibrium constants. If data do not exist for a particular combination of components or chemical reactions, the appropriate parameters can be regressed from experimental data. In the absence of experimental data, Aspen can estimate NRTL interaction parameters using a UNIFAC group contribution method based on the molecular structures of the components.

The latest revision of Aspen Plus includes some updates to the ELECNRTL method. The property method ENRTL-RK is identical to the ELECNRTL method if only one electrolyte is present, but is better equipped to handle mixed electrolytes and has a simplified framework for handling the thermodynamic properties calculations. The ENRTL-RK method requires that some water be present in the system, but as long as the token amount is negligible, the method can be used for anhydrous systems as well.

The ENRTL-RK method needed a couple of property route modifications to accurately characterize the liquid specific heat. The pure component liquid heat capacity property route is specified to DHL10 and the mixture liquid heat capacity property route is specified to DHLMX108. The property routes are compatible with the DIPPR correlation for liquid heat capacity which uses parameters that are easily regressed from experimental or literature data.

One drawback of the electrolyte NRTL property methods is that the methods can be difficult to configure properly. During the course of process simulation development, ION Engineering found a number of problems with the ELECNRTL and another updated method, ENRTL-SR. While the ENRTL-RK method so far seems to avoid those problems, ION is still working with Aspentech technical support to isolate and correct the deficiencies in the other property methods.

2.2. Ionic liquid physical property characterization

Although the nature of the ionic molecular structure of the IL of primary interest to ION is not completely compatible with Aspen Plus, it is possible for the user to define functional groups for various property models that allow Aspen to estimate property parameters. Functional groups were defined for the models and methods shown in Table 1.

Table 1. Physical Property Models and Methods

Property Model	Method
UNIFAC	Activity Coefficient model
UNIFAC-Lyngby	Modified UNIFAC model
UNIFAC-Dortmund	Modified UNIFAC model
UNIFAC- Revision 4	Modified UNIFAC model
Bondi method	UNIFAC model parameter estimation
Joback method	Boiling point and critical property estimation
Reichenberg method	Vapor viscosity estimation
Ruizicka method	Liquid heat capacity estimation

Note: The Universal Functional Activity Coefficient (UNIFAC) method is a semi-empirical system for the prediction of non-electrolyte activity estimation in non-ideal mixtures.

Additionally, there are literature data available for many physical properties of the IL including heat capacity, density, viscosity, thermal conductivity, and surface tension. These data were entered into the Aspen Plus simulation to regress parameters for the physical property methods. Figures 1 through 5 illustrate the fit between the experimental data input and the resulting correlations that were regressed from the data.

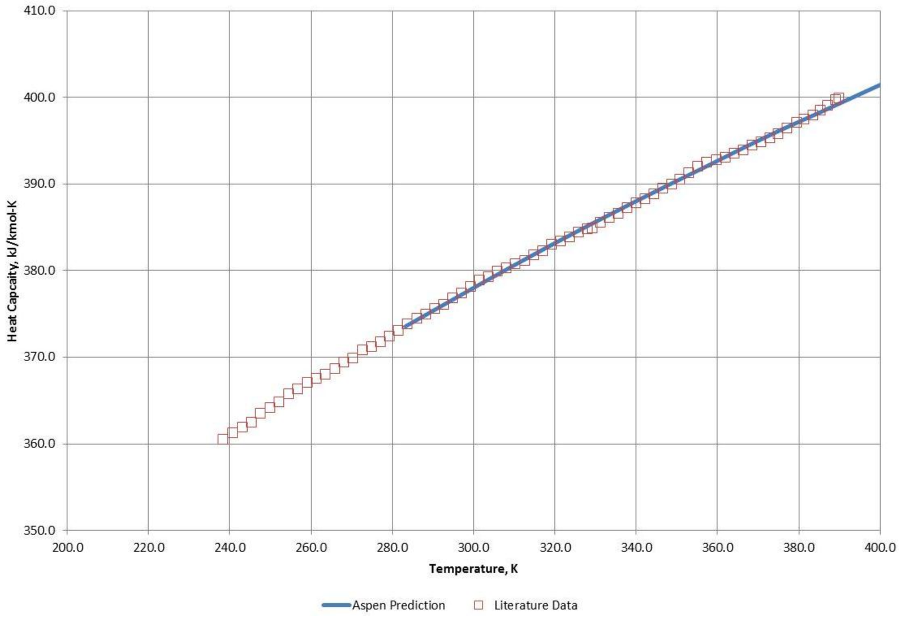

Figure 1. IL Liquid Heat Capacity

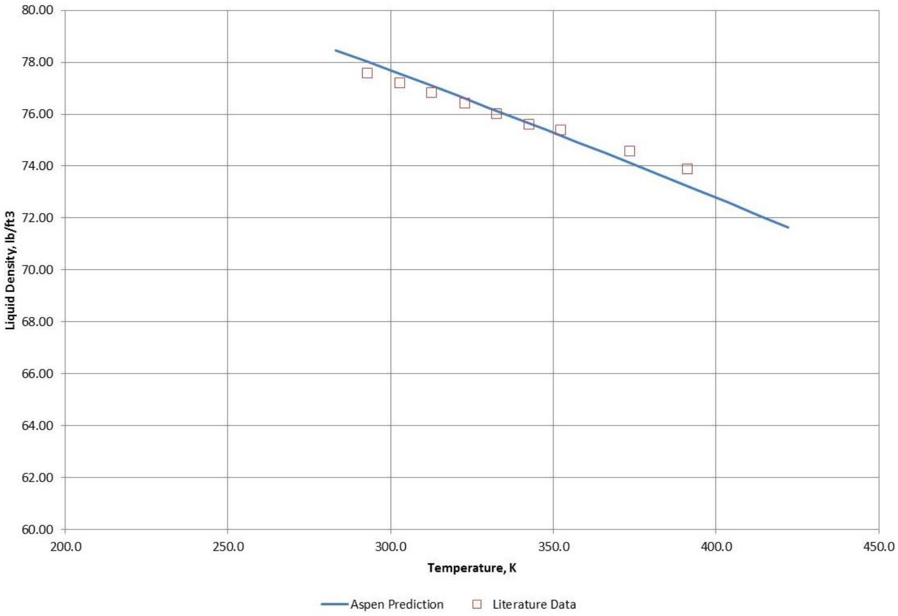

Figure 2. IL Liquid Density

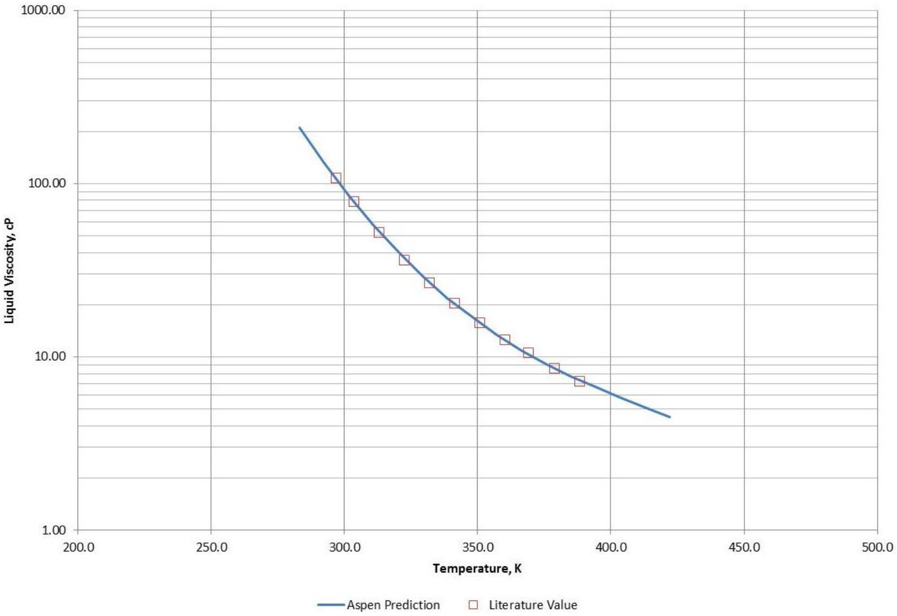

Figure 3. IL Liquid Viscosity

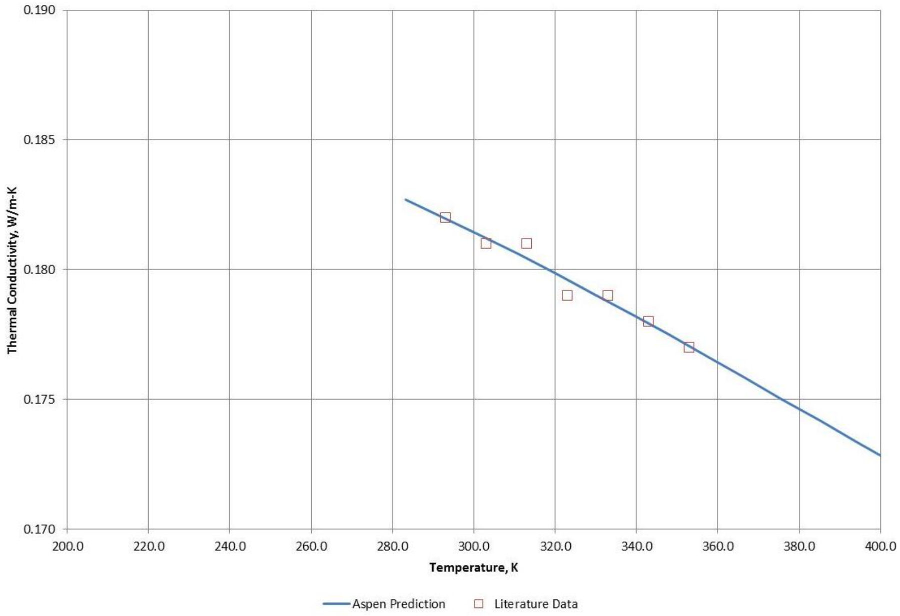

Figure 4. IL Liquid Thermal Conductivity

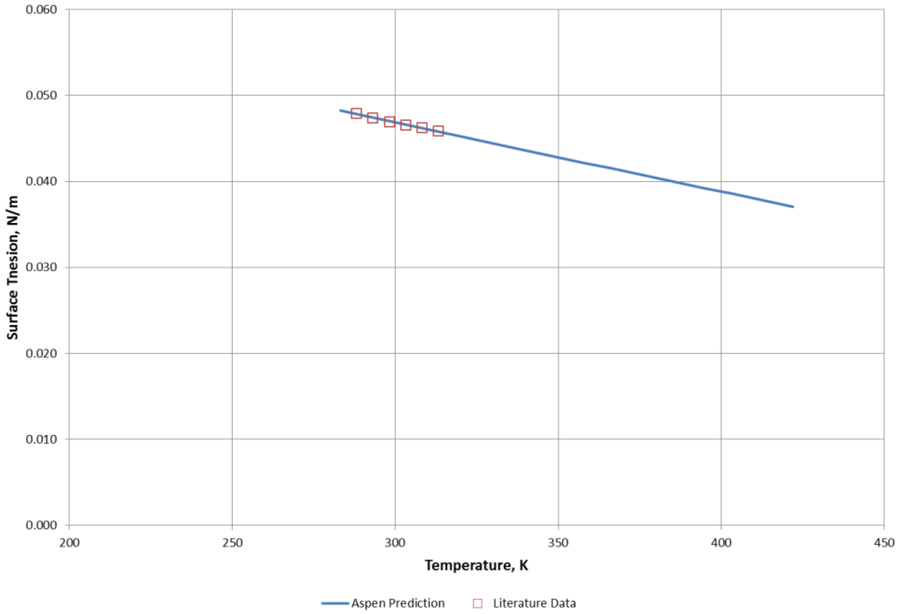

Figure 5. IL Liquid Surface Tension

Figure 6 shows the predicted vapor pressure for the IL liquid as predicted by the default Aspen Plus correlations. The one data point for vapor pressure is from the manufacturer’s MSDS for the IL. While the vapor pressure of the ionic liquid in Solvent A is typically thought of as negligible, the process simulation requires some token value to be supplied.

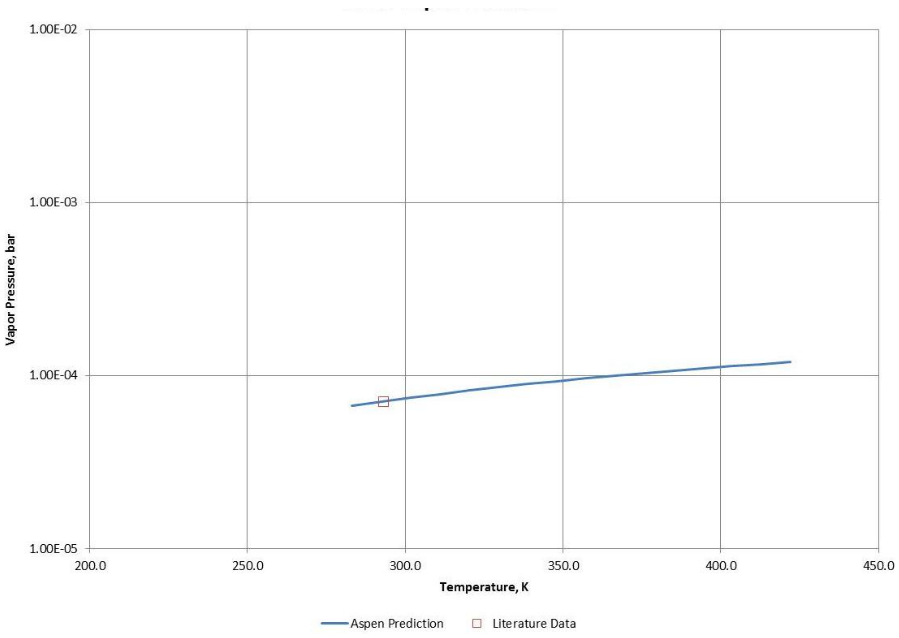

Figure 6. IL Liquid Vapor Pressure

Solubility of gases in ionic liquid

The solubility of carbon dioxide (CO_2) oxygen (O_2) and nitrogen (N_2) in the IL was modeled by declaring the gases Henry's components and regressing solubility data to calculate Henry's Law parameters. Figures 7 through 9 show the agreement between the literature data and the Aspen model predictions for gas solubility using the ENRTL-RK property method with Henry's Law components.

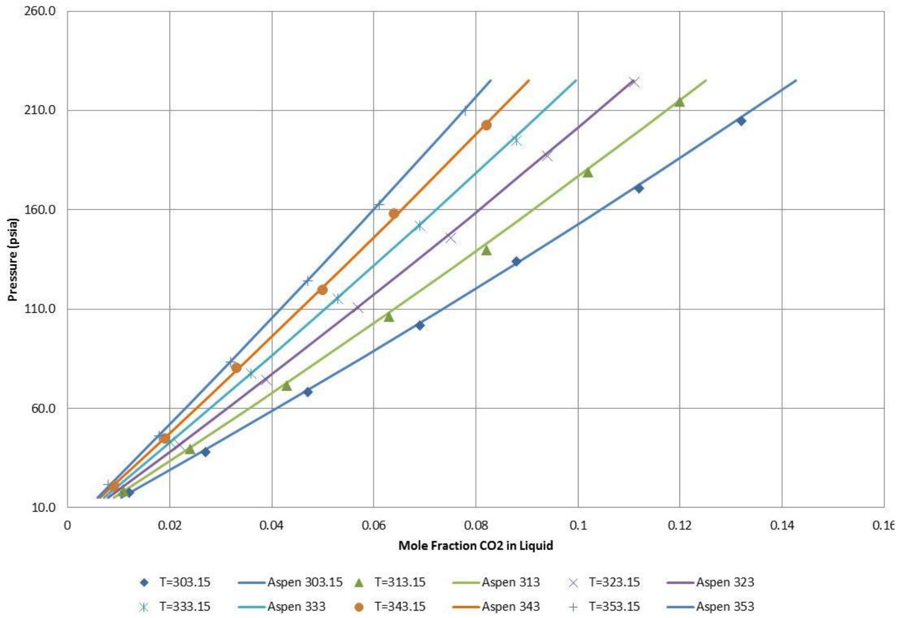

Figure 7. CO_2 Solubility in IL Liquid

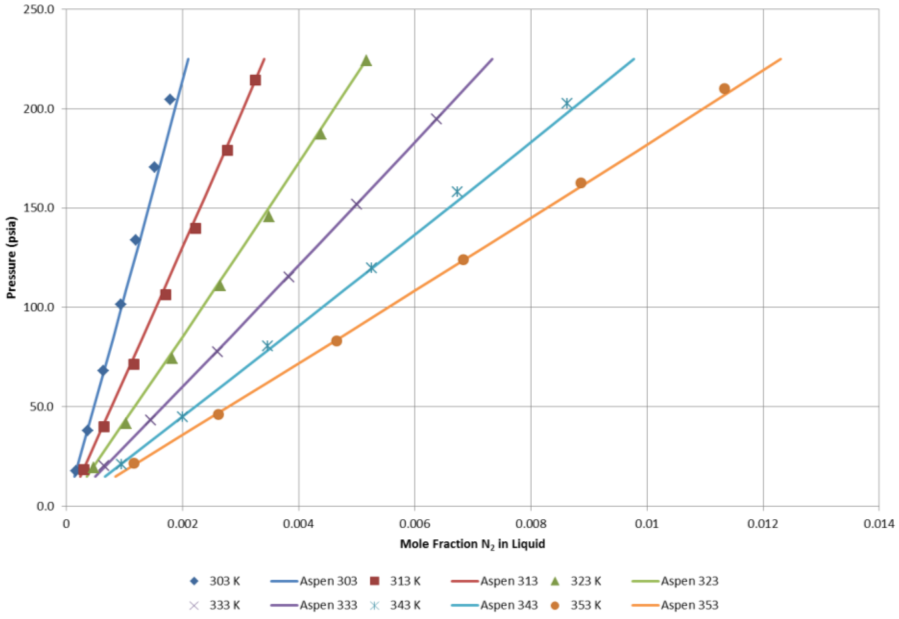

Figure 8. N_2 Solubility in IL Liquid

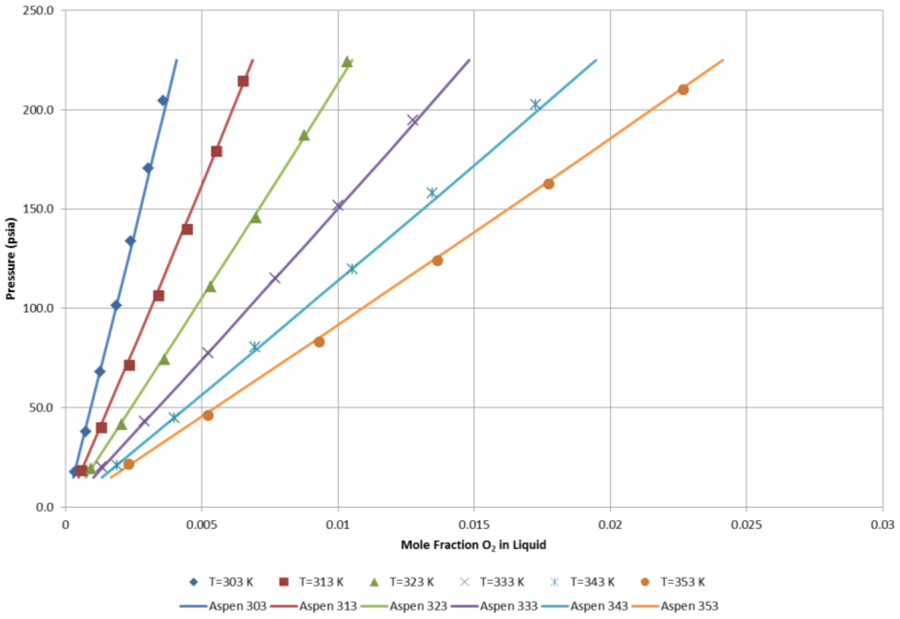

Figure 9. O_2 Solubility in IL Liquid

2.3. Amine physical property characterization

Although the amine of primary interest in Solvent A (Amine A) is present in the Aspen Plus databases of conventional components, a comparison between predicted physical properties and physical property data published by the manufacturer revealed some discrepancies. The physical property data from the manufacturer were regressed to generate parameters for the process simulation that would more closely match those published data. Figures 10 through 13 illustrate the fit between the published data input and the resulting correlations that were regressed from the data for vapor pressure, viscosity, density and vapor-liquid equilibria (VLE) of aqueous Amine A solutions.

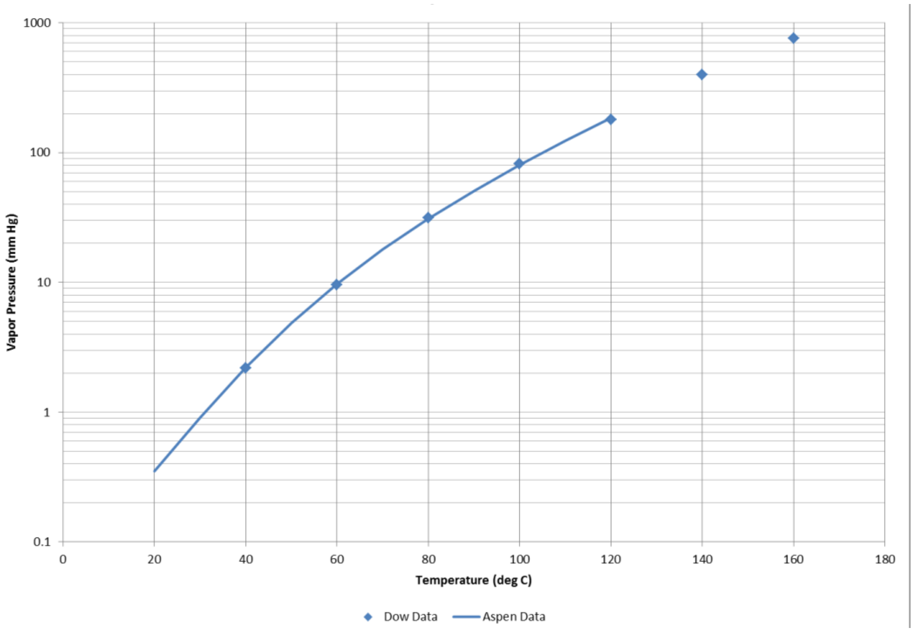

Figure 10. Amine-A Vapor Pressure

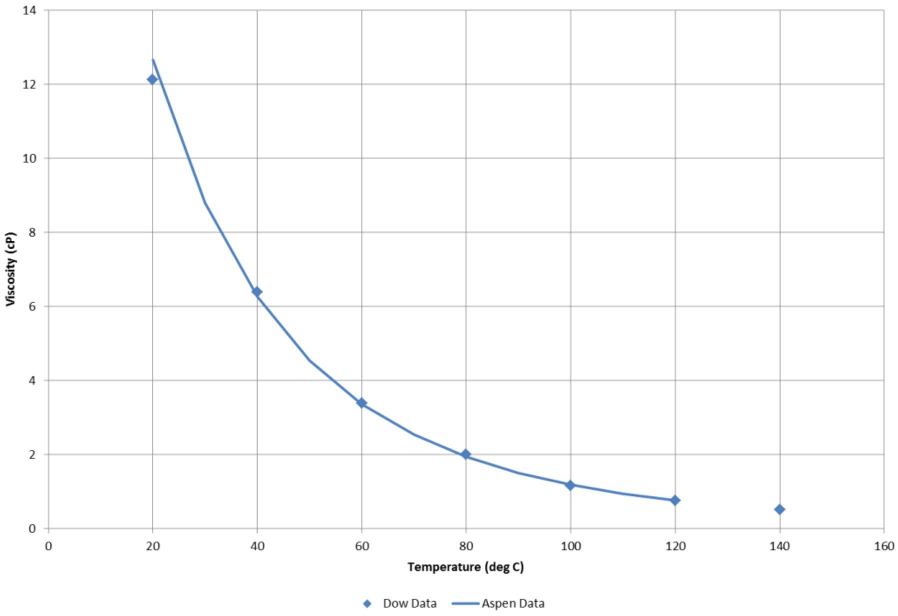

Figure 11. Amine-A Liquid Viscosity

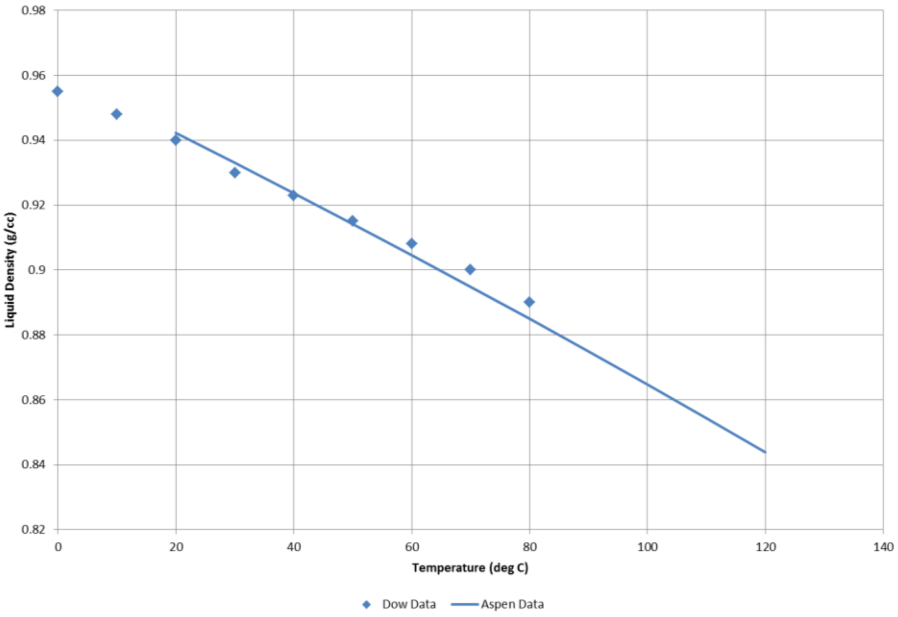

Figure 12. Amine-A Liquid Density

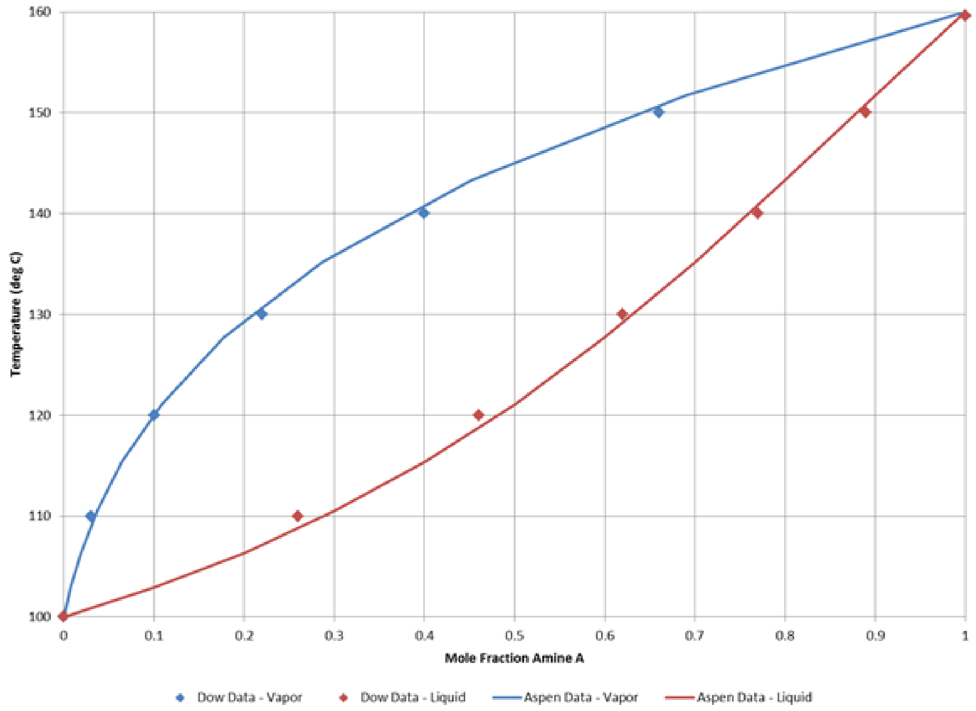

Figure 13. Vapor-Liquid Equilibria of Aqueous Amine-A Solutions

2.4. Solvent mixtures

The ENRTL-RK property method uses binary interaction parameters for pairs of components to calculate the thermodynamic and physical properties of mixtures of those components. The user can regress interaction parameters from experimental data to be used in place of the Aspen Plus default values. Figures 14 and 15 show the agreement between experimental data and Aspen predictions for liquid density and viscosity of IL/amine mixtures.

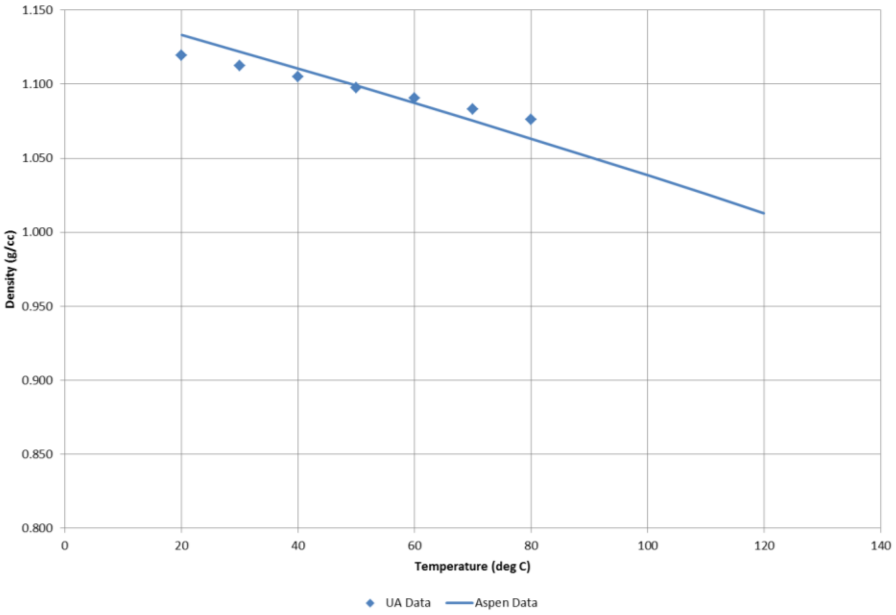

Figure 14. Liquid Density of IL/amine mixture

Binary interaction parameters are also used to calculate the VLE behavior between component pairs. Figure 13 showed the VLE between water and amine. Because both of those components have a vapor pressure, the VLE curve looks like most traditional VLE data. Mixtures containing the IL are different to characterize because of the negligible vapor pressure of the IL.

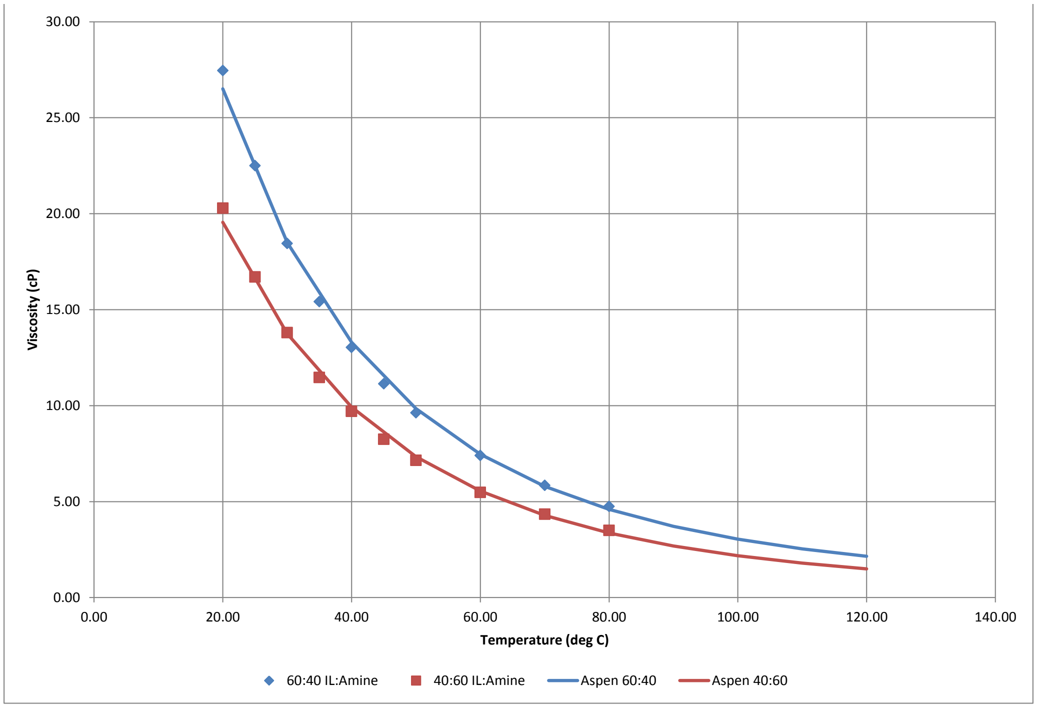

Figure 15. Viscosity of IL/Amine A mixtures

Solubility of CO_2 in IL/amine Mixture

In an anhydrous mixture of IL and amine, CO_2 reacts with the amine to form a carbamate ion and an ammonium ion according to the following equilibrium reaction.

$$2\ \text{Amine-A} + CO_2 \leftrightarrow \text{Amine-AH}^+ + \text{Amine-ACOO}^- \qquad (1)$$

Aspen Plus uses an equilibrium constant, K_{eq}, to calculate the extent of reaction and the concentration of the reactants and products at equilibrium. The equilibrium constant is defined as a temperature-dependent function so that the simulation can accurately represent the reaction across a wide range of operating conditions.

ION Engineering conducted a study to investigate the equilibrium behavior of Reaction 1 in the IL/amine solvent. The results of that study are shown as a series of curves relating solvent loading to the partial pressure of CO_2 above the solvent over a range of operating temperatures. These curves shown in Figure 16 are similar to the partial pressure versus solvent loading solubility charts that are commonly developed for aqueous amine solvents.

The experimental solubility data were used to develop the temperature dependent expression for Aspen to characterize the reaction equilibrium constant. A model sensitivity analysis was used generate the partial pressure versus solvent loading curves with different values for K_{eq} at each temperature. Those values of K_{eq} that best fit the experimental data at each temperature were then regressed to determine the parameters for the temperature dependent K_{eq} expression. The results from the best-fit regression are also shown in Figure 16. Unfortunately, the best-fit values of K_{eq} were not completely linear with respect to temperature, so the temperature-dependent expression introduces a slight deviation from the experimental data, especially for the 100° C temperatures. However, the deviation between the simulation results and the experimental data is minimal in the expected operating areas of interest. The ovals in Figure 16 show the operating areas for absorption (low temperature, low partial pressure) and regeneration (high temperature, high partial pressure) conditions.

Carbon Dioxide Absorption Heat of Solution

The reaction between CO_2 and amines is exothermic when CO_2 is absorbed and endothermic when the CO_2 is released. Additionally, there is a change in enthalpy when CO_2 physically dissolves into the solvent. The combined change in enthalpy resulting from the dissolution of CO_2 into the solvent and the heat of reaction is commonly referred to as heat of solution. The heat of solution is important to the design of CO_2 removal systems for two reasons. First, the heat released during absorption will tend to heat up the solvent in the absorption column thereby hindering its ability to further absorb CO_2. Second, the heat supplied to the solvent to reverse the absorption reaction and release the CO_2 is a significant portion of the total energy input to the system.

The solubility data can also be used to calculate a theoretical heat of solution for the CO_2 absorption reaction using the Van't Hoff equation. A plot of the equilibrium constant versus the inverse absolute temperature (1/T) yields a line with a slope of the negative heat of reaction over the universal gas constant ($-\Delta H_{rxn}/R$). An estimated heat of solution can be obtained by multiplying the slope of the that plot by the universal gas constant. For the IL/amine solvent data, the heat of solution was estimated at 2217 lKlg (910 BTU/lb) CO_2 absorbed. By way of comparison, the reported heats of solution for aqueous monoethanolamine (MEA) are and diethanolamine (DEA) are1919 kJ/kg (825 BTU/lb) CO_2 and 1628 kJ/kg (700 BTU/lb) CO_2, respectively. The estimated heat of solution for Amine A is the right order of magnitude, but higher than what might be expected for the secondary amine in an aqueous solution. It may be that the heat of mixing for the IL/amine solvent is greater than that of water which causes the larger heat of solution. Further experimental work is needed to verify the estimated heat of solution.

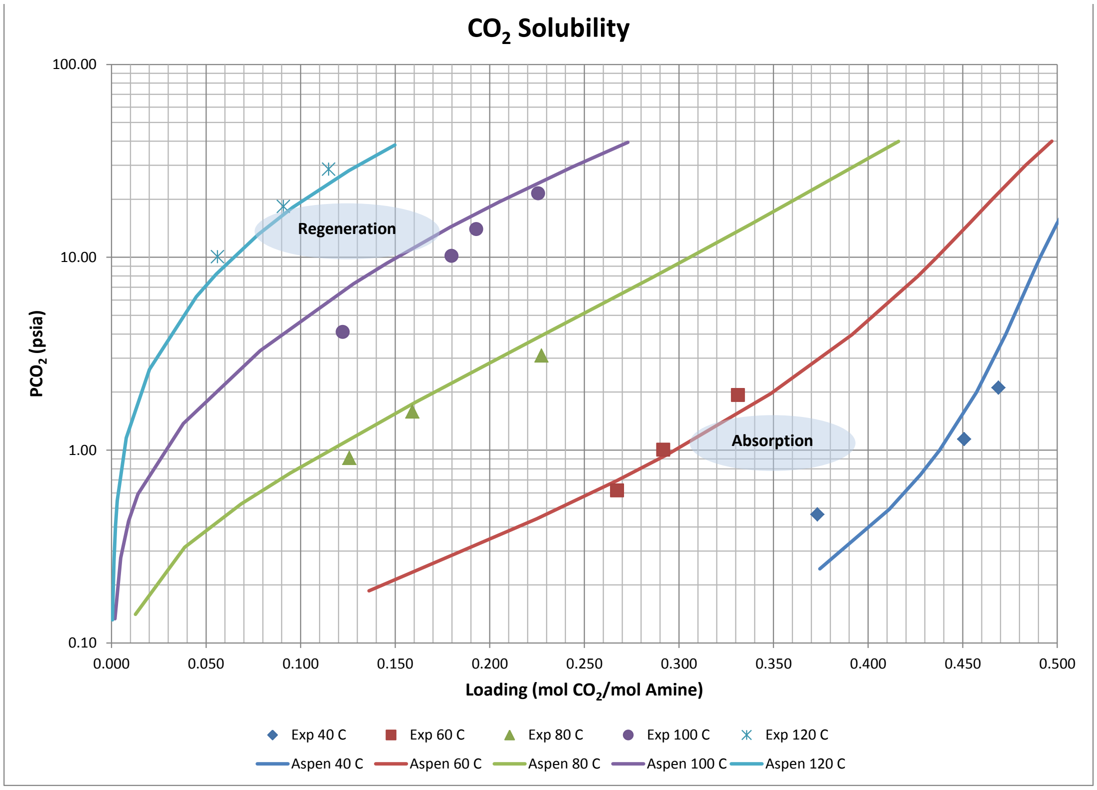

Figure 16. CO_2 Solubility in IL/Amine Solvent

3. Configure process flows to represent lab pilot unit

Several process flows have been developed for simulation with the Aspen Plus model, one corresponding the lab pilot unit (Appendix A-1) and a preliminary process model for the Valmont field test unit (Appendix A-2). The results of test runs in the actual lab pilot unit will be used to validate or refine and improve the process simulation model. The process model for the field test unit will be used for simulation studies and updated to support the more detailed engineering design.

The lab unit process simulation includes virtually every item of equipment on the test unit. Key components of the simulation to be validated with lab unit data are the absorber column and the regeneration flash drums. The lab unit will also help validate physical property assumptions and parameters such as the heat of solution for CO_2 absorption.

The preliminary process model for the field test unit includes the same key equipment (absorber column and regeneration flash drums) as the lab test unit. This model also includes auxiliary equipment such as the flue gas blower and a rich/lean solvent cross-exchanger for heat recovery. This model will be further developed and refined with data and results from the lab test unit and its process simulation.

4. Calibrate model predictions for column performance

A first step in validating the process simulation is to characterize the absorber column performance. An experimental run with aqueous monoethanolamine (MEA) using the lab pilot unit for carbon dioxide (CO_2) capture generated sufficient data to calibrate the simulation model to the column performance. The column can be characterized through the use of stage efficiencies and an approach to reaction equilibrium temperature.

Background

The lab pilot unit was operated in a “once-through” fashion with fresh solvent entering the top of the column. Spent solvent exiting the bottom of the column was sent to waste. Data and samples were collected during the test runs to allow for the calculation of a material balance around the absorber column. Figure 17 shows the limits of the material balance envelope.

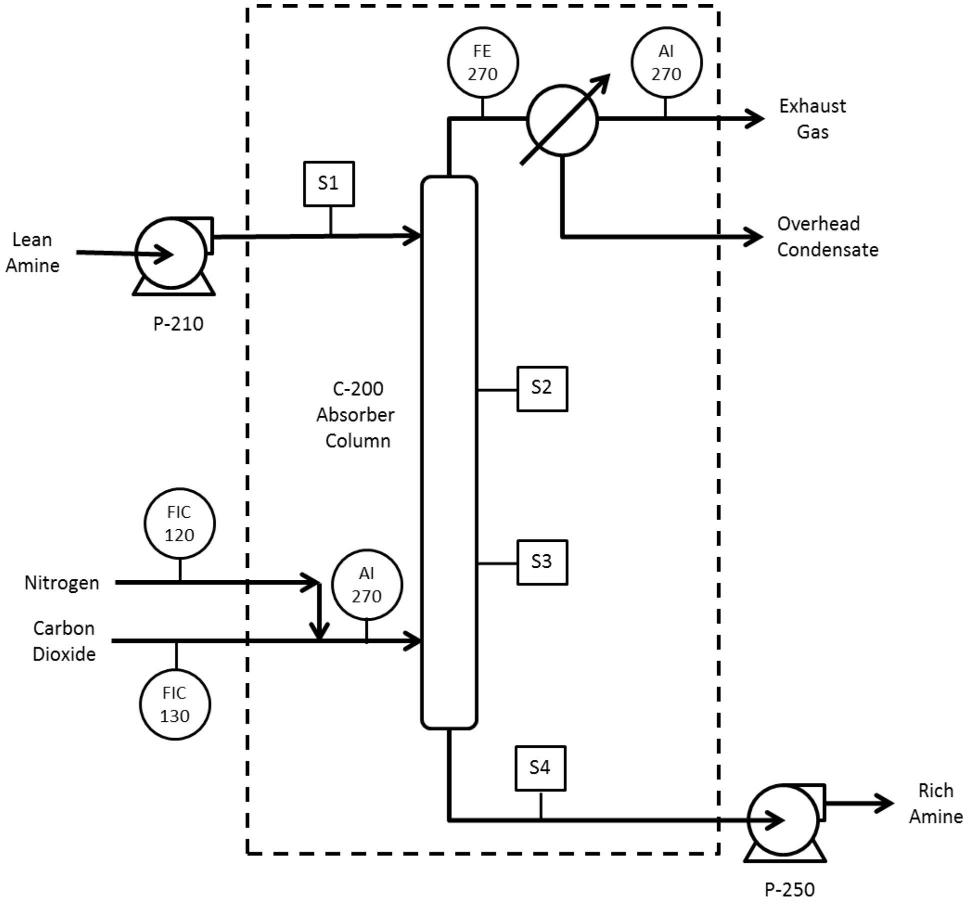

Figure 17. Lab Test Unit Material Balance Envelope

With good material balance closure, the data can be used to characterize the absorber in the process simulation. Key additional data collected for the absorber process simulation are the temperatures throughout the height of the column and the intermediate amine loadings collected at S2 and S3. Figures 17 and 18 show the relative location of the temperature points in the column profile.

4.1. Process simulation parameters

The process simulation for the lab pilot unit absorber is developed in Aspen Plus v7.2. The simulation is based on the model for CO_2 capture with MEA that is available to Aspen Plus users from Aspentech. The model includes physical properties and interaction parameters for the simulation components and the equilibrium expressions for all the amine and CO_2 reactions.

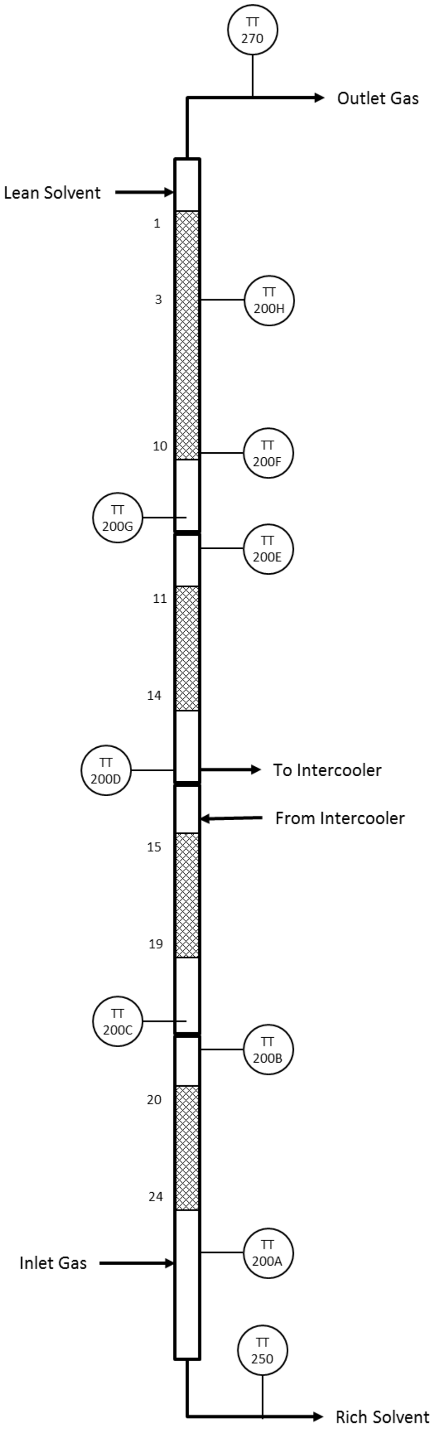

Figure 18. Absorber Column Diagram

Several parameters can be adjusted to calibrate the absorber process simulation. First is the number of theoretical stages in the column. Second is the approach to equilibrium for the CO_2 reactions with the amine. Third is the heat loss from the column to the ambient surroundings. Last is the vaporization efficiency of the top stages.

Column theoretical stages

The lab unit absorber column is approximately 19’-0” from flange to flange and contains 10’-0” of total packed bed height. There are four beds within the column, with the first being 4’-0” in height and the remaining three 2’-0” each. The bed material is a stainless steel knitted wire similar to Goodloe® packing produced by Koch-Glitsch.

In a packed tower, the number of theoretical stages is related to the height of packing by a factor known as Height Equivalent to a Theoretical Plate (HETP). For this exercise, several HETP values were investigated ranging from 3” HETP, or 40 theoretical stages, to 10” HETP, or 12 theoretical stages.

Apparent reaction equilibrium temperature

The reaction kinetics between CO_2 and amines are considered to be relatively fast as compared to the mass transfer limitations of the gas absorption into the liquid phase. An initial simulation assuming equilibrium at every stage in the absorber overpredicted the CO_2 absorption even with as few as two theoretical stages in the column.

Aspen Plus provides for a temperature approach to equilibrium for the reaction chemistry that was adjusted to match the overall absorber material balance. In all cases, the simulation approached equilibrium from the high-temperature side, or as expected, the side less favorable for CO_2 absorption.

Heat Loss to Surroundings

Although the lab pilot unit is insulated, at the CO_2 absorption reaction temperatures, the fluid in the column is losing heat through the column walls to the ambient surroundings. When the process simulation was executed with no heat loss from the column, the predicted temperature profile was uniformly higher than the actual temperatures observed. The rate of heat loss to the surroundings was estimated in the process simulation to give the best fit to the observed temperature profile.

Stage Efficiency

The stage efficiency relates the actual performance to the theoretical equilibrium performance at each stage in the absorber. Unfortunately for process simulation developers, measuring a departure from equilibrium within the column is not a straightforward task. Most often, the stage efficiencies in the simulation are adjusted to match secondary operating indicators such as the column temperature profile and overall column performance. The intermediate liquid sample points (S2 and S3) on the lab test unit column provide additional useful insight into the performance throughout the height of the column that can be used to tune the simulation parameters.

The first stage efficiency was chosen to match the observed vapor temperature exiting the column. Vaporization efficiencies throughout the remainder of the column were chosen to match the liquid loadings and the column temperature profile. While these assumptions cannot be independently validated, the results show a reasonable match between the process simulation and the observed absorber performance.

Additional data inputs for temperature, pressure and flow rates as the basis for the process simulation documented in Appendix B.

4.2. Process simulation methods

The main goal of the aqueous amine experiment was to obtain data that could be used to characterize the absorber column. The important characteristic of the absorber column is the number of theoretical stages. Once developed, the simulation was run on absorber columns with the number theoretical stages ranging from 12 to 40. For each case, a design specification in the simulation adjusted the approach to equilibrium temperature to match the CO_2 absorption rate in the column to the experimental results. Vaporization efficiencies were assigned to the stages to match the observed temperature profile and liquid loadings. Finally, the heat loss from the column was estimated to give the best fit with the observed temperature profile in the column.

The process simulation is unable to match both the temperature profile and the liquid loading data from the aqueous MEA test run. Key indicators are the location of the temperature bulge and the CO_2 loading in the liquid sample collected from the S2 sample point. The absorber column with the best balance between the temperature profile and liquid loading data has 24 theoretical stages, which calculates to a HETP of 5 inches. According to the Goodloe® packing specifications, the knitted wire packing can provide HETP values anywhere from 4 to 9 inches. The use of 5 inch HETP, while on the aggressive side of the packing specifications is not unreasonable.

4.3. Process simulation results

Absorber Material Balance

The process simulation overall material balance is in good agreement with the material balance calculated from the experimental data. The simulation results in 30.9 gmols/hr CO_2 captured or 89.4% of the CO_2 feed to the column. This is in good agreement with the experimental results which showed between 87% and 91% of the CO_2 absorbed in the aqueous MEA solution.

One of the tuning parameters for the simulation is the approach to reaction equilibrium temperature. Aspen Plus uses a temperature dependent function to calculate the equilibrium constant (K_{eq}) for each equilibrium reaction in the simulation. The equilibrium constant calculation can be adjusted by including a temperature approach to equilibrium. That is, the equilibrium constant is calculated at the operating temperature plus the temperature approach value. This is a common approximation for handling equilibrium reactions that are rate-limited, as is the case for CO_2 absorption by amines.

The equilibrium approach temperatures needed to match the material balance with different numbers of theoretical stages was fairly consistent. As expected, fewer theoretical stages are less conducive to mass transfer, so a closer approach to equilibrium is needed to match the material balance.

Absorber Temperature Profile

Figure 19 shows the comparison between the observed temperatures and the temperatures predicted by the simulation over the height of the absorber column. The process simulation correctly predicts the location of the temperature bulge caused by the exothermic reaction of the CO_2 with the amine once the appropriate stage efficiencies were incorporated into the model.

The shape of the temperature profile is also affected by the heat loss from the fluid in the column to the surroundings. As the process simulation was run for different column heights, one optimization routine was to vary the assumed heat loss to achieve the best fit to the observed temperature profile. The "best-fit" heat loss was 1,200 kJ/hr +/- 100 kJ/hr for all column heights. In all cases, the heat loss was applied uniformly across each stage rather than resorting to a stage-by-stage heat loss estimation to force a fit to the observed temperature data.

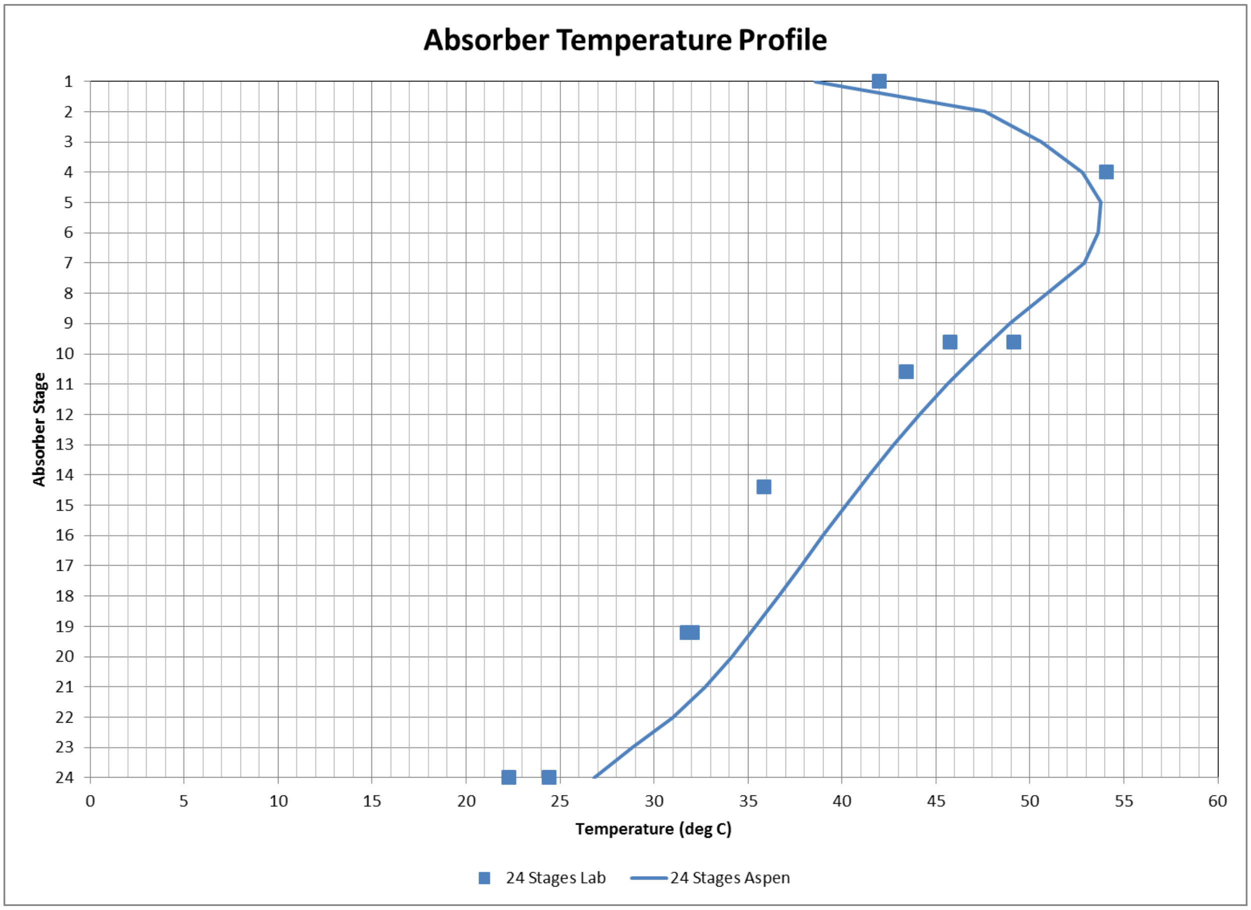

Figure 19. Absorber Temperature Profile (15% aqueous MEA)

Absorber Amine Loadings

The comparison between observed and predicted solvent loadings in the absorber column is shown in Figure 20. The observed solvent loading on the first stage (Stage 0) is the CO_2 loading in the fresh solvent fed to the column. The simulation solvent loadings are in the liquid leaving each stage. Even with the reduced stage efficiencies referenced above, the simulation tends to overpredict the absorption in the top part of the column. Additional simulation work may be able to narrow the gap between the experimental data and the simulation prediction. These discrepancies aside, there is good agreement between the observed and predicted outlet solvent loading, as would be expected for an experimental run with good overall material balance closure.

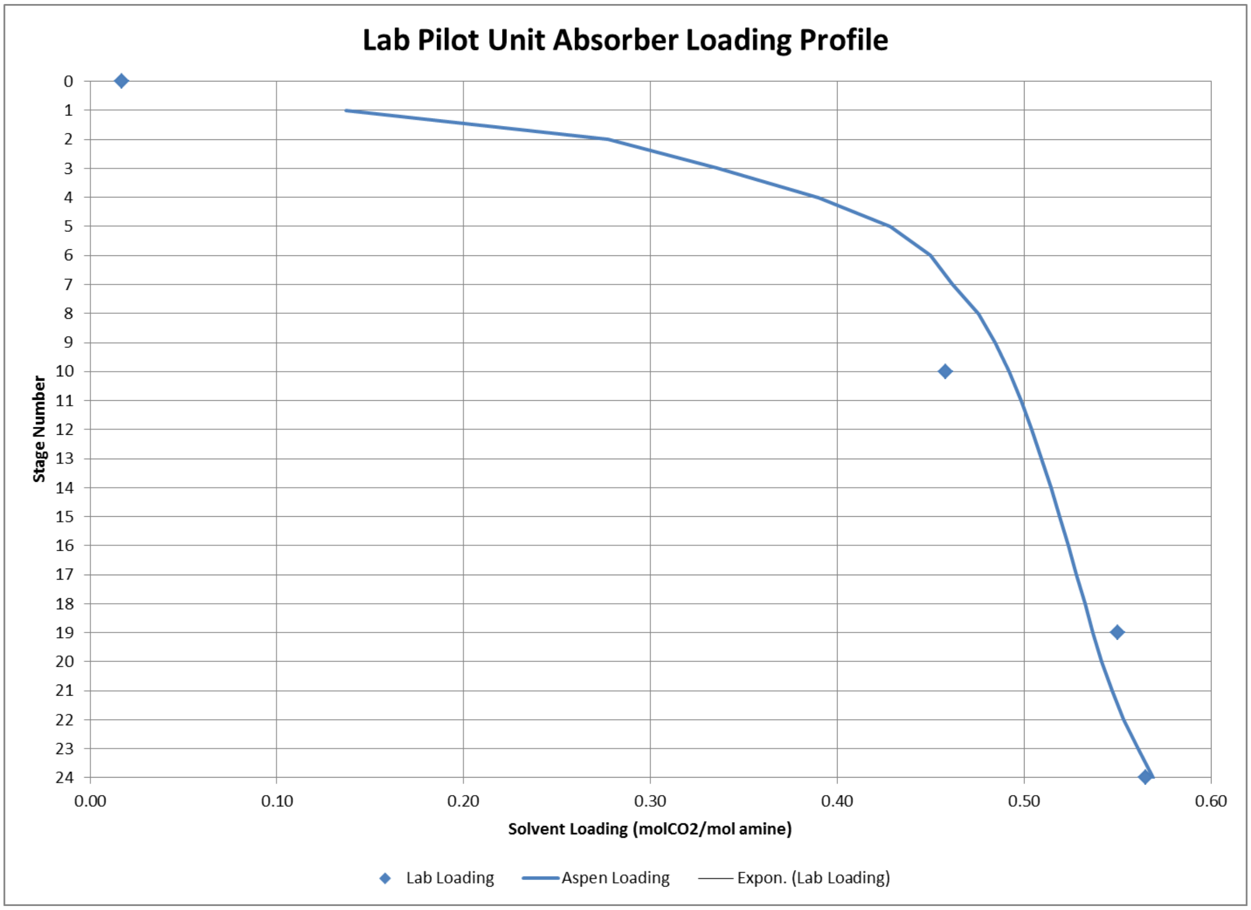

Figure 20. Lab Unit Absorber Solvent Loading Profile (15% aqueous MEA)

5. Process simulation conclusions and next steps

The modified Aspen model can be used to predict the performance of ION's novel solvents in CO_2 capture applications.

The comparison of literature and experimental data with predictions from the Aspen Plus simulation shows that sufficient property estimation parameters are available or can be regressed from the data to allow a good prediction of physical and thermodynamic properties for the IL, amine, and IL/amine mixtures that are the basis of ION Engineering's proposed technology.

Further work will use experimental results from the lab pilot unit to validate and refine the simulation model for ION's novel solvents.

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Appendices

Appendix A: Aspen process simulation flow sheets

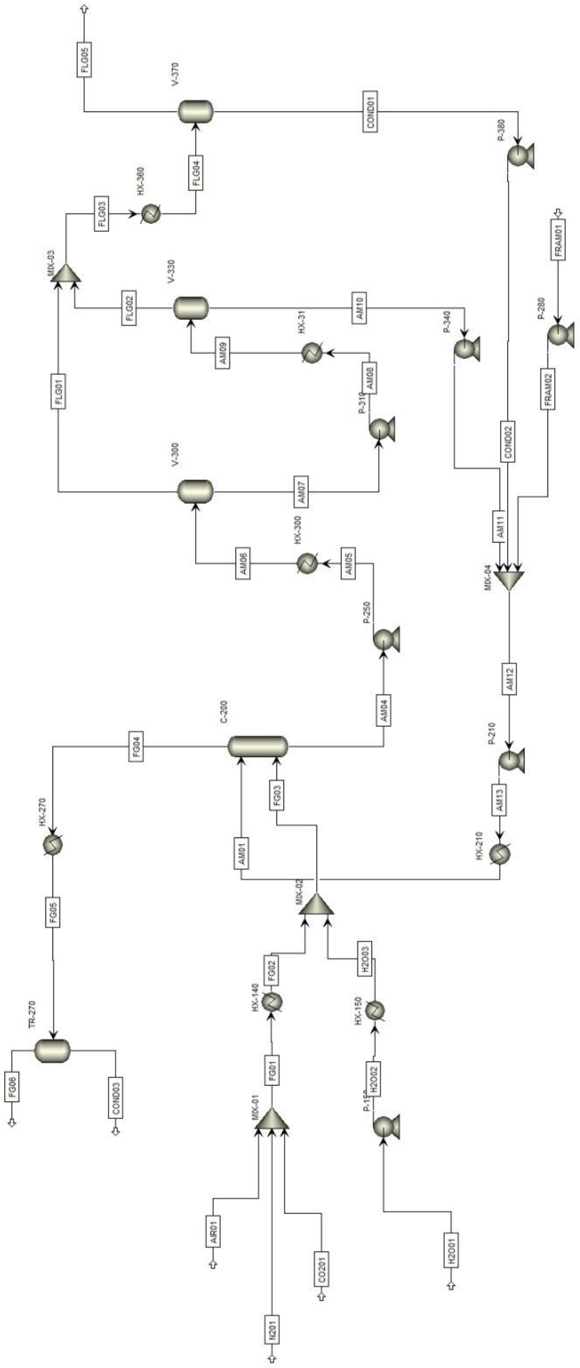

Figure 2A-1. Unit Initial Aspen Model Process Configuration Corresponding to Lab Pilot Unit

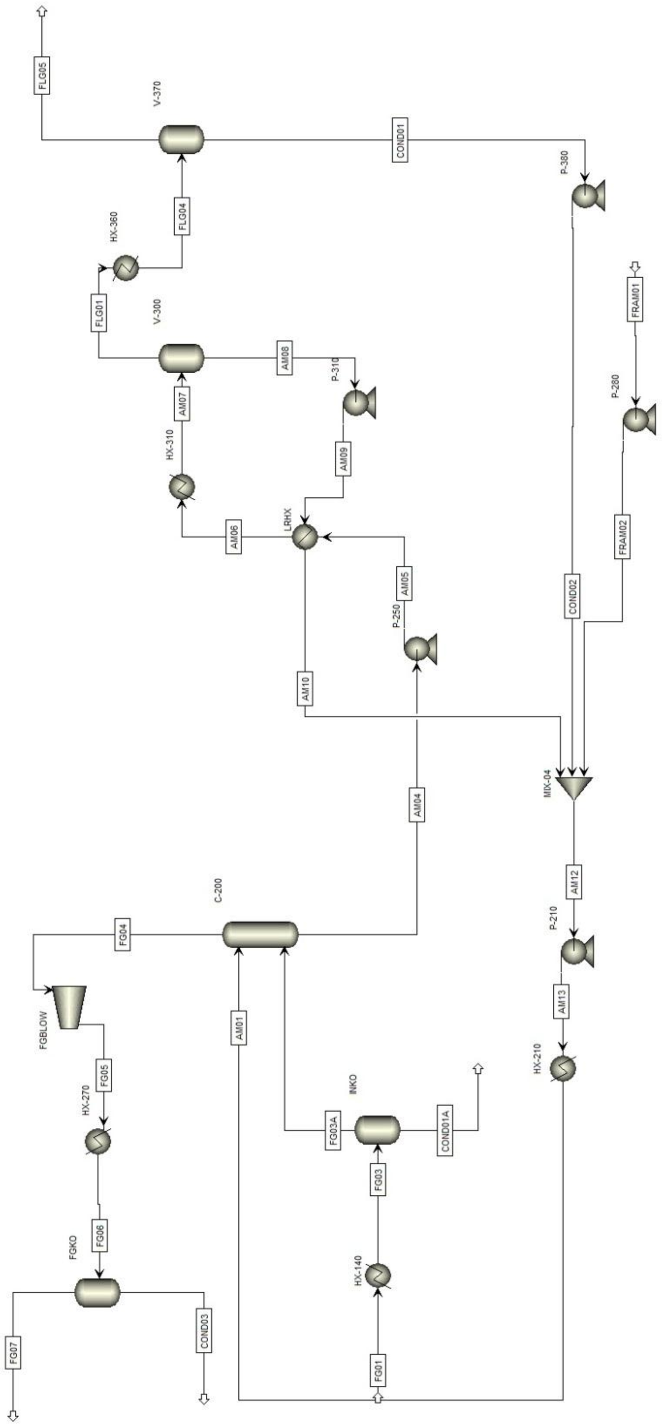

Figure A-2. Preliminary Aspen Model Process Flow Sheet for Design of Valmont Field Test

Appendix B: Aspen Plus simulation data

The values used as the basis for the process simulation for characterization of the absorber column.

Table B-1 Aspen Plus Input Data

Description	Instrument Location	Units	Value
Nitrogen Flow Rate	FIC-120	mol/hr	262.9
CO_2 Flow Rate	FIC-130	mol/hr	34.6
Mixed Gas Temperature	TI-165	deg C	40.0
Mixed Gas Pressure	PI-165	kPa(g)	12.2
Solvent Flow Rate	Calculation	gph	5.8
Lean Solvent Temperature	TI-211	deg C	24.8
Absorber Pressure	PI-270	kPa(g)	10.8
Absorber Pressure Drop	PDT-200	kPa	1.1

ION Engineering
Bold Science for Clean Energy

Appendix T3: Topical Report for Task 5.3

Thermal Energy Requirement for Solvents B and C Compared to Aqueous Amine

DOE Award: DE-FE0005799
ION Engineering

Project Title: Novel Solvent CO_2 Capture
Principal Investigator: Alfred (Buz) Brown, PhD
Co-Authors: Nathan Brown
Jerrod Hohman
Greg Staab

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Abstract

ION Engineering is developing technology for carbon dioxide (CO_2) capture using a novel solvent comprised of a mixture of non-volatile, non-aqueous compounds and amines. One of the most important factors in determining the impact of solvent-based, CO_2-capture technologies on the cost of electricity is the parasitic energy load required to regenerate the CO_2-rich solvent.

A study of the theoretical regeneration energy demand shows that the ION Engineering solvents potentially require total regeneration energy 20% less than that of an optimized aqueous amine process with the net heat input demand 22-24% less than an optimized aqueous amine process.

Using two simple process optimization strategies, ION's Solvent C closely approaches a net heat input requirement of 2.5GJ/tonne $CO_{2.}$

Executive Summary

ION Engineering is developing technology for carbon dioxide (CO_2) capture using a novel solvent comprised of a mixture of non-volatile, non-aqueous compounds and amines. One of the most important factors in determining the impact of solvent-based, CO_2-capture technologies on the cost of electricity is the parasitic energy load required to regenerate the CO_2-rich solvent (the regeneration energy as discussed in this report).

ION Engineering conducted a study of the regeneration energy for two solvents. This study provides a hypothetical, size independent comparison of solvent systems based on operation at equilibrium conditions in both the absorber and the regeneration system. The heat of reaction, the sensible heat, and the latent heat of vaporization are presented and compared for both solvents and an optimized aqueous MEA process. The results from the study show potential energy savings that may be realized for a particular CO_2 solvent technology.

In brief, this study shows that the ION Engineering solvents could potentially:

- Reduce the total regeneration energy by 15% to 20% as compared to an optimized aqueous amine process.
- Reduce the net heat input demand more than 20% as compared to the optimized aqueous amine process.
- Additional heat integration and process improvements may reduce the net heat input demand by an additional 7%-8%.

The net heat input required for solvent regeneration is largely driven by the heat of reaction between the amine and the CO_2. For aqueous amine systems, the heat of reaction makes up about 50% of the net heat input demand. With ION's solvents, the heat of reaction makes up between 70% and 80% of the net heat input demand demonstrating that ION has successfully reduced energy requirements by using advanced non-aqueous solvents. While both ION Engineering solvents currently exceed 2.5 GJ/tonne CO_2 net heat input, additional process optimization strategies and improving the amine component of the combined solvent offer the greatest potential for further reductions in parasitic thermal energy consumption.

Report

1. Introduction

One of the most important factors in determining the impact of solvent-based, CO_2-capture technologies on the cost of electricity is the parasitic energy load required to regenerate the CO_2-rich solvent. The thermal energy required to regenerate the solvent is usually supplied by steam from the power plant that could otherwise be expanded through a turbine to generate power. That parasitic loss of power either reduces the total plant power output or requires additional feedstock to produce enough steam to cover the parasitic loss. In either case, the thermal regeneration energy demand increases the cost of electricity, so lowering solvent regeneration energy is important in the overall goal to minimize impact of CCS on cost of electricity.

This report examines the thermal regeneration energy demand for two ION solvents, Solvent B and Solvent C. In each case, the energy demand is calculated for the CO_2 capture system at equilibrium conditions in both the absorber and the regeneration system. Because CO_2 absorbers do not operate at equilibrium conditions, these results should be considered to be hypothetical cases. Deviations from equilibrium in the absorber and the regeneration system will tend to change the solvent circulation rate. However, as will be explained below, a change in solvent circulation rate does not necessarily have a large impact on the net heat input required for regeneration. Therefore, the equilibrium case is still useful to gauge the potential energy savings that can be realized for a particular CO_2 solvent technology.

The regeneration energy demands for the two solvents are compared to the regeneration energy demand for an advanced aqueous monoethanolamine (MEA) process. Typical operating conditions for the advanced aqueous MEA process were obtained from the literature[1] and used to construct a process simulation. The results from the process simulation were used to calculate the total regeneration energy and the net heat input demand for the aqueous MEA process.

Other parasitic energy demands typical to CO_2 capture solvent processes are not within the scope of this analysis. Some examples of these other energy demands include: solvent cooling and condensation; CO_2 compression power; and liquid solvent pumping power. Additionally, many primary and secondary aqueous amines require reclaiming to purify the solvent of heat-stable salts. At this time, ION does not know what, if any, percentage of solvent will need to be reclaimed and that energy demand has also been excluded from the evaluation for Solvents B and C.

2. Basis for Thermal Regeneration Energy Analysis

The total thermal energy required to regenerate a CO_2 absorbing solvent from the rich, or CO_2-loaded, state to the lean, or CO_2-unloaded, state is comprised of three separate components. The first is the energy that must be supplied to the endothermic chemical reaction to dissociate the CO_2 from the absorbing amine compound. The second it the sensible heat of the solvent, or that energy required to raise the bulk fluid temperature to the appropriate regeneration temperature. The third is the heat required to vaporize the water, amine, and/or solvent at regeneration conditions. Each component of the thermal regeneration energy is discussed in more detail in the following paragraphs.

2.1 Heat of Reaction

While the heats of reaction are readily available for many well-known and widely-used amines, there is very little in the literature regarding the amine of choice (Amine A) for ION's Solvent B and Solvent C formulations. Recognizing this gap, ION has contracted with an outside testing laboratory to measure the heat of reaction for Amine A; however, those results will not be available until later in the Phase 2 project. In order to obtain a first approximation of these reaction energies, ION conducted a series of semi-quantitative tests to estimate the heat of reaction especially relative to the well-known heat of reaction for the widely used monoethanolamine (MEA).

A combined heat of reaction/heat of solution was measured for aqueous amines and the ION solvent systems by absorbing a measured quantity of CO_2 into a known mass of solvent in a well-insulated vessel while stirring. The temperature of the solvent was monitored throughout the experiment to determine the temperature rise of the mixture due to CO_2 absorption. The temperature rise and heat capacity of the mixture were used to determine the total heat release from the exothermic reaction/absorption of carbon dioxide. The results of the semi-quantitative testing indicated that the heat of reaction for Amine A is comparable to the heat of reaction for aqueous MEA within the accuracy of the test method.

Because Amine A is not as well-known or widely used as the more traditional amines, the databases in the Aspen Plus® process simulation software do not contain data for the products of the CO_2 absorption reaction. These products, namely the resulting carbamate salts, were characterized in the simulation as “user-defined” electrolyte components within the ENRTL-RK property method. The reference heats of formation for the anion and cation electrolyte components were adjusted within the framework of the equilibrium reaction chemistry to obtain the desired value for the heat of reaction. The simulation heats of reaction for aqueous MEA and ION Amine A were subsequently verified against the literature and experimental values, respectively.

2.2 Sensible Heat

The sensible heat of the solvent is calculated by the simulation as a molar average of the specific heat of each component in the solvent formulation. For the standard compounds including water, CO_2, and Amine A, the specific heat is calculated in the simulation using the specific heat parameters for each compound available in the Aspen Plus® databases. Alternate expressions for liquid and electrolyte specific heats were provided for the user-defined components including the bulk solvent and the carbamate salt ions. The carbamate salt ions were assumed to have a specific heat similar to that of MEA carbamates. The bulk solvent specific heats were matched to literature data as shown in Figures 1 and 2. The calculated solvent specific heats will be further validated by an outside testing laboratory later in Phase 2.

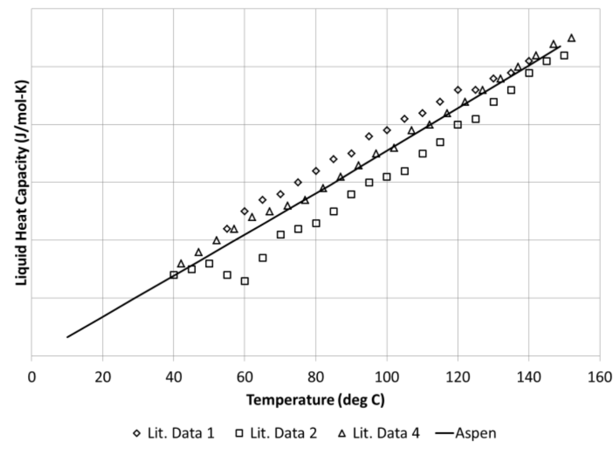

Figure 1. *Bulk Solvent B Specific Heat*[2]

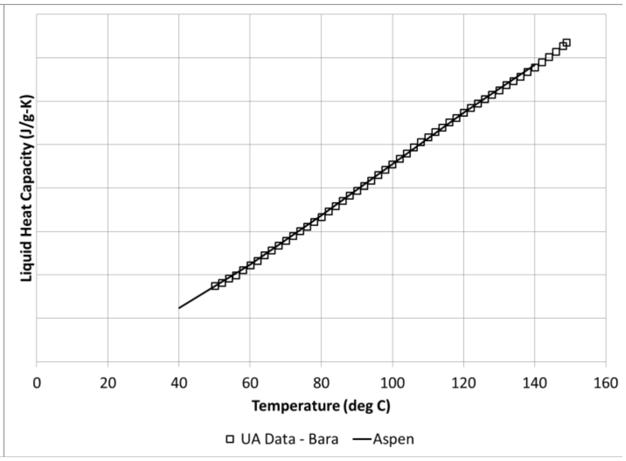

Figure 2. *Bulk Solvent C Specific Heat*

2.3 Heat of Vaporization

In traditional aqueous amine technologies, significant amounts of the bulk solvent (water) are vaporized during the solvent regeneration. With ION's approach of using a low-volatility bulk solvent, the heat of vaporization of the bulk solvent can be neglected. However, since there is water present in all flue gas to some degree or another, some of that water will be absorbed into the solvent in the absorber column and therefore have to be driven off during the regeneration of the solvent. Thus, the heat of vaporization component of the regeneration energy cannot be completely eliminated, even with the use of a non-aqueous, low vapor pressure solvent.

The important attribute to characterize in the process simulation is the interaction between the non-aqueous bulk solvent and the water in the system. ION developed a method to measure binary pair vapor-liquid equilibrium (VLE) data that could be regressed into activity coefficient parameters to be used in the process simulation. This enables the process simulation to predict how much water will be absorbed from the flue gas in the absorber and then subsequently vaporized out of the solvent in the regeneration system. Figures 3 and 4 show the agreement between the experimental and predicted data for both the bulk solvent-water pair and the bulk solvent-Amine A pair.

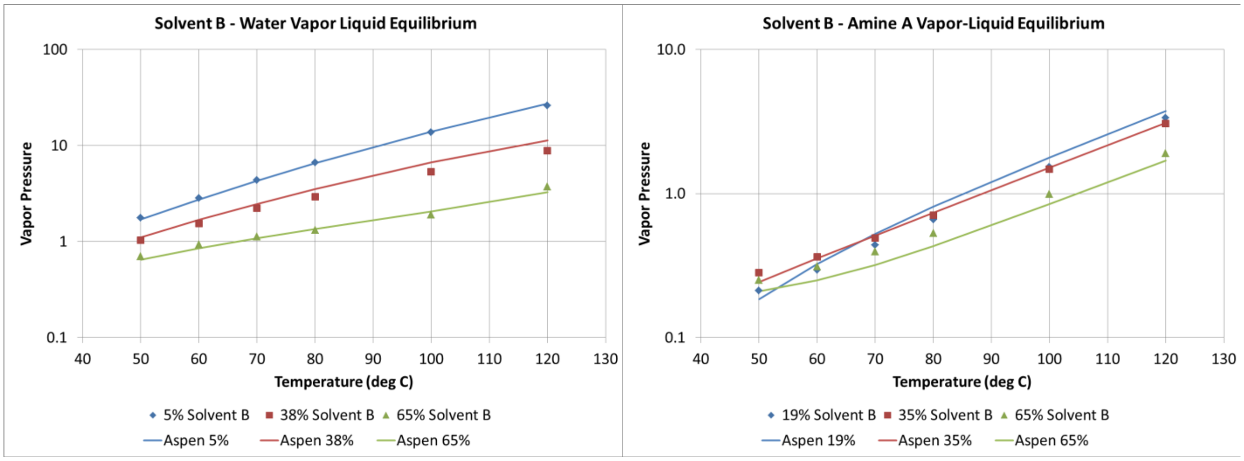

Figure 3. *Solvent B VLE*

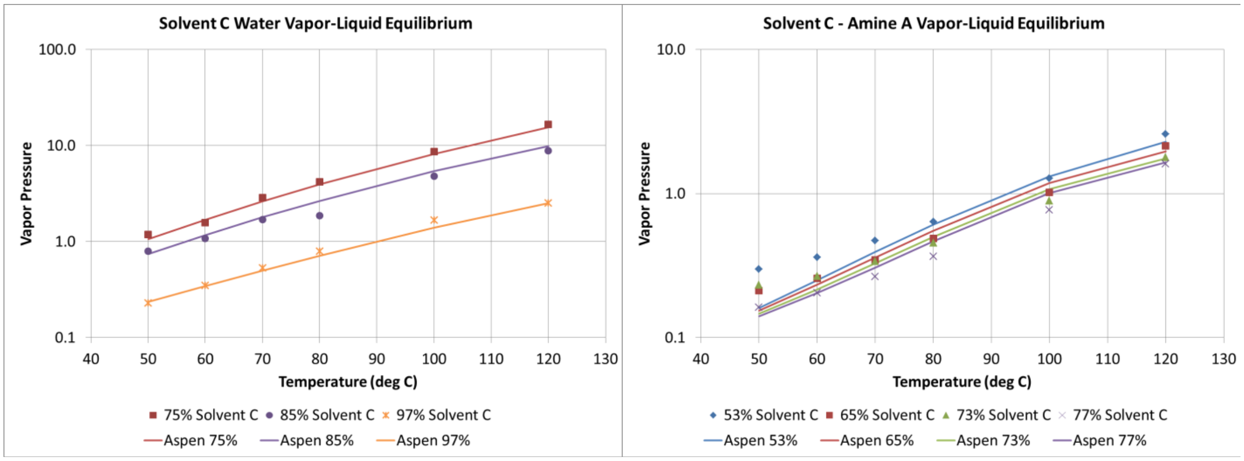

Figure 4. *Solvent C VLE*

3. Solvent Regeneration Energies

3.1 Total Regeneration Energy

Figure 5 shows the total regeneration energy requirement for ION Solvents B and C along with a representation of the actual regeneration energy requirement for an optimized aqueous MEA system. Although not a direct comparison, the total regeneration energy requirement for Solvent B is almost 15% lower than the total regeneration energy for an optimized aqueous amine process. Likewise, the total regeneration energy requirement for Solvent C is almost 21% lower than optimized aqueous MEA.

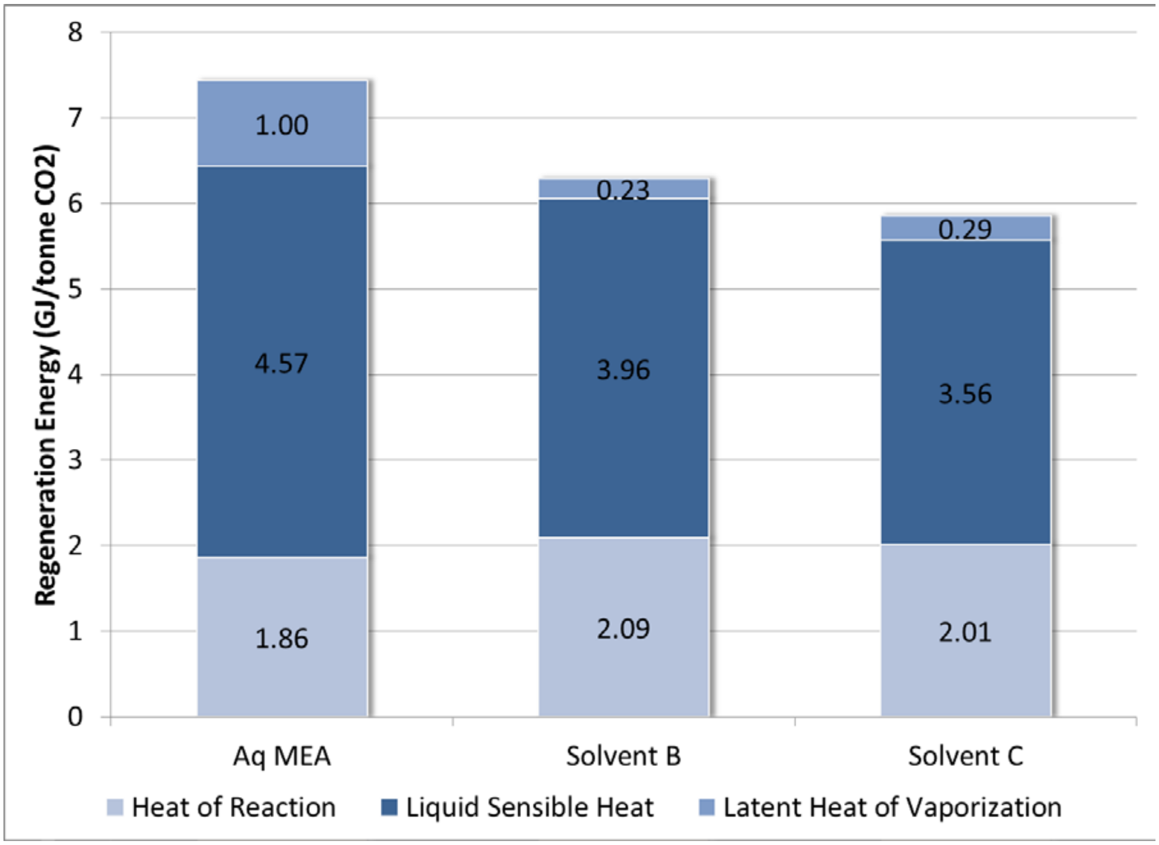

Figure 5. *Total Regeneration Energy*

3.2 Net Heat Input

A more useful metric for comparison of solvent regeneration energy is the net heat input to the process. In general, both the heat of reaction and the heat of vaporization are unrecoverable energy demands in that both energies must be supplied at higher temperatures than are available for recovery within the CO_2 removal process unit. While most of the sensible heat can be recovered within the CO_2 removal process, it is not possible to recover all the sensible heat due to temperature approach limitations of the traditional lean/rich cross heat exchanger.

One drawback of the net heat input requirement analysis is that the metric is process dependent. For this evaluation, the process consisted of an absorber column paired with ION's dual flash regeneration technology. The absorber included a single intercooler that extracted liquid about halfway down the column, cooled the liquid to remove the exothermic heat of reaction, and returned the liquid to the absorber. A lean/rich solvent cross heat exchanger was used to recover the sensible heat from the lean solvent by cooling against the incoming rich solvent to an 8° C temperature approach. There was no additional heat integration with the rest of the power plant or CO_2 compression train as is often proposed for CO_2 capture solvent technologies. Those common heat integration proposals may decrease the net heat input, but need to be evaluated against the increased capital cost.

Figure 6 shows the recovered and net heat input for ION's solvents B and C as well as the recovered and net heat input for an optimized aqueous MEA process. While again this is not a direct comparison, the net heat input requirement for Solvent B is nearly 25% less than the net heat input required for the optimized aqueous MEA process. Likewise, the net heat input for Solvent C is almost 22% less than the heat input for the optimized aqueous MEA process.

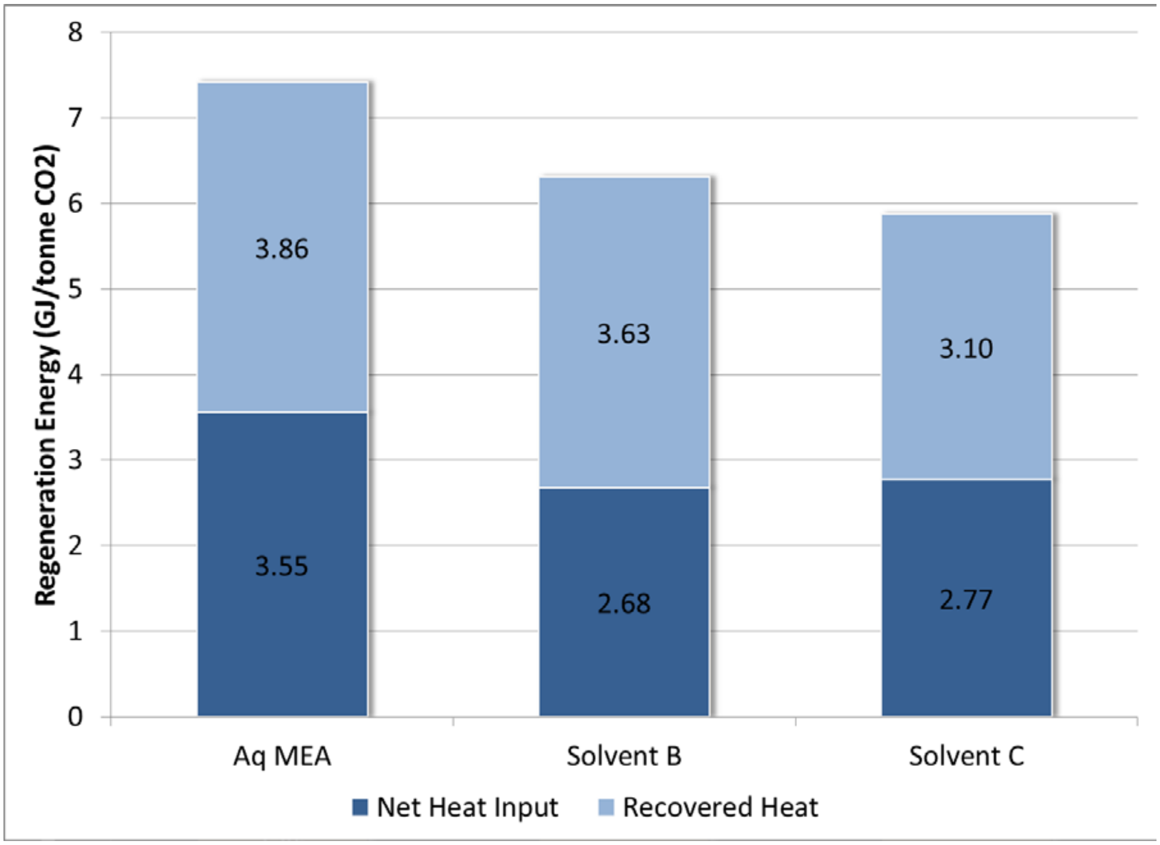

Figure 6. *Recovered and Net Heat Input Comparison*

Comparing Figures 5 and 6 gives some insight to the limitations on net heat input reduction. Across all three solvent systems, the net heat input is the sum total of the heat of reaction, the latent heat of vaporization and 10%-15% of the sensible heat. Although the non-aqueous bulk solvent reduces the energy required for both the sensible heat and the latent heat of vaporization, the heat of reaction remains dependent on the amine component of the combined solvent. Since the heat of reaction is the largest component of the net heat input, modifying the amine component of the combined solvent would appear to offer the most potential to further reduce the required regeneration energy.

Finally, Figure 7 shows the comparison between the net heat input for an optimized aqueous MEA process and an optimized Solvent C (equilibrium) process. For this case, an additional intercooler was added to the absorber to increase the solvent carrying capacity and the lean/rich solvent heat exchanger temperature approach was reduced to 3° C. These two modifications together decrease the net heat input requirement by about 7.5% for Solvent C, from 2.77 GJ/tonne CO_2 to 2.56 GJ/tonne CO_2. As discussed above, required net heat input is approaching the limit of the heat of reaction plus the latent heat of vaporization. For aqueous amine systems, the heat of reaction makes up about 50% of the net heat input demand; whereas, with ION's non-aqueous solvents, the heat of reaction makes up between 70% and 80% of the net heat input demand. This demonstrates that ION has successfully reduced regeneration energy requirements by using advanced non-aqueous solvents. Additionally, it appears that a different amine with a lower heat of reaction will have the greatest impact on net heat input and may be critical to achieving a net heat input less than 2.5 GJ/tonne CO_2. In addition to the lower heat of reaction, the amine will also need to be suitably reactive towards CO_2 and inert to the other components of the combined solvent mixture.

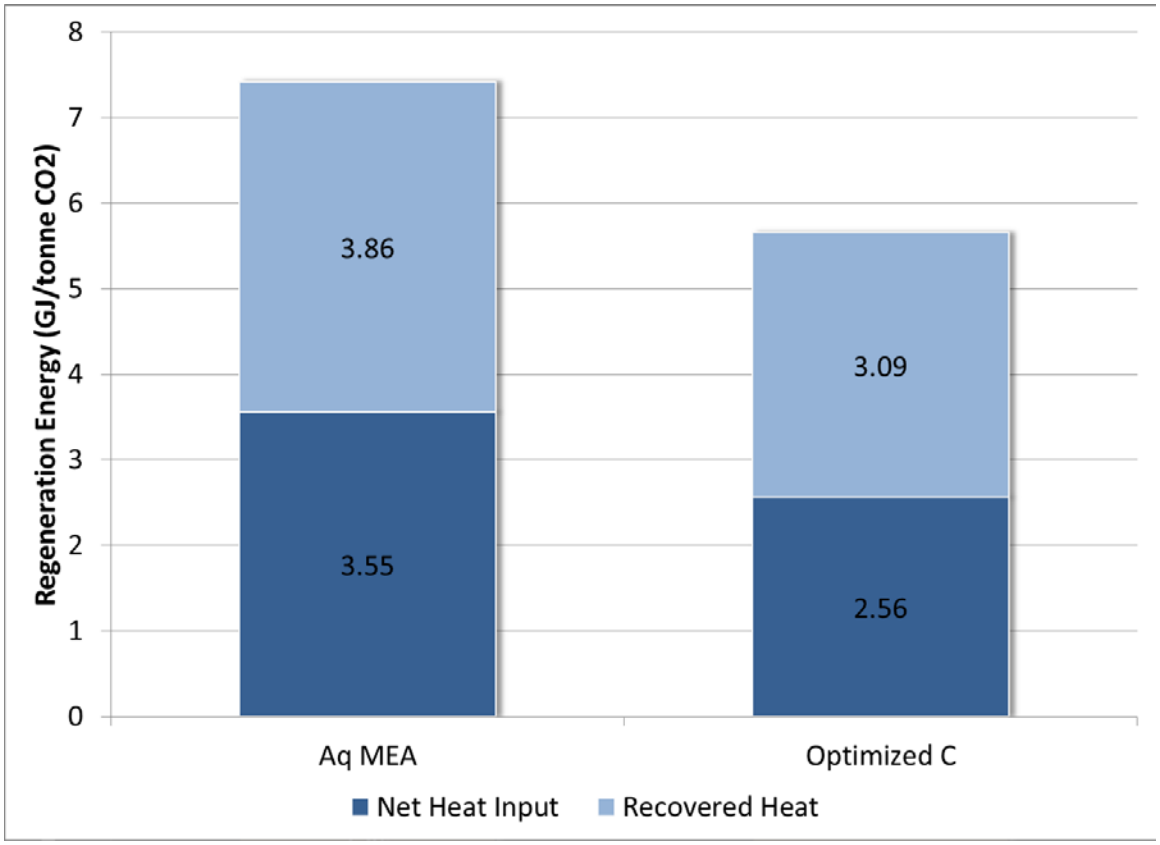

Figure 7. *Optimized Net Heat Input Comparison*

3.3 Water Management

Another important aspect of ION's non-aqueous CO_2 capture solvent technology is management of the water that is introduced into the solvent system by absorption from the flue gas. In short, there are two extremes that can be considered. The first is to purge all the water that is produced in the regeneration system by condensation from the flashed CO_2. One obvious drawback of a water purge is an increased rate of amine loss in the condensed water as well as a need to treat the produced water prior to disposal. The second is to completely recycle the condensed water back into the liquid solvent and allow it to accumulate to its equilibrium level. Complete recycle increases the water vaporization rate and commensurate energy demand in the regeneration system.

An evaluation of Solvent C showed that the recycling the produced water increases both the total energy demand and the net heat input demand for the system as compared to the water purge case. Although higher water content in the solvent led to better regeneration, a leaner solvent did not decrease the solvent circulation rate enough to offset the increased energy demand for the heat of vaporization. Both Solvents B and C were evaluated in a water purge process configuration to minimize the net heat input demand to the process.

4. Thermal Regeneration Energy Analysis Conclusions

- ION Engineering Solvents B and C show total regeneration energies that are 15% and 21% respectively less than an optimized aqueous MEA process.
- Both ION Engineering Solvents B and C show a net heat input reduction of more than 20% as compared to an optimized aqueous MEA process.
- With two simple process optimization strategies, Solvent C approaches a net heat input of 2.5 GJ/tonne CO_2.
- The heat of reaction between CO_2 and the amine is currently the largest component of the net heat input demand. By further optimization of the amine component of ION's Solvent C, it may be possible to further reduce the net heat required to below 2.5 GJ/tonne CO_2.

5. Next Steps

- Update the process simulation with the actual heat of reaction as measured by the outside testing laboratory, if the value proves to be substantially different than what was measured by ION Engineering.
- Evaluate additional heat integration and process optimization opportunities to further reduce the net heat input demand. By evaluating the impact on cost of electricity, the comparison will include the effect of both capital and operating costs.
- Develop a plan that would consider alternative amines for use in the ION's solvent system. Specifically, candidate amines should have a lower heat of reaction yet retain sufficient CO_2 carrying capacity to minimize the impact on circulation equipment size and cost.

References

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Appendix A

Excerpt of full report including complete results for ION solvent in Post-Combustion Coal-Fired flue gas testing at the Energy & Environmental Research Center, Grand Forks, ND.

Pavlish, B.M.; Kay, J.P.; Strege, J.R.; Fiala, N.J.; Stanislowski, J.J.; Snyder, A.C. *Subtask 2.5 – Partnership for CO_2 Capture – Phases I and II*; Final Report (Sept 1, 2010 – April 30, 2013) for U.S. Department of Energy National Energy Technology Laboratory Cooperative Agreement No. DE-FC26-08NT43291; EERC Publication 2013-EERC-04-12; Energy & Environmental Research Center: Grand Forks, ND, April 2013

7.0 POSTCOMBUSTION TESTING – COAL-FIRING

7.5 ION Engineering

Over the past decade, there has been significant interest in exploring a new class of nonaqueous solvents for postcombustion carbon capture. Early research efforts targeted the use of ionic liquids (ILs) and other novel organic solvents as alternative physical solvents for gas processing and CO_2 capture applications. The IL platform offered some unique opportunities with respect to controlling physical and chemical properties of the solvent. In addition, ILs have essentially zero vapor pressure, and there is little risk of loss because of volatilization, which could theoretically eliminate the need for unit operations for solvent recovery, such as condensers, water washes, and chillers.

Although hundreds of different ILs have been explored in laboratory and small-scale tests for CO_2 capture, drawbacks to these solvents have become apparent. For the vast majority of ILs, physical solubility is the dominant mechanism of gas absorption. This renders the vast majority of ILs unsuitable for postcombustion CO_2 capture. Efforts had been made to develop amine-functionalized task-specific ionic liquids (TSILs) as a means of increasing CO_2 solubility for postcombustion applications. While TSILs were able to improve CO_2 uptake at low partial pressures, they suffered from high viscosities and prohibitively expensive synthetic procedures.

A more straightforward, cost-effective approach to improving CO_2 solubility in IL solvents was reported in 2008 (30). This approach involved simply blending the IL with a commodity amine (e.g., MEA) to combine the benefits of IL nonvolatility with the CO_2 capacity of traditional aqueous amine systems. Using this approach, it was believed that these IL-amine solvent systems would result in a low energy penalty solvent for postcombustion CO_2 capture by eliminating much of the latent energy lost in the regeneration process without significantly increasing the liquid flow rates required by incorporating an amine to preserve the CO_2-carrying capacity of the new solvent.

It was determined by ION and others that, despite broad claims of IL stability in the literature, many amines are capable of attacking and degrading ILs, resulting in loss of capacity of the solvent for CO_2 and undesirable changes in physical and chemical properties.

An alternative class of organic solvents was already under development as potential improvements to the IL–amine strategy. This work focused replacing ILs with imidazoles, a large class of organic molecules not previously studied in combination with amines for industrial gas separations. Similar to the ILs, imidazoles have desirable and tunable chemical and physical properties, including very low vapor pressures and viscosities comparable to water. Imidazole–amine blends have been demonstrated to provide a stable, nonaqueous solvent with low volatility and high capacity for CO_2. Additionally, results generated by ION and Dr. Bara indicate that imidazoles promote CO_2 capture, as demonstrated by CO_2 loadings of imidazole–amine mixtures that exceed stoichiometric expectations of comparable aqueous–amine solvents.

Several test runs were performed in order to evaluate ION Engineering's lead CO_2 capture solvent. The solvents being developed by ION Engineering represent a new class of amine-based solvents known as nonaqueous solvents. While these "nonaqueous" can tolerate aqueous environments and may even contain water, the technology is distinguished by an engineered solvent matrix consisting of an amine that reversibly bonds with CO_2 and an organic solvent, which facilitates the "CO_2 –>/<– amine" reaction during the absorption and/or desorption process. The primary aim in designing this type of solvent technology is to minimize latent heats (i.e., unrecoverable energy losses) throughout the process, which can be accomplished by minimizing the amount of water in the solvent matrix. By minimizing the water in the active mixture, less energy is required to regenerate or strip the CO_2 off of the working components of the solvent. However, because some water is required to facilitate the CO_2 absorption process, a trade-off does exist between reducing regeneration energy and achieving a reasonable CO_2-carrying capacity that is suitable for commercial operation. In order to fully understand the performance and operability of this new type of solvent, 5 weeks of testing was planned and executed.

Four of the early weeks of testing were used to evaluate the solvent in the EERC's current system as is with no modifications to equipment. Results from these tests indicated very promising reductions in energy required when compared to similar capture while using the MEA solvent (which is currently used as a baseline for relative comparison). During the first week of testing, several parametric-style tests were performed to evaluate capture performance at varying L/G ratios and varying energy inputs to the system. During this week of testing, both coal and NGCC flue gas were generated in order to evaluate the solvent under both of these types of flue gas. During the coal-generated flue gas testing, a Wyoming PRB coal was fired in order to generate a flue gas stream that contained a range of components. Table 18 shows the range of gas conditions at the inlet of the absorber. For Week 1 of testing, the PTC system was equipped with an SCR unit to control NO_x levels, an ESP to remove the majority of the ash generated, and a WFGD to scrub the SO_2 to a level of approximately 0 ppm. During Week 1 of testing, understanding the degradation of the solvent was not a focus of testing; that parameter was tested in a following test campaign.

Table 1. Typical Flue Gas Concentrations at the Inlet to the Absorber

Flue Gas Component	Coal-Derived	NGCC-Derived	Notes
CO_2	13%–15%	3%–4%	All values are on a volume basis and are measured dry.
O_2	3%–5%	14%–15%	
NO_x	0–100 ppm	0–100 ppm	
SO_x	0–80 ppm	0 ppm	
CO	10 ppm	<10 ppm	

The CO_2 capture system was set up the same way as for the earlier solvents tested in the Phase II program. The DCC was used to control the inlet absorber flue gas to a temperature of 110°F (43°C). The gas entered the absorber at the bottom and traveled through ~13 feet (~4 m) of structure packing provided by Sulzer from the MellaPak CC line of packing. At the top of the absorber column, an indirect cooling section was used to try to maintain an outlet temperature of 112°F (44°C) providing for a +2° delta between the inlet and outlet. This delta T is a slow-reacting control and, therefore, was not always maintained in this region. During this first week of testing, several L/G ratios were evaluated by manipulating the gas and/or the solvent flow rates.

Figure 37 shows the results from this first week of testing while firing the PRB coal and treating 75 scfm of flue gas. The results of this testing were very promising, providing for a decrease in regeneration energy of 40% to 50% when compared to the MEA baseline case. A reduction in the liquid circulation rate was also shown in these results, with liquid flows being 25% to 40% lower than MEA at a capture rate of 90%.

A flue gas flow rate of 100 scfm was also tested which is a significant increase in velocity through the column. Figure 38 shows the result which again indicated very promising reductions in both L/G ratios as well as regeneration energy. The best results show a reduction in regeneration energy as much as 55% lower than that of MEA at 90% capture with L/G ratios being as much as 45% lower. Because the objective of the ION solvent is to minimize water in the matrix, several solvent samples were taken and measured for water content. Throughout testing, the water concentration increased, even while maintaining a 1° to 5°F delta in temperature between the inlet and outlet flue gas to try to maintain a water balance. Toward the end of Week 1 testing, it appeared that the water concentration had stabilized, but at a significantly higher concentration than the initial solvent contained. These results can be seen in Figure 39.

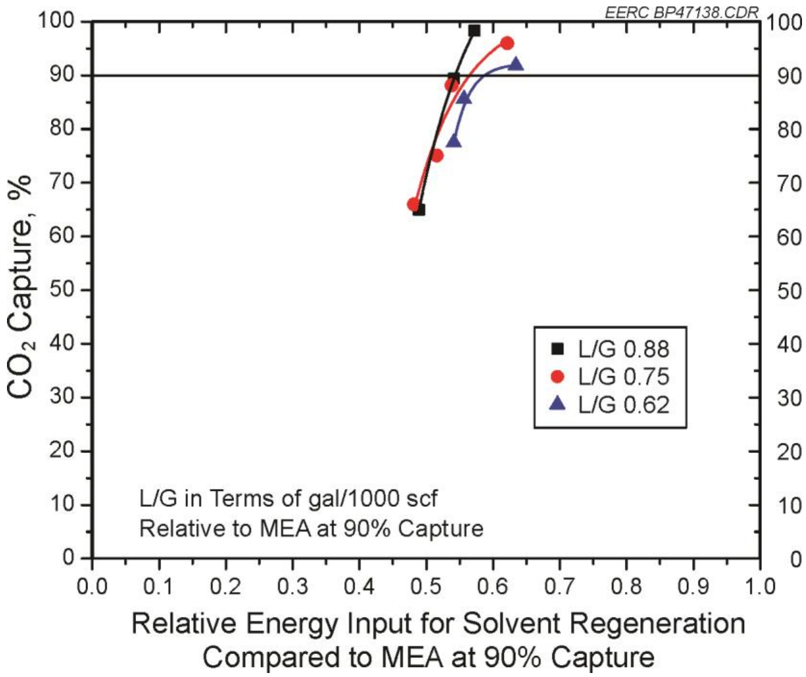

Figure 1. Summary of Week 1 pilot-scale results at 75 scfm gas flow.

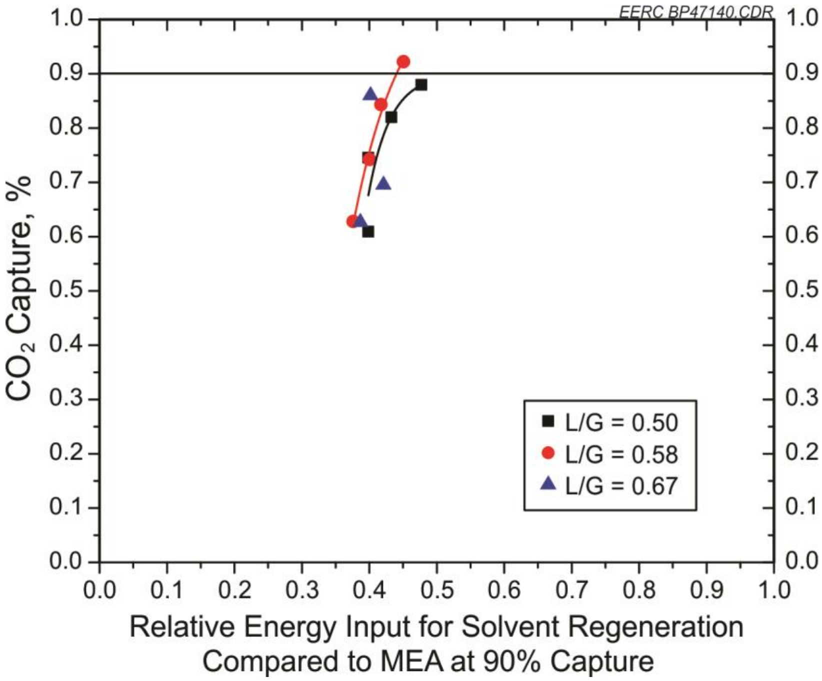

Figure 2. Summary of Week 1 pilot-scale results at 100-scfm gas flow.

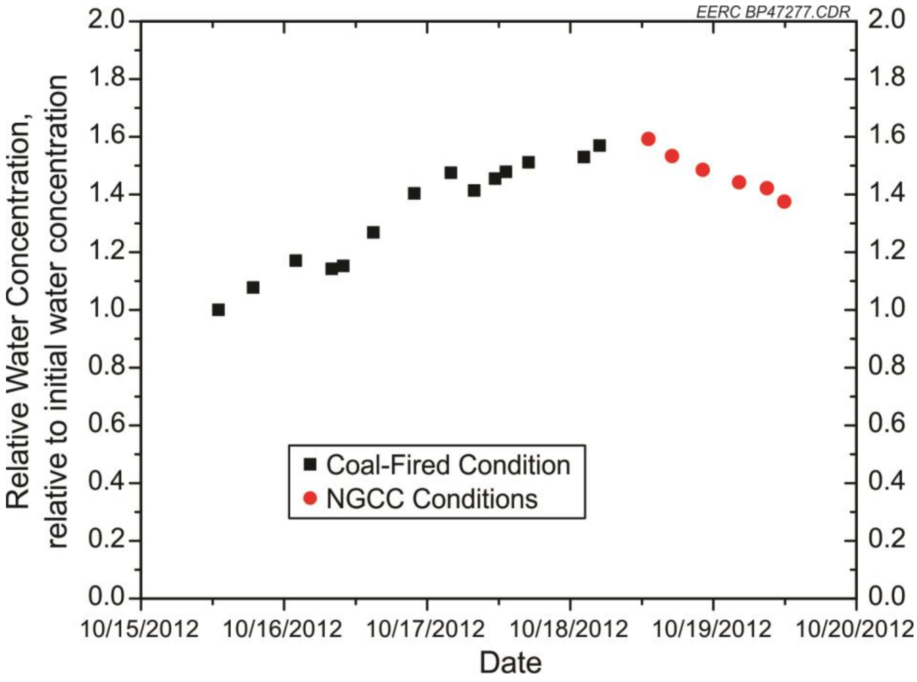

Figure 3. Summary of the change in solvent water concentration for Week 1 testing.

Toward the end of Week 1, the flue gas was switched from a coal-derived flue gas to a NGCC-simulated gas. This was done by combusting natural gas in the PTC at very high excess air levels. This created a flue gas that contained a range of CO_2 from 3% to 5% with high oxygen concentration of ~15%. Table 18 shows the range of NGCC flue gas components entering the absorber. A similar set of parametric tests was performed while under the NGCC gas conditions in order to evaluate solvent performance. Further discussion of work performed under NGCC conditions can be found in Section 10.

Based on the results from Week 1, a longer-term test run was planned for both the PRB coal and NGCC gas conditions in order to demonstrate steady-state capture for a 72-hour continuous run for both flue gases. The test run started by dialing in the steam and liquid flow rates determined to be the most efficient from Week 1 of testing, while matching the coal-derived gas conditions from Week 1 (100 scfm flue gas rate). Because the starting solvent was slightly different in water concentration from Week 1 (higher initial water content), additional steam was required to reach 90% capture. It was decided that a delta T between the inlet and outlet gas of +2°F would be targeted to maintain the water balance. Throughout the week of testing, capture performance began to slowly decrease as the water content of the solvent began to increase. During the week of testing, the water concentration of the solvent increased by roughly 50% from starting values. The test was ended early as it appeared the water content would not stabilize. During this time, capture dropped from 90% to a final value of ~72%. Figure 40 shows the capture performance as water concentration is increased in the solvent at a set L/G ratio. The testing team decided to not move forward with the long-term NGCC test until the water concentration could be stabilized by optimizing the operating temperature profile.

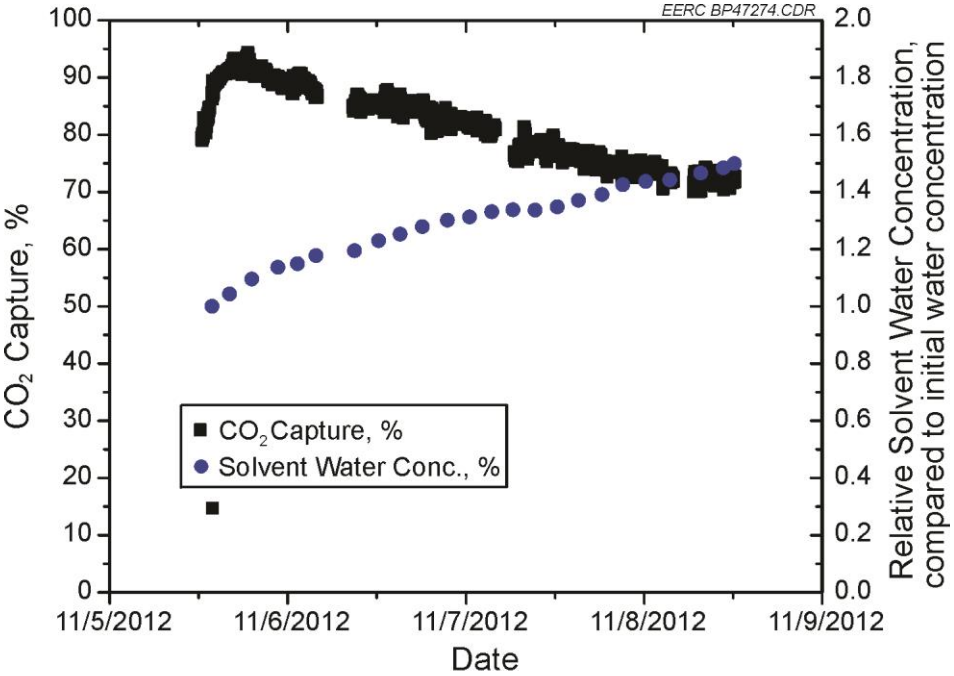

Figure 4. Capture rate during the long-term steady-state test as water concentration increased.

Week 3 of testing was designed to determine an operating protocol that would allow for the control of water in the system, because it was unknown if it was the solvent that was hydrophilic or simply the way the system needed to be operated in order to control the water concentration. The unknowns created a very dynamic Week 3 test program based on water concentration as the output. The inlet and outlet flue gas temperatures to the absorber were used as the primary method of controlling the water concentration in the solvent matrix. A maximum delta T between the inlet and outlet gas was targeted as calculated by Equation 1:

$$Delta\ T = Absorber\ Outlet\ Gas - Absorber\ Inlet\ Gas \qquad \text{[Eq. 1]}$$

Throughout the week of testing, several delta T's were targeted to determine the impact of water in the solvent. This was controlled by either cooling the inlet gas more or less and operating the top of the absorber column temperature at either 105° or 110°F (41° or 43°C). Testing started with the inlet gas cooled to 75°F (24°C) and the outlet gas set to 105°F (41°C). The water concentration dropped at a rate of approximately 0.5%/hr at these initial test conditions. The inlet gas was then adjusted to 85°F (29°C) and then 95°F (35°C), the system was allowed to reach steady-state at each inlet gas condition, and steady-state operation was maintained for 2 hours before moving to the next flue gas temperature. The 2-hour steady-state periods at each flue gas inlet temperature allowed the water concentration in the circulating solvent to be measured and the gain or loss of water in the solvent to be determined at a given inlet flue gas condition. As shown in Figure 41, the water concentration of the solvent decreased substantially at the 75°F (24°C) inlet gas condition, increased at the 95°F (35°C) inlet gas condition, and appeared to remain steady with a slight decreasing tendency at the 85°F (29°C) inlet gas condition. Based

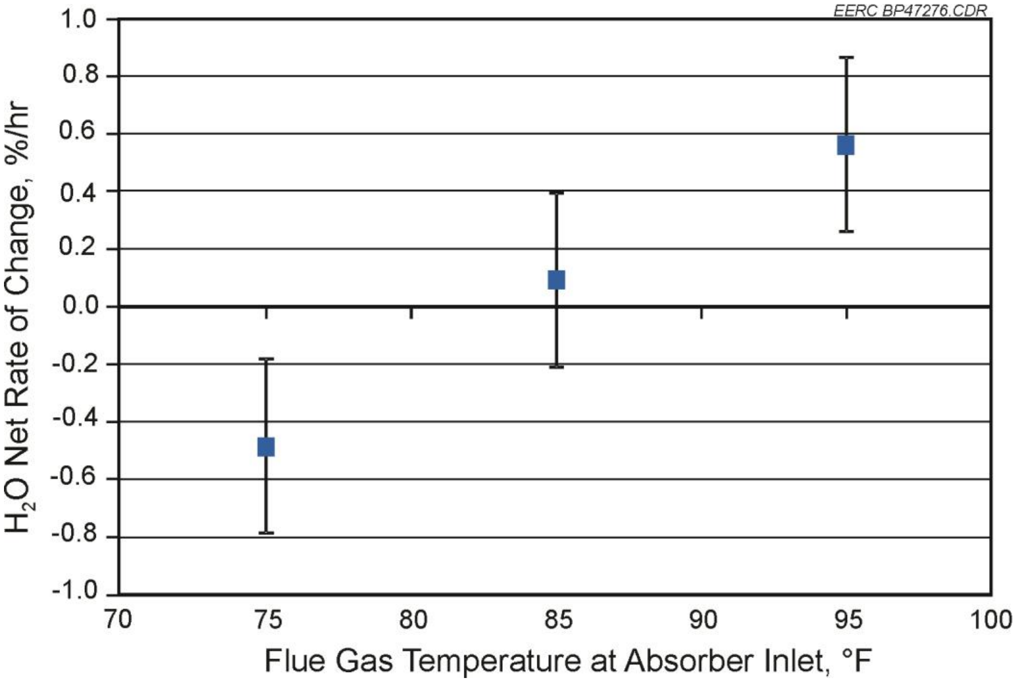

Figure 5. Controlling rate of change in solvent water concentration by varying flue gas temperature at the inlet of the absorber column.

on these results, it can be said that the water concentration could be controlled in the solvent. Furthermore, these results suggest that by periodically monitoring water concentration in the solvent and adjusting the inlet flue gas temperature, fine control of the water concentration in ION's solvent should be achievable.

Several other temperature profiles were tested during this week to determine the best possible control point. Figure 42 shows the inlet and outlet gas temperature as well as the water concentration in the solvent. It can be seen that during low inlet temperatures, the water concentration decreases and seems to be stable when the inlet temperature is equal to 95°F (35°C) while the outlet temperature is above 105°F (41°C). However, as the outlet temperature drops to below 105°F (41°C), the water concentration rises quickly. Adjustments to lower the inlet temperature as well as raising the outlet temperature caused the concentration of water to drop quickly. This supports the ability to control the water concentration in the solvent and indicates that controlling water concentration in the solvent is possible across a range of operating conditions.

Another way to look at this is to investigate the change in water concentration vs. varying delta T's in the system. Figure 43 shows this trend. Based on this figure, the water concentration can be maintained at several different temperature profiles but should be more stable with a delta T between 15° and 20°F. This is where the solvent appears to switch from a trend of gaining water to a trend of losing water.

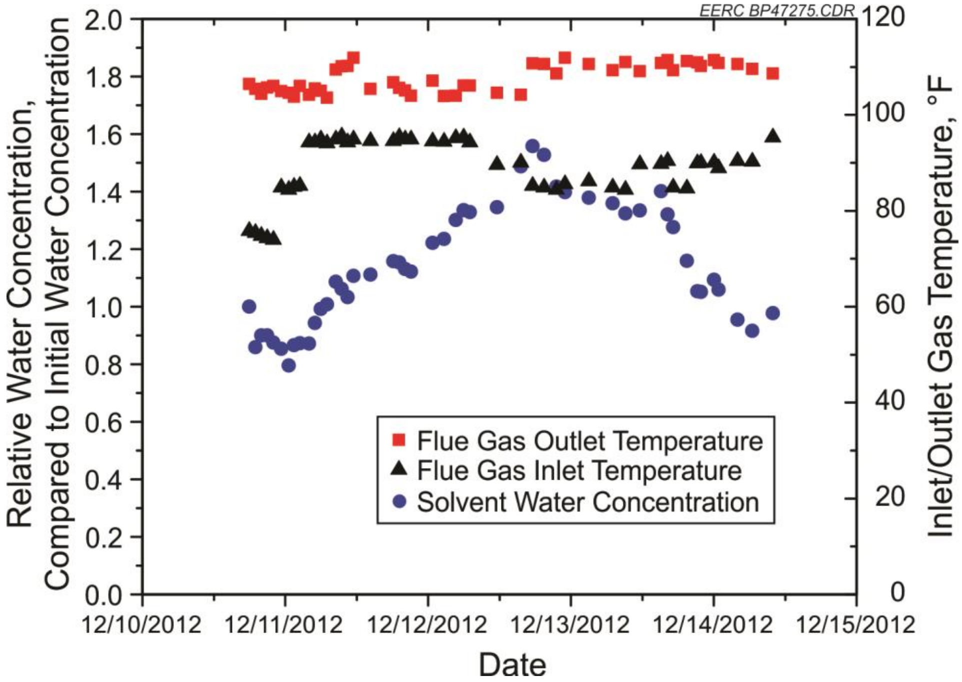

Figure 6. Water concentration results as gas temperatures are changed.

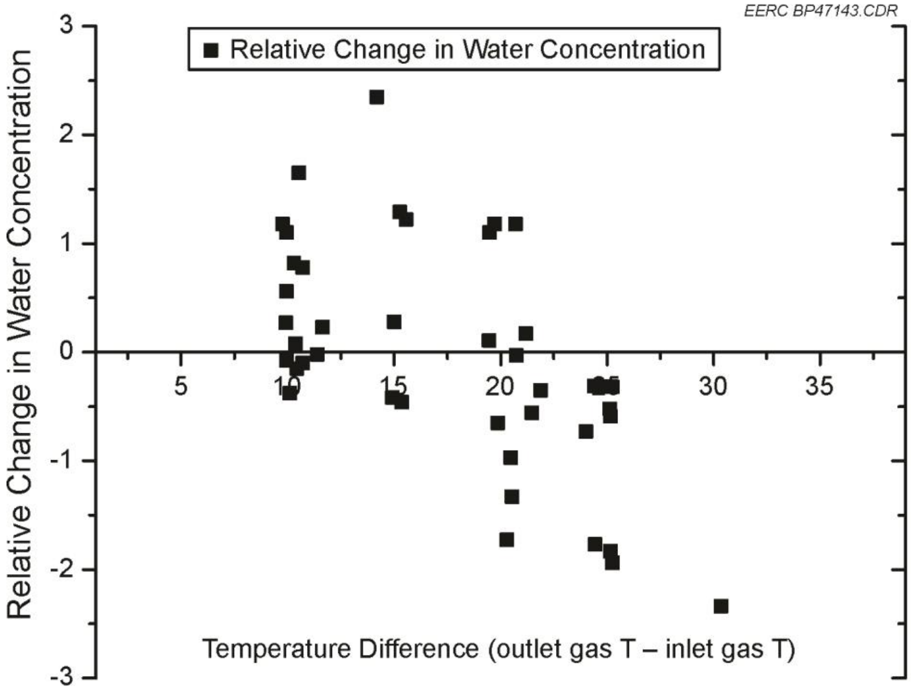

Figure 7. Gain and loss of water at various temperature profiles in the system.

Based on the results of the Week 3 testing, another long-term test period was planned. The parameters of this test were chosen to be the same as in Week 2 (coal-fired gas at 100 scfm); however, the inlet gas was primarily targeted to be 85°F (29°C) while the outlet temperature was maintained at 105°F (41°C).

Based on the rich and lean loading values of the solvent, as determined using the total inorganic carbon analyzer, it was determined that the solvent performance was not achieving its maximum rich loading which may be caused by the short residence time in the column. However, even with this occurring, the results still support large reductions over MEA in both L/G ratio and regeneration energy. This indicates faster overall kinetics than that of MEA but suggests that further gains in regeneration energy reductions could be realized. It was decided that a second absorber column would be built and operated in series, effectively increasing the overall height of the absorber column. Figure 44 shows the modified piping and instrumentation diagrams, including the second absorber column.

7.5.1 Week 4 ION Testing: Steady State Run

The Week 4 test of ION Engineering solvent was a 72-hour test similar to the Week 2 test, maintaining constant system conditions and 90% CO_2 capture if possible. The test was interrupted periodically to clean out the test furnace, ESP, and associated piping daily for approximately 2-hour intervals. During each maintenance period, the 72-hour clock was stopped. Solvent samples during the test were collected at 4 hour intervals during testing.

The target absorber inlet and outlet temperatures were 85° and 103°F (29° and 39°C), respectively, maintaining a delta T of 18°F to keep water concentration in the solvent as stable as possible. Absorber delta T was chosen based on the results of Week 3 testing. Choosing a delta T of 18°F allowed operating engineers a temperature buffer of 2°–3°F to maintain operation between the 15°–20°F range determined in Week 3. Temperature control at the top of the column is slow-reacting, necessitating the buffer. The plot at the bottom of Figure 45 shows the sample water concentration as a percentage of the initial water concentration to begin the 72-hour test. Water level in the solvent was maintained within 10% of the starting concentration level. The demonstrated ability to keep water relatively constant supported the data generated during Week 3.

Test results and conditions for Week 4 testing are also presented in Figure 45. Coal-derived flue gas flow rate was set to 100 scfm at the absorber inlet. Regeneration energy input and L/G ratio were each initially set based on test conditions from Week 2 of ION Engineering testing. Adjustments were made at the beginning of the 72-hour test to L/G and regeneration energy to reach approximately 90% CO_2 capture. For the remainder of the test, only small adjustments were made to steam input and solvent flow rates in order to maintain steady-state conditions.

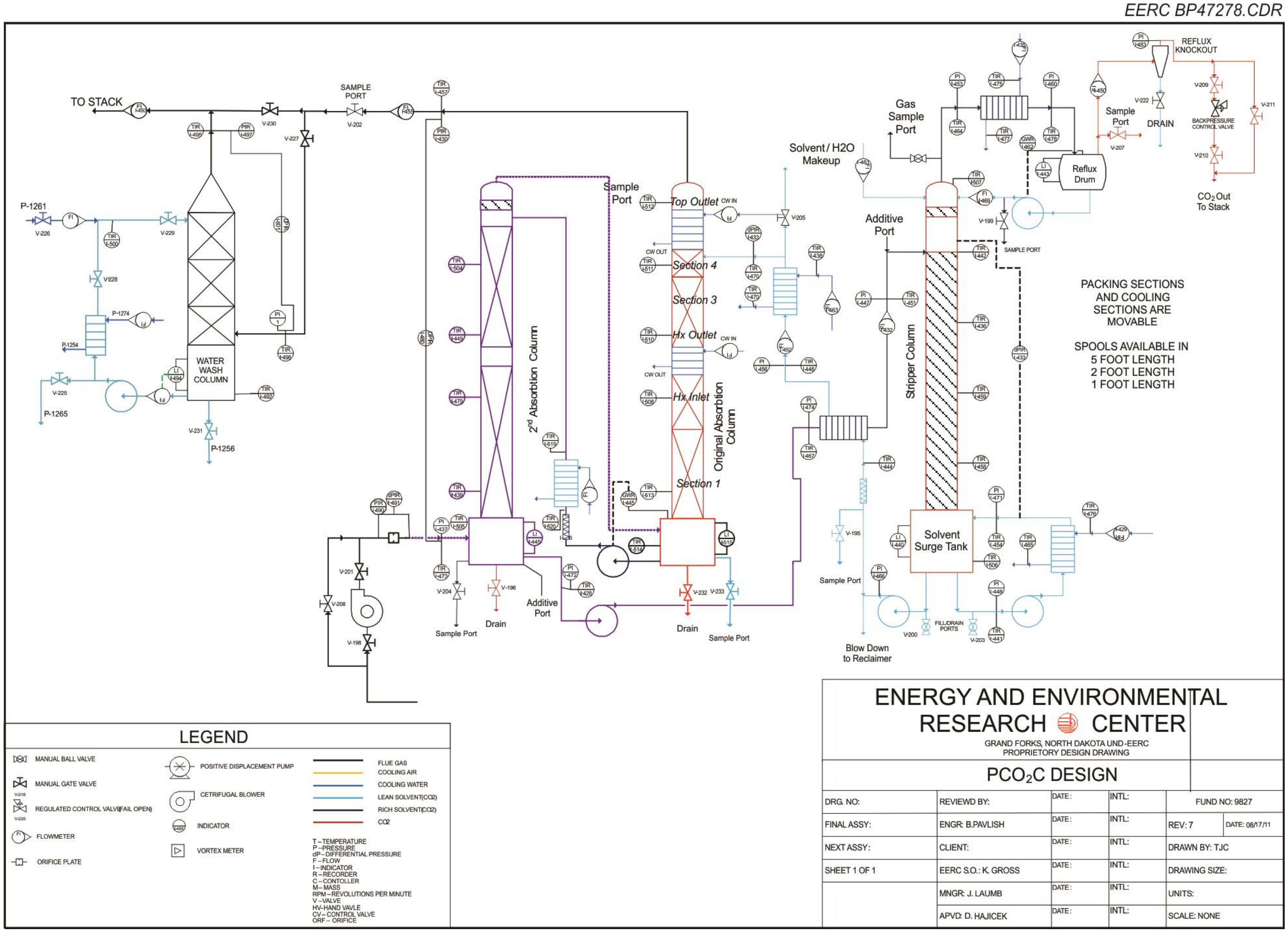

Figure 8. Modified P&ID showing the addition of the second absorber column.

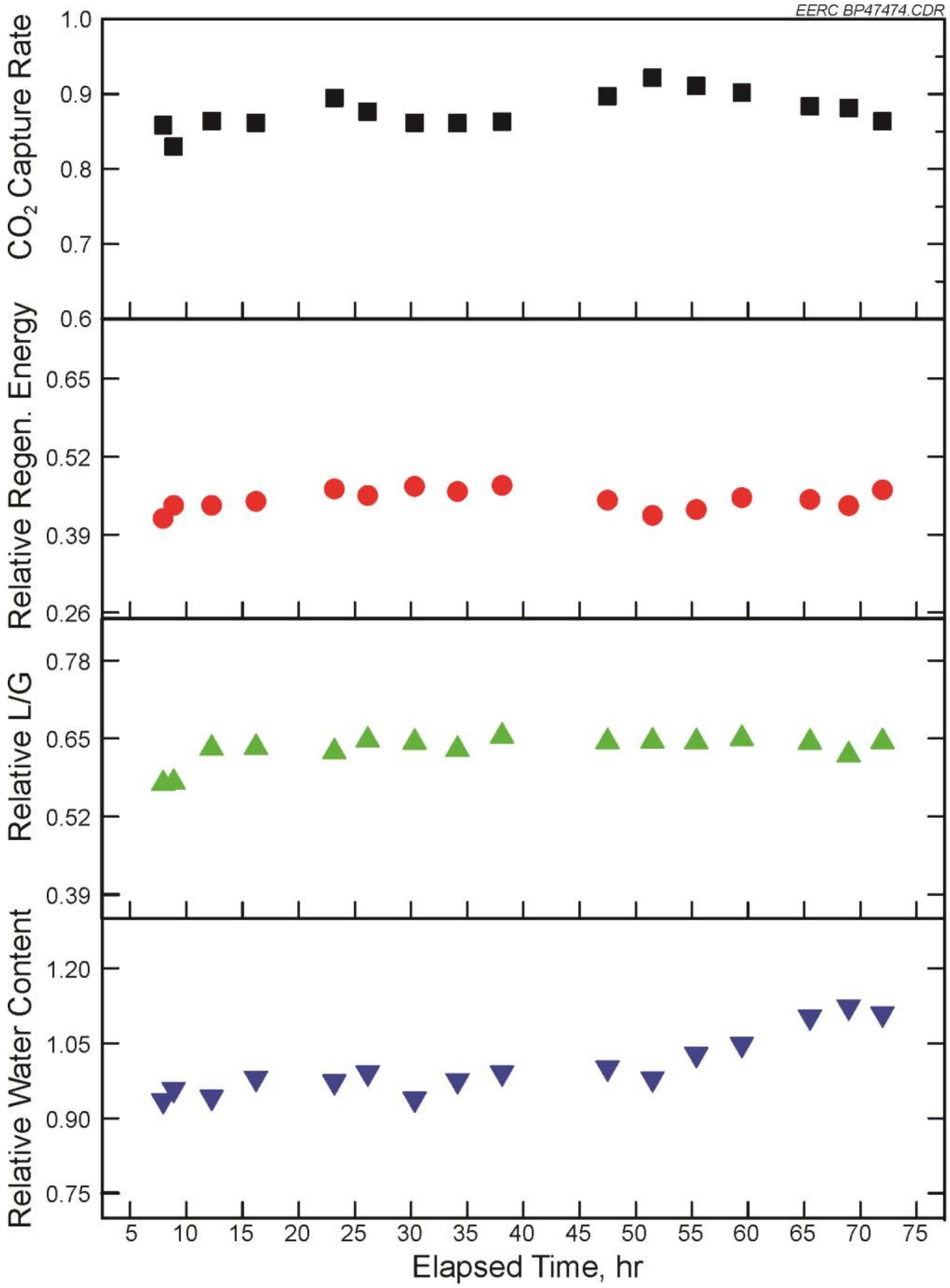

Figure 9. Steady-state test conditions for 72-hour test.

Figure 45 shows CO_2 capture was maintained between 85% and 92% throughout the 72-hour test. Compared with baseline testing of MEA at 90% capture on the same equipment, the required regeneration energy for the solvent to reach 90% capture was 65% lower. The L/G ratio was also significantly lower than MEA testing, about 35% lower than MEA. At larger scale, these advantages over 30 wt% MEA will lead to lower capital costs when considering pump sizes and a smaller parasitic load requirement with decreased steam usage.

7.5.2 Week 4 Heat Stable Salt Analysis

Solvent samples were collected every 4 hours during the 72-hour test run. A number of the lean solvent samples were analyzed for the presence of HSS ions. These ions build up over time during postcombustion capture processes and degrade the solvent. Both organic and inorganic HSS ions were found upon analysis of solvent samples. Figure 46 shows the concentration of organic HSS ions acetate, formate, and oxalate, as well as inorganic HSS ions fluoride and chloride.

The organic ions as well as the fluoride and chloride ions were found in relatively small amounts. The concentrations of each HSS increased or stayed the same over the course of the test campaign. Of the organic HSS ions, formate was found in the largest concentrations, ranging from 66 to 150 ppm. The acetate HSS ion concentration rose from 15 to 54 ppm, while the other HSS ions shown in Figure 46 all showed concentrations below 25 ppm. It is not surprising to find larger amounts of formate compared to acetate and oxalate because formate anions are the first compounds formed from oxidative degradation of MEA; acetate and oxalate are formed from subsequent degradation steps after formate anions are formed. Similar mechanisms are assumed to be present in the solvent. Similar sample analyses were performed in Phase I of the PCO_2C project. Figure 47 shows the data from MEA.

During MEA testing, formate, acetate, and oxalate followed similar trends, with formate being represented in the solvent in the highest concentration. There was no significant difference in organic HSS ion formations between the MEA test from PCO_2C Phase I and the ION solvent test.

Solvent samples were also analyzed for the presence of nitrate and nitrite HSS ions. Figure 48 shows both nitrate and nitrite in concentrations ranging from 2 to 8 ppm. This is consistent with the low NO_x levels in the flue gas at the absorber inlet. Similar conditions were run during MEA testing in PCO_2C Phase I, producing similarly low nitrate and nitrite levels, shown in Figure 49.

There was a significant difference in the concentration of chloride between MEA and ION solvent tests. In Phase I, it was reported that the amount of chloride ion in solution was in the range of about 100–220 ppm during the test period. This suggests that a significant amount of the chloride in the flue gas formed a HSS and remained in the SASC system. The fuel used for each test was Antelope PRB subbituminous coal, which typically has a chlorine level of around 20 ppm. The solvent showed chloride levels below 11 ppm.

Sulfate, sulfite and thiosulfate HSS ions result from SO_x compounds in the treated flue gas. Solvent samples were analyzed for sulfate and thiosulfate. Attempts were made to quantify the sulfite concentration in the lean solvent samples. Because of the unstable nature of the sulfite HSS ion, the total sulfate/sulfite concentration was found with the sulfite represented as the difference between that number and the sulfate ion concentration. This calculation results in sulfite HSS concentrations between 5 and 19 ppm during coal-fired testing. The sulfate concentration was low for NGCC testing during the first day of the test, but coal-fired testing resulted in a steady increase in concentration from 40 to 488 ppm by the end of the test. Figure 50 shows sulfate and sulfite concentrations, with absorber inlet flue gas SO_2 concentration shown for reference.

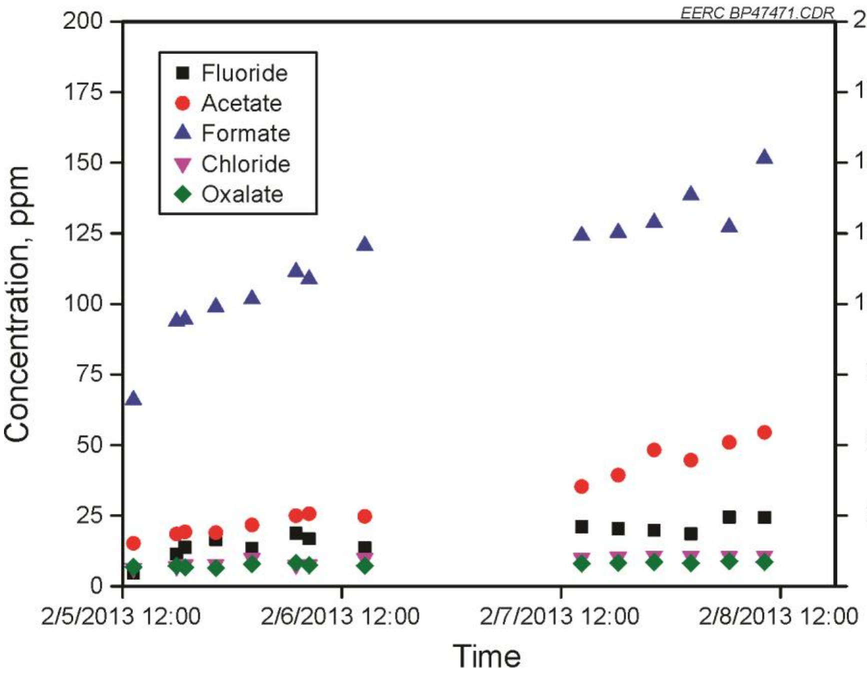

Figure 10. Concentration of HSS ions in lean ION samples.

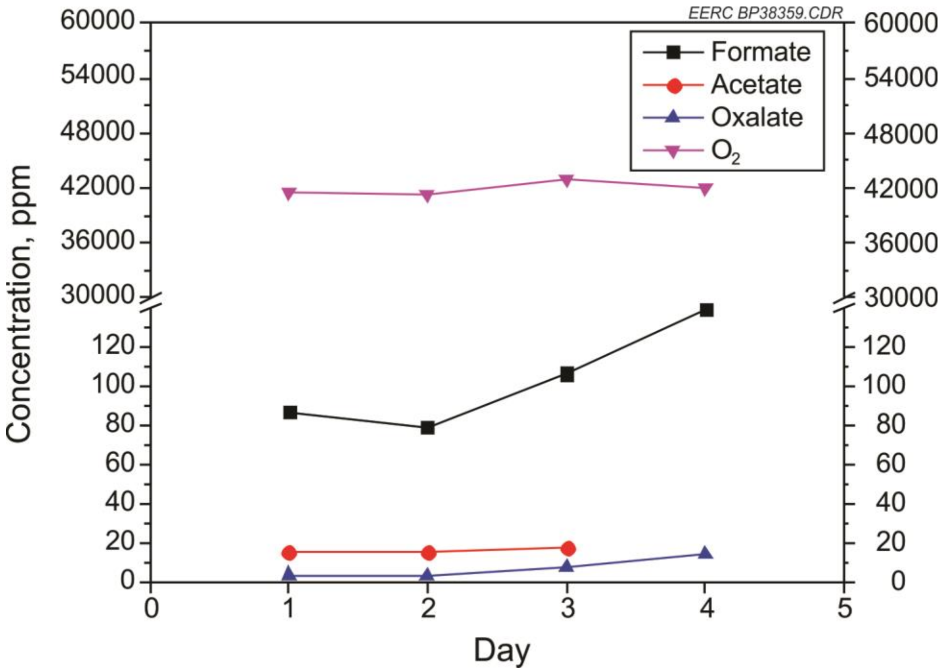

Figure 11. Concentration of organic anions in lean MEA solutions.

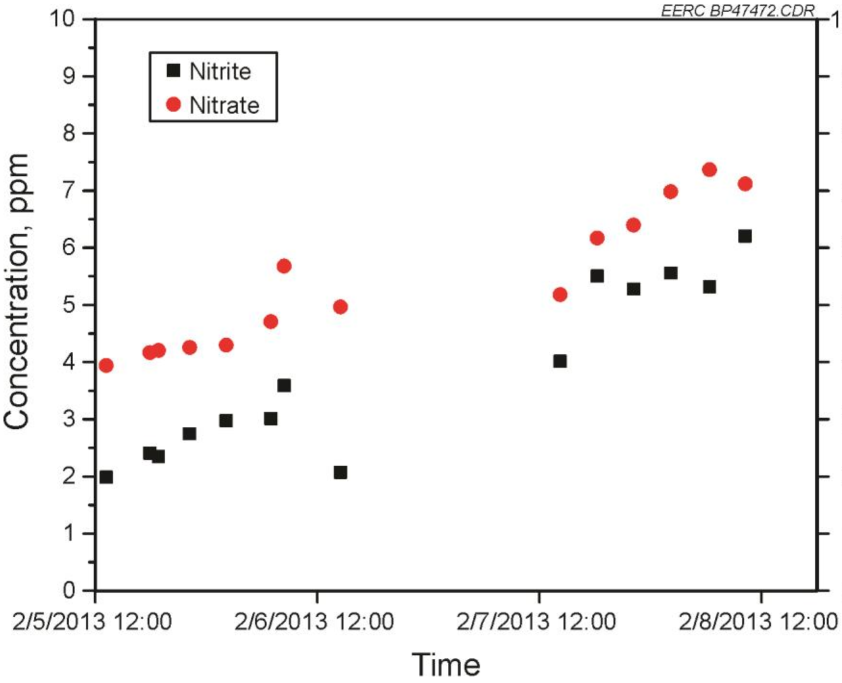

Figure 12. Concentration of nitrate and nitrite HSS ions in lean ION solvent samples.

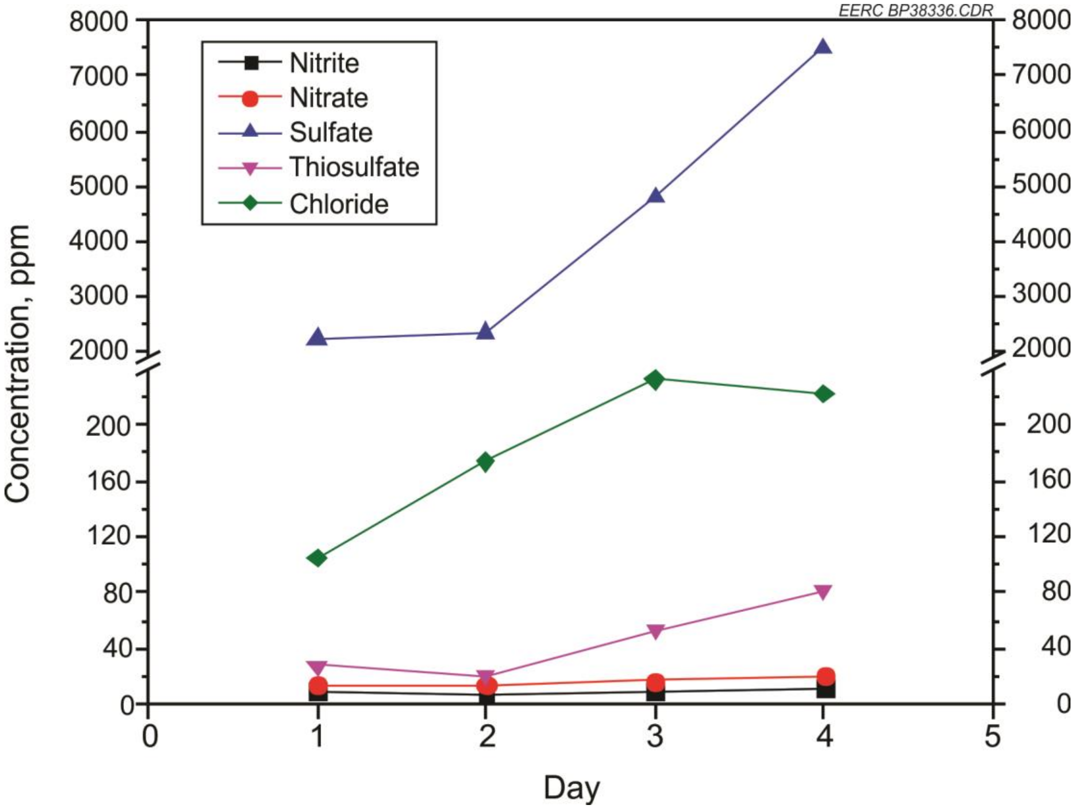

Figure 13. Concentration of inorganic anions in lean MEA solutions.

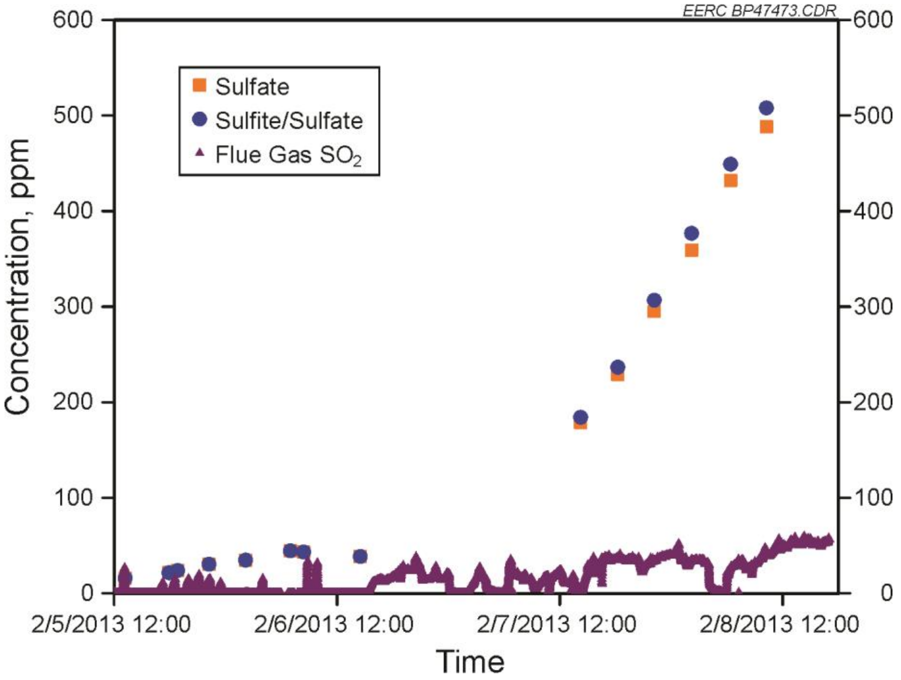

Figure 14. Concentration of sulfate and sulfite HSS ions in ION solvent samples.

For comparison, Figure 51 shows sulfate and thiosulfate HSS ion sample concentrations from MEA testing, along with flue gas SO_2 concentration. Flue gas SO_2 concentrations for both tests were similar, but the resulting HSS ion concentrations were significantly different. MEA samples had sulfate concentrations 10 to 15 times higher than the ION solvent. This represents a significant potential advantage for ION solvent in commercial applications. Samples in both cases were analyzed for the presence of thiosulfate HSS ions, but the solvent thiosulfate levels were undetectable in most samples. In the MEA samples, thiosulfate levels increased from 25 to 85 ppm, again significantly higher than the ION solvent.

7.5.3 CO_2 Loading Analysis

During Week 4 of testing, several samples were taken, and the CO_2 loading was determined in both the rich and lean samples. During this testing it can be seen that the rich loadings were 13 to 14 g carbon/kg of solvent. Several factors can affect the rich loading, such as temperature and column residence time. The lean loadings for this test period varied slightly early on in the testing and were below 3 g carbon/kg solvent. Toward the end of testing, the rich loading increased slightly toward the 14 g carbon/kg solvent range while the lean loadings were consistently around 3.2 g carbon/kg solvent. These results are shown in Figure 52. It was noted from this test and earlier testing that the absorber column may have been limiting the maximum rich loadings achievable for the ION solvent. In an ideal system, the rich loading should not change with a change in lean loading. If this is the case, it can be noted that there is sufficient packing height (residence time) for the solvent to be fully enriched with CO_2, or the solvent is

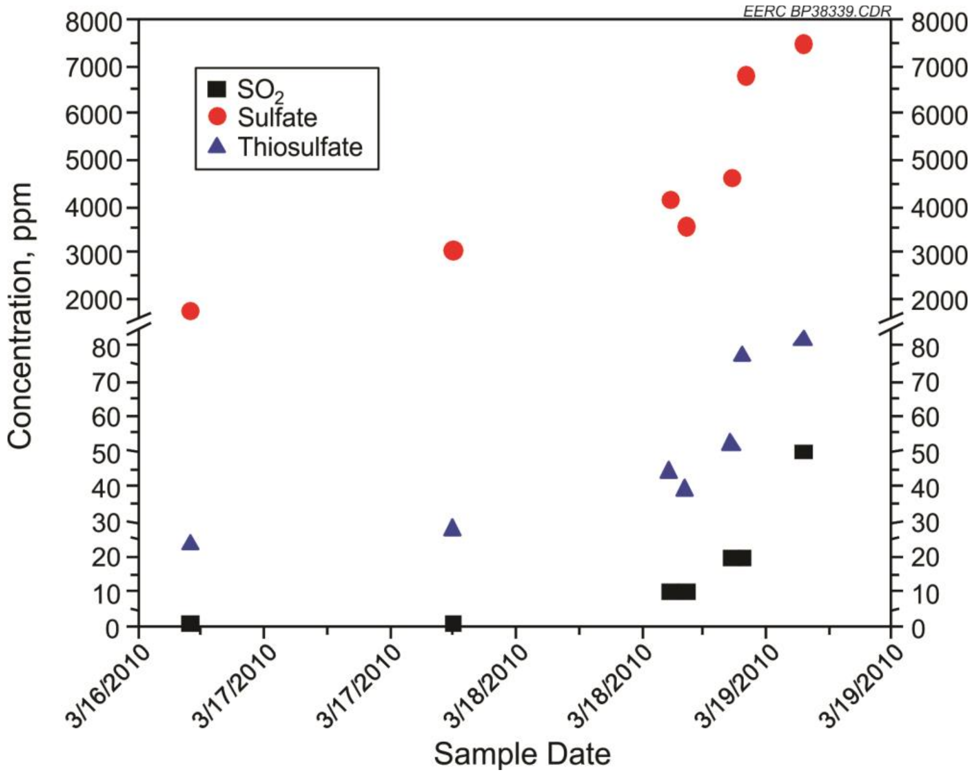

Figure 15. Sulfate and thiosulfate concentration at various SO_2 injection levels.

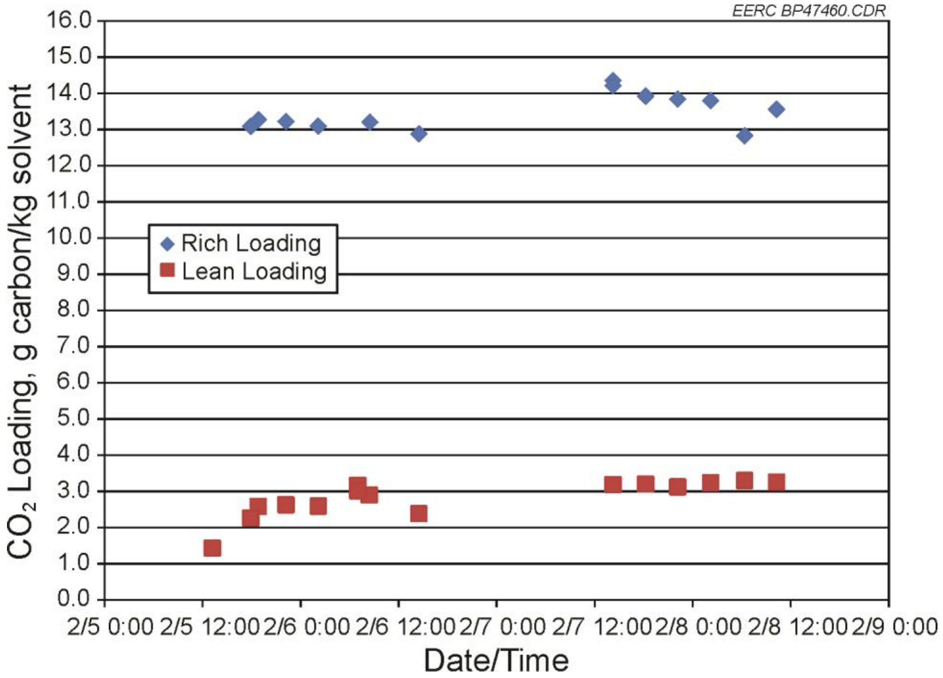

Figure 16. Rich and lean loadings during the Week 4 steady-state run.

kinetically fast to reach a steady-state loading. For the ION solvent, it was clear that we were not at the maximum potential; however, it was also noted that the solvent was kinetically faster than MEA as the rich loading was not nearly as sensitive to the lean loading of the solvent. This can be seen in Figure 53. The rich loading varies slightly with changing lean loading (change in regeneration energy), however, remains close to a rich loading of 16 g carbon/kg solvent.

MEA is much more sensitive to changing the lean loading as it is more kinetically limited than the ION solvent. Figure 54 shows that when the regeneration energy is increased, the lean loading drops from 0.28 mol CO_2/mol MEA to 0.20 mol CO_2/mol MEA. However at the same time, the rich loading decreases from 0.45 to 0.37 mol of CO_2/mol MEA. This is a function of the MEA solvent needing more residence time or column height to capture the same amount of CO_2. Based on this and the knowledge that the ION solvent had the potential to hit higher rich loadings, a second absorber column was added to the system and operated in series to essentially double the packing height in the system. This was an overdesign for the ION solvent; however, it was decided to overdesign the column at this stage to determine what the maximum loading for the solvent was.

The second column was constructed similarly to the original column, with a 10-inch ID (25-cm) 316L SS column built in flanged sections with a solvent surge tank at the base. The new column is insulated and heat-traced to minimize wall temperature effects inherent to this scale. The column added a total of 13 feet (139 m) of packing. The new configuration has the flue gas flowing first into the new column, then back to the original column before going through the water wash section and out to the stack.

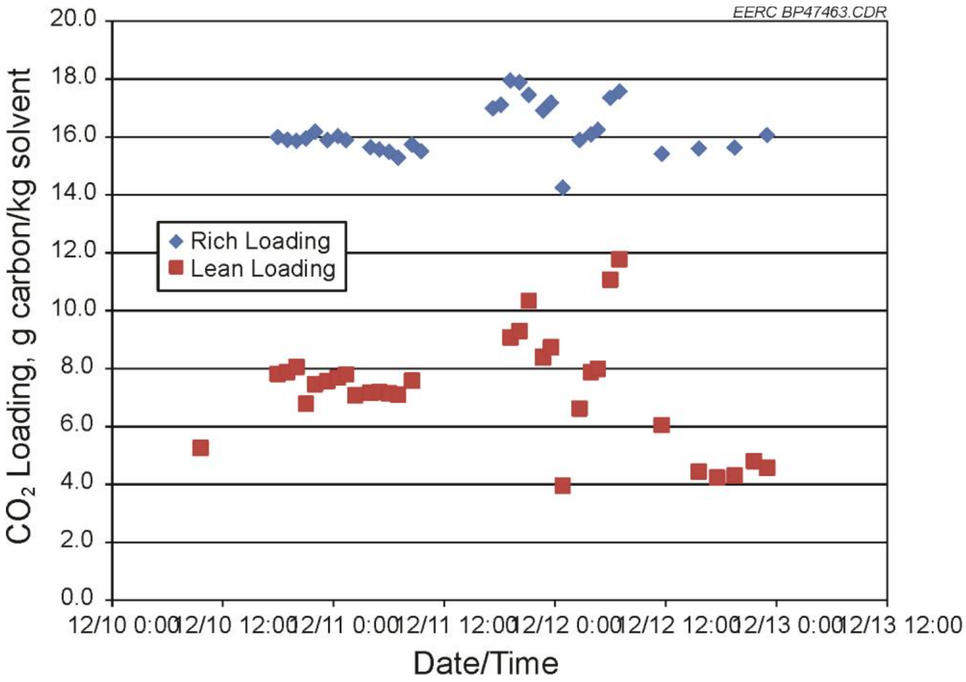

Figure 17. Rich and lean loading showing the impact of rich loading with varying regeneration energy for the ION solvent.

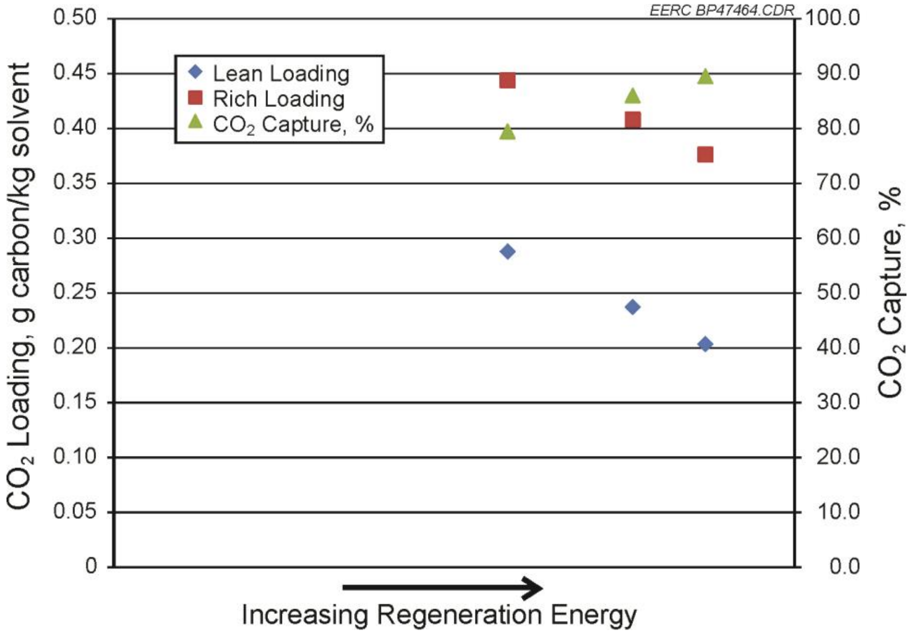

Figure 18. Rich and lean loadings for MEA showing diminishing rich loadings with decreasing lean loadings.

The lean solvent line is unchanged from the original single-column configuration, but the rich solvent in the new configuration goes from the original column through a water-cooled heat exchanger which was added to the intermediate rich solvent line between the two absorber columns. After going through the new column, the rich solvent is pumped through the cross flow heat exchanger to the stripping column. Solvent samples with the two-column configuration are taken at the base of both absorber columns, giving a rich sample and an intermediate-rich sample. Solvent sampling from the stripper column for lean solvent is unchanged.

The second column can be seen in Figure 55. It was located as closely as possible to the original column to minimize the amount of flue gas and solvent piping necessary to complete the system. Flue gas piping between the two absorber columns is insulated to minimize heat loss between columns.

7.5.4 Week 5 Testing: Extended Absorber Analysis

Week 5 of testing with the ION solvent was used to evaluate the addition of the second column in order to determine the maximum rich loading and the benefits of not overstripping. Because of time and budget constraints, there was not enough time to repeat the MEA benchmark with the additional packing height installed. Therefore, these results were not used to determine cost benefits; however, they were used more in the research sense of how the system would be designed and scaled up for the next level of demonstration. It was felt that the results gathered earlier in testing were sufficient to demonstrate the benefit of the ION solvent over MEA and provided enough information for the coal-based modeling. Several parameters were tested during Week 5 to determine an optimum loading profile for the solvent. During the range

Figure 19. PCO_2C pilot-scale system with second absorber column.

of conditions, the results indicated that the rich loading could be increased an additional 20%when compared to the single column testing. It is unclear how much of the additional packing was required to reach this maximum; however, it is assumed (based on single column loadings) that only a small portion was needed to reach this maximum condition. Figure 56 shows the range of rich and lean loadings as conditions were varied throughout the week of testing.

Running the system with higher rich loadings allowed for 90% CO_2 capture to be achieved with lower amounts of energy. This is caused by the ability to strip the solvent less, while still maintaining the necessary working capacity of the solvent to capture 90% of CO_2. Utilizing the solvent with a more optimum working capacity yielded an additional 10% to 12% reduction in regeneration energy when compared to earlier results. This will make for significant savings in annual operating expenses for a modest increase in absorber capital. Figure 57 shows the

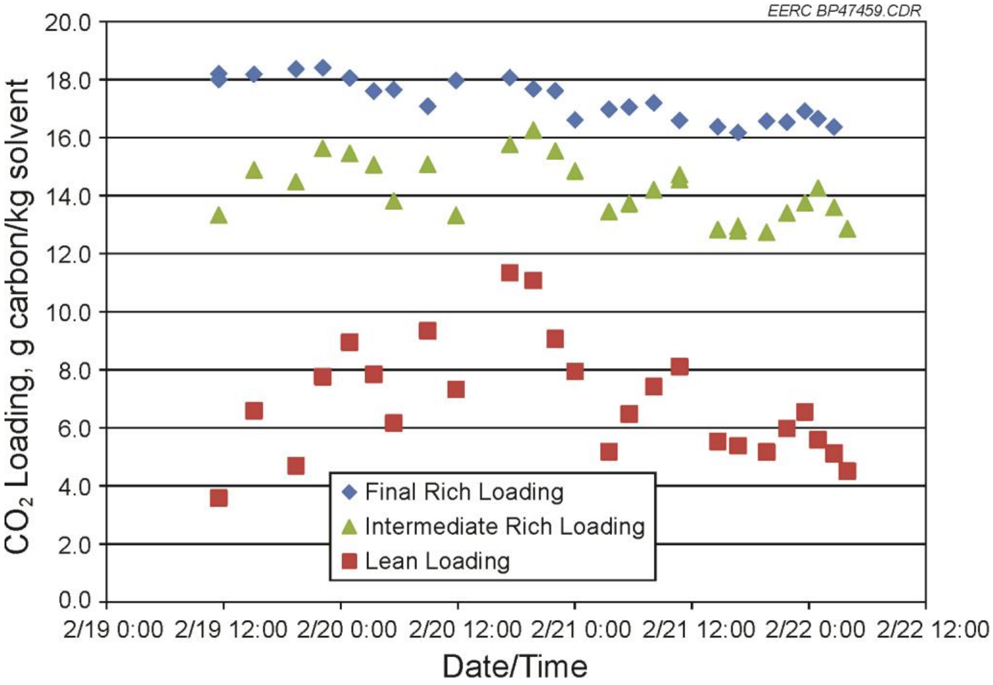

Figure 20. Rich and lean loadings for the ION solvent during the expanded column testing.

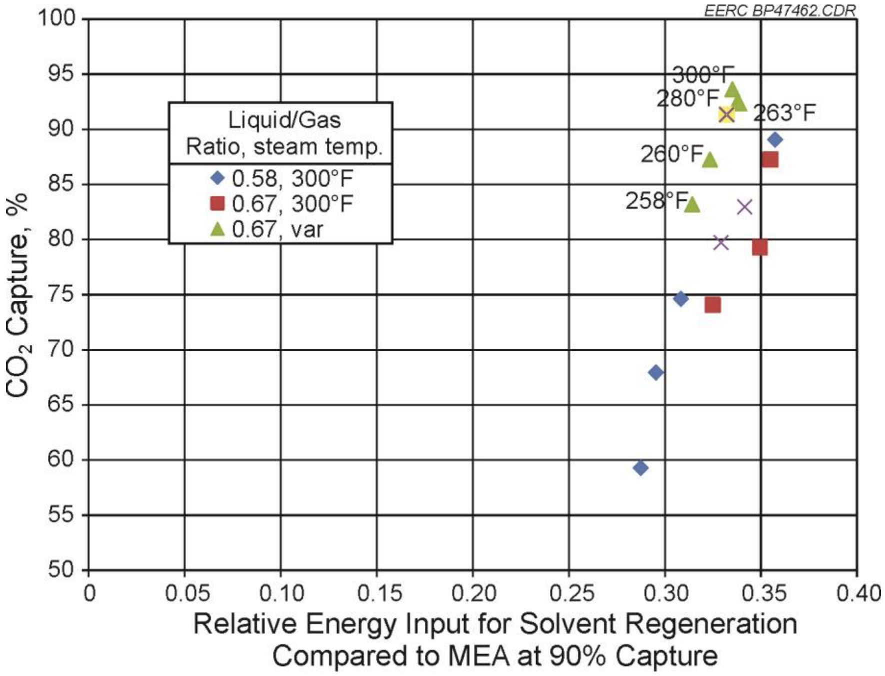

Figure 21. Results for evaluating the ION solvent at 100 scfm with the extended absorber column.

parametric results during the 100 scfm flue gas flow rate testing. During this test, the steam quality was adjusted to determine if a lower-quality steam could be used to regenerate the solvent. This test was performed by reaching a steady-state condition with the base case steam conditions (55 psig and 300°F [149°C] steam). Once this condition was reached, the steam conditions were decreased by decreasing the pressure of steam supplied to the reboiler. Doing this test showed decreased capture performance and decreased the regeneration energy. An overall increased system efficiency was noticed during this testing and can also be seen in Figure 57.

During Week 5, the flue gas flow rate through the column was also reduced to 75 scfm to determine the impact of velocity (reaction time in the column). In the case of the ION solvent, lower velocity tends to decrease the overall performance. This would be true for a kinetically fast solvent as it may not need the extra time to capture the same amount of CO_2. The lower velocities may also impact mixing in the absorber; however, in a structured packed column, mixing tends to be much less of a concern. The ION solvent still performed significantly better than MEA during this test. With the additional absorber height, the regeneration energy was decreased by 15% to 20% for the 75-scfm gas flow. Again, this was attributed to the increased rich and lean loadings (no need for overstripping). It is likely that the MEA base case solvent would also perform slightly better in this configuration; however, there is less room for improvement. Commercially, MEA is operated at rich loadings of 0.44 mol CO_2/mol amine and lean loadings of ~0.22 mol CO_2/mol amine. For the steady-state point chosen as the base case analysis for 75 scfm, the MEA solvent was operated with rich and lean loadings of 0.41 and 0.23 mol CO_2/mol amine, respectively, which is close to commercial. The results for the 75-scfm testing can be seen in Figure 58.

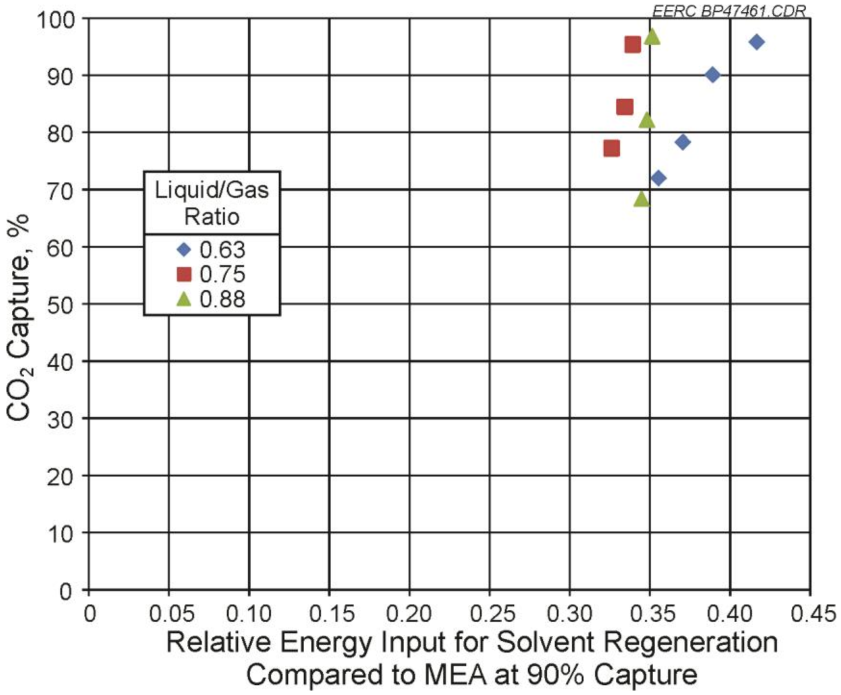

Figure 22. Results from the 75-sfcm flue gas testing with the extended absorber column.

8.0 POSTCOMBUSTION MODELING – COAL-FIRING

8.5 ION Solvent Performance/Model Results

The results of the pilot-scale work were used in an Aspen Plus-based process model to develop the mass and energy balance for Case 10 ION solvent. It was determined through the pilot-scale studies that the ION solvent required 75% of the liquid flow requirements of MEA and 57% of the regeneration energy requirements for MEA. This information was used to resize the CO_2 capture, steam cycle, and boiler models to account for lower steam requirements. A reduction in steam usage also reduced the amount of coal needed to generate the steam; therefore, less CO_2 was produced, and even less solvent was needed to capture the CO_2. This process proceeded in an iterative manner until the plant was sized for 90% capture and 550-MW net power output.

The results of the study are presented in similar format to the DOE report for rapid comparison of the differences of each technology option. A complete mass and energy balance around the system is presented along with overall efficiency calculations.

8.5.1 Block Flow Diagram and Stream Table

Figure 73 shows the overall block diagram for the Case 10 ION solvent pc combustion plant with CO_2 capture. The figure is accompanied by Table 26, which gives detailed information about the composition, temperature, and pressure of each stream in the system. The block flow diagram does not represent a complete mass balance of the system and is intended as a visual aid for understanding the layout of the power plant.

The system modeled represents a pc power plant with a subcritical steam cycle and a CO_2 capture system. The boiler is wall-fired with primary air and secondary air that represents OFA used to control NO_x emissions. SCR with ammonia injection is used to control NO_x emissions at the boiler exit. A standard pulse-jet baghouse is used for flue gas particulate control. A WFGD with limestone injection is used to control sulfur levels entering the CO_2 capture system. Case 10 ION solvent uses a standard absorber tower and stripper column.

The results show that a coal feed rate of 518,438 lb/hr with a reboiler steam usage requirement of 1,112,770 lb/hr resulted in a plant with a net power output of 550 MW. The flue gas exiting the stack of the plant contained mainly nitrogen and water. Approximately 90% of the CO_2 is captured in the CO_2 capture system, compressed to 2415 psia, and is ready for pipeline transport.

8.5.2 Heat and Mass Balance Diagrams

Diagrams showing the overall heat and mass balance for the power plant are shown in Figures 74 and 75. The heat and mass balance diagrams follow Case 10 of the DOE report very closely, and the numbers for the figures were derived from the models developed in Aspen Plus. The energy balance information is derived from the Aspen Plus models and also estimated based on the modeling effort. The enthalpy reference point for all streams is natural state at 77°F (25°C) and 14.696 psia.

8.5.3 Plant Performance Summary

The addition of CO_2 capture technology to the base plant greatly increases the auxiliary power load; therefore, a bigger overall power plant is needed to produce the 550 MW net of power required for the study. Table 27 shows the overall power plant performance summary for Case 10 ION solvent; Cases 9 and 10 from the DOE report are also included for comparison. The performance of the ION solvent in the model as compared to baseline MEA was based on pilot-scale data. The EERC-modeled Case 10 ION solvent performed significantly better than the DOE-developed Case 10 model. This difference is because of the improved CO_2 capture

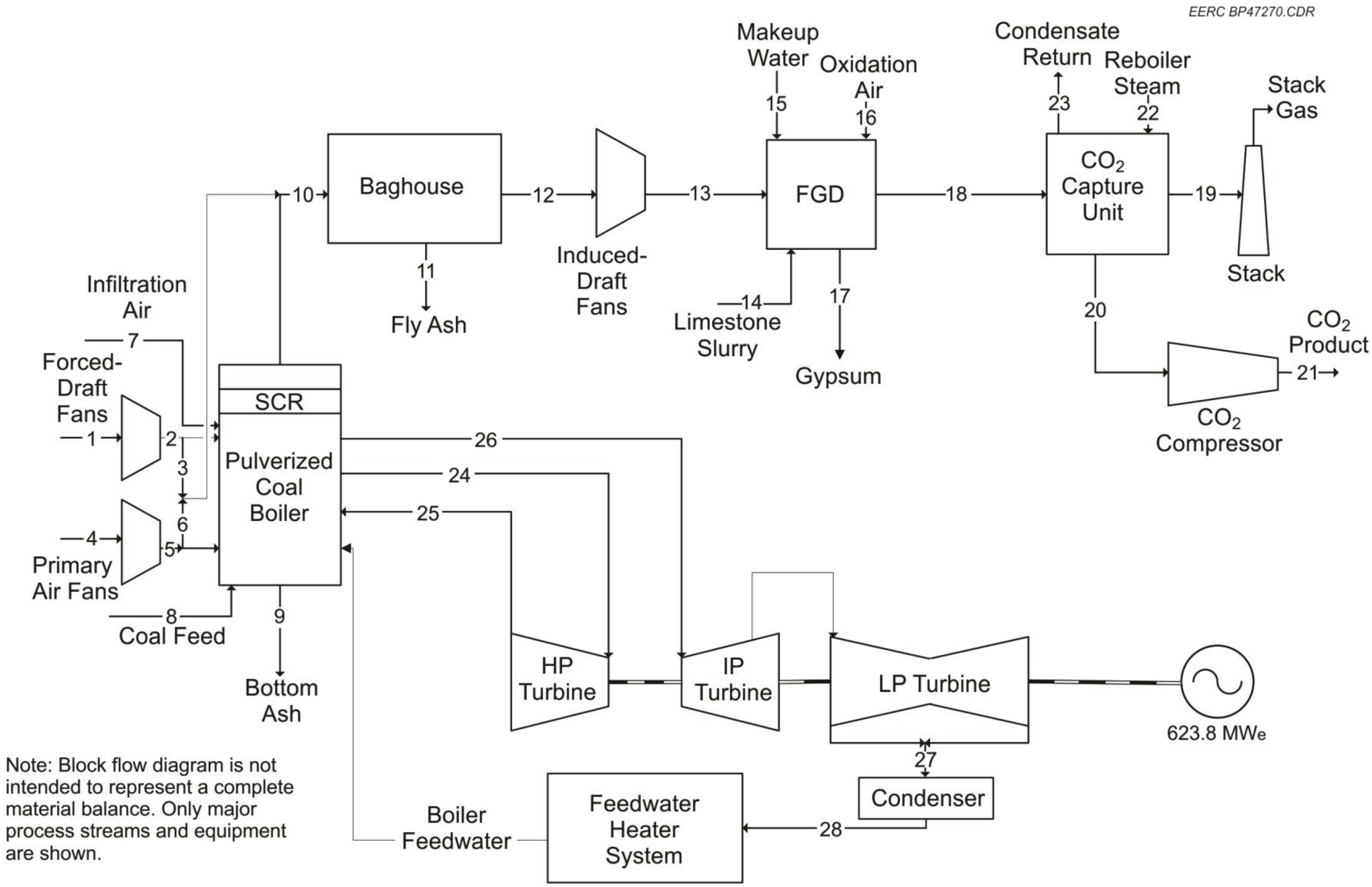

Figure 23. Block flow diagram for Case 10 ION solvent, pc combustion plant with CO_2 capture.

Table 2. Case 10 ION Solvent Stream Table, Subcritical Unit with CO_2 Capture

V-L Mole Fraction	1	2	3	4	5	6	7	8	9	10	11	12	13	14
Ar	0.0092	0.0092	0.0092	0.0092	0.0092	0.0092	0.0092	0.0000	0.0000	0.0087	0.0000	0.0087	0.0087	0.0000
CO_2	0.0003	0.0003	0.0003	0.0003	0.0003	0.0003	0.0003	0.0000	0.0000	0.1453	0.0000	0.1453	0.1453	0.0000
H_2	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
H_2O	0.0099	0.0099	0.0099	0.0099	0.0099	0.0099	0.0099	0.0000	0.0000	0.0884	0.0000	0.0884	0.0884	1.0000
N_2	0.7732	0.7732	0.7732	0.7732	0.7732	0.7732	0.7732	0.0000	0.0000	0.7305	0.0000	0.7305	0.7305	0.0000
O_2	0.2074	0.2074	0.2074	0.2074	0.2074	0.2074	0.2074	0.0000	0.0000	0.0240	0.0000	0.0240	0.0240	0.0000
SO_2	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0021	0.0000	0.0021	0.0021	0.0000
Total	1.0	1.0	1.0	1.0	1.0	1.0	1.0	0.0	0.0	1.0	0.0	1.0	1.0	1.0
V-L Flow Rate, kgmol/hr	61,982	61,982	1836	17,851	17,851	2457	1343	0	0	86,082	0	86,082	86,082	3645
V-L Flow Rate, kg/hr	1,788,519	1,788,519	52,972	51,511	51,511	70,892	38,756	0	0	2,557,685	0	2,557,685	2,557,685	65,666
Solids Flow Rate, kg/hr	0	0	0	0	0	0	0	235,160	4562	18,241	18,241	0	0	28,373
Temperature, °C	15	20	20	15	26	26	15	15	15	170	15	170	182	15
Pressure, MPa, abs	0.10	0.11	0.11	0.10	0.11	0.11	0.10	0.10	0.10	0.10	0.10	0.10	0.11	0.10
Enthalpy, kJ/kg*	–97.5	–92.8	–92.8	–97.5	–86.8	–86.8	–97.5	–	–	–2512.5	–	–2512.5	–2499.5	–
Density, kg/m^3	1.2	1.2	1.2	1.2	1.3	1.3	1.2	–	–	0.8	–	0.8	0.8	–
V-L Molecular Weight	28.856	28.856	28.856	28.856	28.856	28.856	28.856	–	–	29.714	–	29.715	29.715	–
V-L Flow Rate, lbmol/hr	136,646	136,646	4047	39,355	39,355	5416	2961	0	0	189,779	0	189,779	189,779	8036
V-L Flow Rate, lb/hr	3,943,010	3,943,010	116,784	113,562	113,562	156,291	85,442	0	0	5,638,730	0	5,638,730	5,638,730	144,769
Solids Flow Rate, lb/hr	0	0	0	0	0	0	0	518,438	10,057	40215	40,215	0	0	62,552
Temperature, °F	59.0	67.3	67.3	59.0	78.0	78.0	59.0	59.0	59.0	337.4	59.0	337.4	359.2	59.0
Pressure, psia	14.7	15.3	15.3	14.7	16.1	16.1	14.7	14.7	14.7	14.4	14.7	14.2	15.3	15.0
Enthalpy, Btu/lb[a]	–41.9	–39.9	–39.9	–41.9	–37.3	–37.3	–41.9	–	–	–1080.2	–	–1080.2	–1074.6	–
Density, lb/ft^3	0.076	0.078	0.078	0.076	0.081	0.081	0.076	–	–	0.05	–	0.049	0.052	–

[a] Reference conditions are 77°F and 14.696 psia.

Continued. . .

Table 26. Case 10 ION Solvent Stream Table, Subcritical Unit with CO_2 Capture (continued)

V-L Mole Fraction	15	16	17	18	19	20	21	22	23	24	25	26	27	28
Ar	0.0000	0.0128	0.0000	0.0081	0.0097	0.0003	0.0003	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
CO_2	0.0000	0.0005	0.0004	0.1351	0.0163	0.9957	0.9957	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
H_2	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
H_2O	1.0000	0.0062	0.9996	0.1550	0.1324	0.0039	0.0038	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000
N_2	0.0000	0.7505	0.0000	0.6774	0.8132	0.0001	0.0001	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
O_2	0.0000	0.2300	0.0000	0.0234	0.0283	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
SO_2	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
Total	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
V-L Flow Rate, kgmol/hr	14,731	1049	11,066	93,992	78,437	11,496	12,588	21,439	21,439	110,356	101,474	101,474	48,578	67,061
V-L Flow Rate, kg/hr	265,393	30,461	199,362	2,706,867	2,131,798	504,744	552,664	386,241	386,241	1,988,100	1,828,073	1,828,073	875,143	1,208,130
Solids Flow Rate, kg/hr	0	0	41,343	0	0	0	0	0	0	0	0	0	0	0
Temperature, °C	15	181	57	57	53	21	35	300	152	566	363	566	39	39
Pressure, MPa, abs	0.10	0.31	0.10	0.10	0.11	0.16	15.27	0.52	0.52	16.65	4.28	3.90	0.01	1.69
Enthalpy, kJ/kg[a]	–16,007.1	98.4	–	–3111.5	–1385.8	–8956.5	–9185.4	–12,916.3	–15,338.3	–12,506.4	–12,861.4	–12,384.1	–13,517.1	–15,814.7
Density, kg/m^3	1003.1	2.4	–	1.1	1.1	2.9	798.3	2.0	915.0	47.7	15.7	10.3	50.3	993.2
V-L Molecular Weight	18.015	29.029	–	28.76	27.23	43.91	43.91	18.015	18.015	18.015	18.015	18.015	18.015	18.015
V-L Flow Rate, lbmol/hr	32,477	2313	24,397	207,217	172,925	25,345	25,345	47,266	47,266	243,294	223,711	223,711	107,096	147,845
V-L Flow Rate, lb/hr	585,092	67,154	439,519	5,967,620	4,699,810	1,112,770	1,112,770	851,515	851,515	4,383,010	4,030,210	4,030,210	1,929,360	2,663,470
Solids Flow Rate, lb/hr	0	0	91,146	0	0	0	0	0	0	0	0	0	0	0
Temperature, °F	59.0	357.0	135.0	135.0	126.7	69.0	95.0	572.6	306.0	1050.0	686.0	1050.0	101.7	102.5
Pressure, psia	14.7	45.0	14.8	14.8	15.5	23.5	2214.5	75.0	75.0	2415.0	620.5	565.5	1.0	245.0
Enthalpy, Btu/lb[a]	–6881.8	42.29	–	–1337.7	–595.8	–3850.6	–3949.0	–5553.0	–6594.3	–5376.8	–5529.4	–5324.2	–5811.3	–6799.1
Density, lb/ft^3	62.622	0.149	–	0.067	0.067	0.184	49.834	0.124	57.12	2.975	0.982	0.643	3.138	62.005

[a] Reference conditions are 77°F and 14.696 psia.

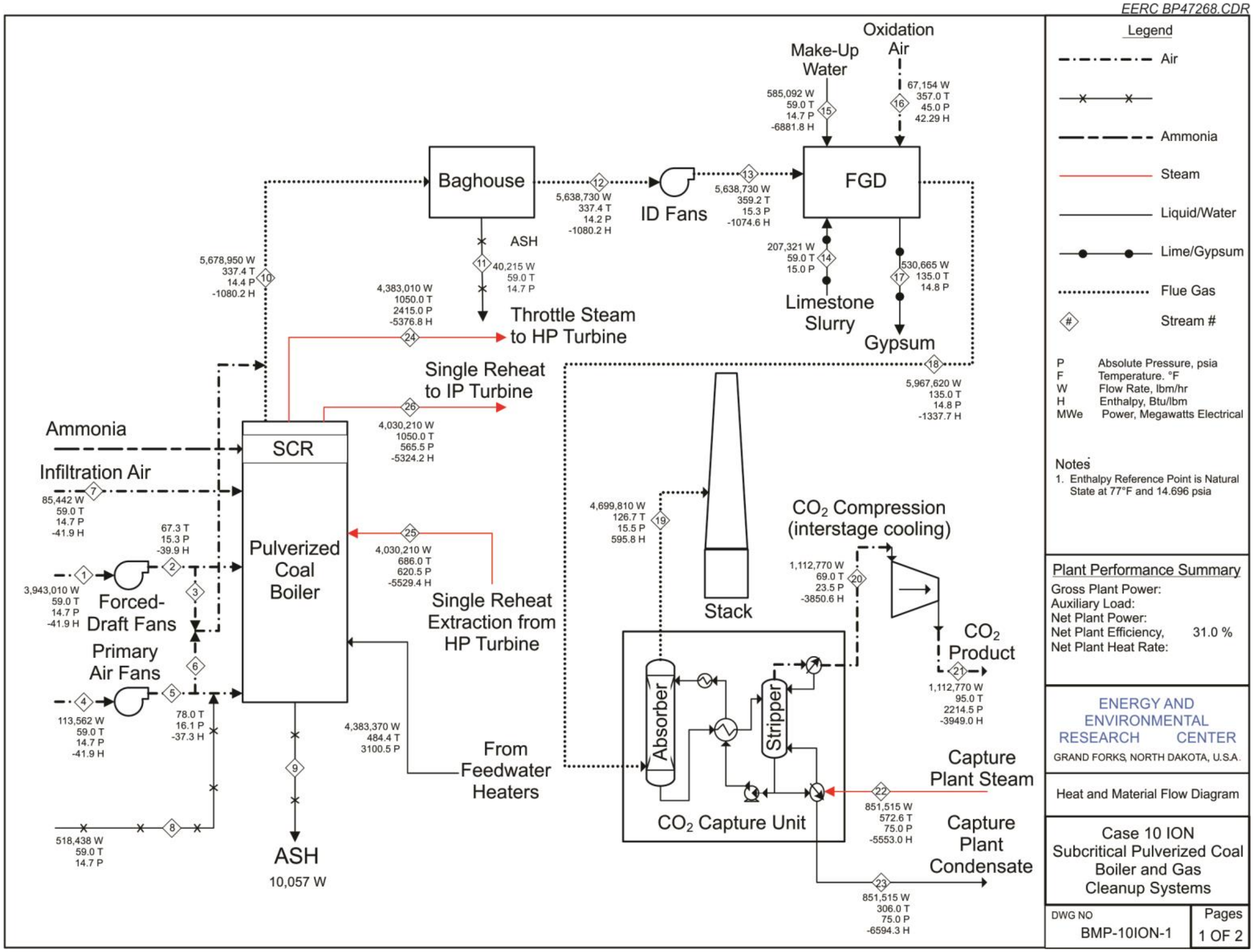

Figure 24. Combustor heat and material flow diagram for Case 10 ION solvent.

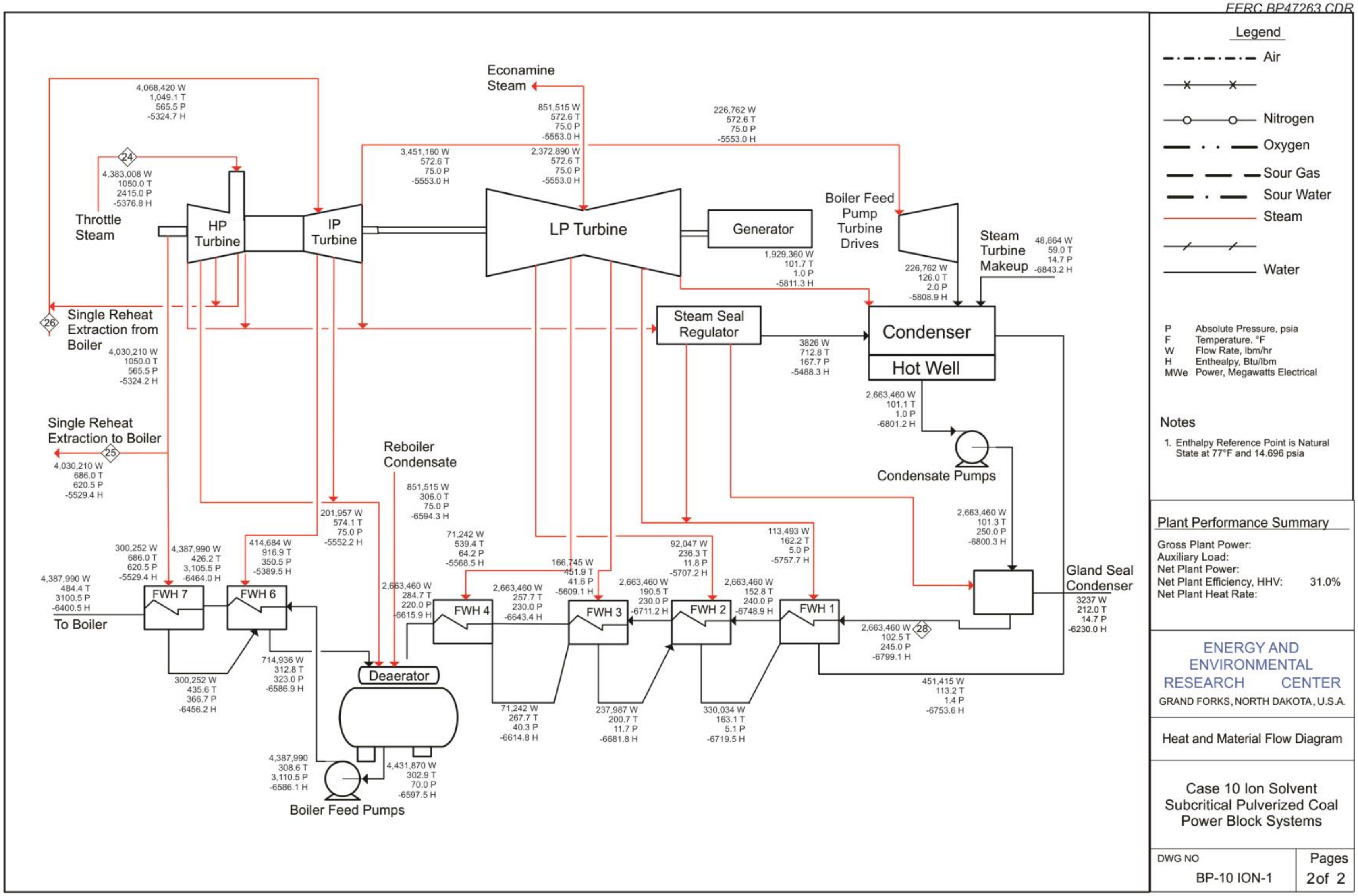

Figure 25. Steam cycle heat and material flow for Case 10 ION solvent.

Table 3. Overall Plant Performance, Case 10 ION Solvent

	Case 9	Case 10	Case 10 ION Solvent
Total (steam turbine) Power, kWe	582,600	672,700	623,772
Auxiliary Load Summary, kWe			
Coal Handling and Conveying	450	540	491
Pulverizers	2970	4180	3522
Sorbent Handling and Reagent Preparation	950	1370	1142
Ash Handling	570	800	675
Primary Air Fans	1400	1,960	1656
Forced-Draft Fans	1780	2,500	2109
Induced-Draft Fans	7540	12,080	9612
SCR	50	70	59
Baghouse	70	100	84
WFGD	3180	4470	3769
CO_2 Capture Auxiliaries	–	22,400	10,223
CO_2 Compression	–	48,790	22,267
Miscellaneous BOP	2000	2000	2000
Steam Turbine Auxiliaries	400	400	400
Condensate Pumps	890	700	803
Circulating Water Pump	5250	11,190	7961
Ground Water Pumps	530	1020	754
Cooling Tower Fans	2720	5820	4135
Transformer Losses	1830	2350	2067
Total Auxiliaries, kWe	32,580	122,740	73,727
Net Power, kWe	550,020	549,960	550,045
Net Plant Efficiency, HHV	36.8%	26.2%	31.0%
Net Plant Heat Rate, Btu/kWh	9277	13046	10996
Condenser Cooling Duty, 10^6 Btu/hr	2432	1928	2202
Consumables			
Coal Feed Rate, lb/hr	437,378	614,994	518,438
Limestone Sorbent Feed, lb/hr	43,410	62,618	62,552
Thermal Input, kWth	1,495,381	2,102,644	1,772,522
Raw Water Withdrawal, gpm	5896	11,224	8328
Raw Water Consumption, gpm	4680	8620	6478

performance of the ION solvent, requiring less liquid flow and regeneration energy. The overall efficiency of the plant was improved by 4.8 percentage points, from 26.2% to 31.0%. This change also results in a slightly smaller overall plant size and, therefore, further reduces the overall energy needs.

The total steam turbine power output for Case 10 ION Solvent is 623.8 MW, which represents a reduction of 48.9 MW over Case 10, with the same net power production of 550 MW. Auxiliary power requirements for the CO_2 capture system and the total output of the steam turbines were modeled in detail using Aspen Plus. The power requirements for some of the smaller systems were estimated based on the information provided in the DOE report. The coal feed rate for Case 10 ION solvent was reduced by about 97,000 lb/hr over Case 10, and this reduction contributes to the overall efficiency increase of the system.

9.0 ECONOMIC EVALUATION – COAL-FIRING

9.1 Description of Aspen Process Economic Analyzer

In order to estimate the impact that process improvements in CO_2 capture technology can have on the economics of a power plant, APEA software package was used. It is a useful project scoping tool that enables engineers to evaluate the economic impact of their process designs. APEA is most valuable in the early phases of conceptual design to compare competing technologies and evaluate alternative process configurations. Models that have been constructed in Aspen Plus for calculating mass and energy balances were imported into APEA for economic analysis.

Once imported, APEA then assigned specific equipment types to each process block from a large database of various real-world components. For example, APEA assigned a floating head shell and tube heat exchanger for the cross heat exchanger in the CO_2 capture model. APEA determined from its database of equipment that this was the most appropriate type based on flow rates, materials, heat-transfer area, and other factors. The software package also estimates the size of the process equipment. For the discussed heat exchanger, dimensions of the tubes and shell were calculated, which included the required thickness of the materials in order to withstand the temperatures and pressure that the heat exchanger would be required to endure. When necessary, the user had the ability to manually revise specific types of equipment, materials of construction, sizes of equipment, and costs.

Operating costs, annual cash flows, and project profitability can be calculated by APEA. Various investment parameters such as tax rates, operator wages, and interest rates; economic life of the project; overhead charges; and others were entered. Raw material and product streams can be specified. APEA's detailed economics module allowed the user to perform interactive economic scenarios for sensitivity analyses. APEA can report key economic metrics, including payout time, interest rate of return, net present value, and income and expenses on changing any economic premise. APEA performed the economic evaluation over a specified time line of the project, from planning phases through the entire life of the process facility.

9.2 Key Economic Assumptions

Because of constraints on resources and time, the entire power plant was not modeled and economically analyzed from scratch. A thorough NETL report, Cost and Performance Baseline for Fossil Energy Plants (33), was referenced to estimate the costs for the majority of the power plant. The cost estimates in the report had a base year of 2007. An inflation adjustment rate of 5.2% was applied to update the base year to 2010. Case 10, pc power plant with Econamine-based CO_2 capture, was used as a baseline for comparisons to an analysis of pc power plants with novel CO_2 capture solvents.

For the new solvents developed for the CO_2 capture plant, APEA was used to estimate the capital and operating costs. Interpolation between Cases 9 and 10 in the NETL report was used to estimate costs for all other areas of the power plant such as the pc boiler, heat recovery steam generator (HRSG), steam turbines, etc. For each case in the report, the plants were variably sized so that the net electrical output of the plant was 550 MW_e. Therefore, the coal consumption rate and equipment costs in Case 10 were greater than Case 9 in order to make up for the steam and electricity consumed in the CO_2 capture plant. Since the novel CO_2 capture solvents analyzed in this report were more efficient than Case 10, the costs fell between Cases 9 and 10. Consequently, a linear interpolation of the costs of the plant based on the coal feed rate that was modeled with Aspen Plus would provide reasonable estimates. The following equation was used for linear interpolation, where *y* was the cost and *x* is the coal feed rate.

$$y = y_9 + (y_{10} - y_9)\frac{(x - x_9)}{(x_{10} - x_9)} \qquad \text{[Eq. 9]}$$

For estimating costs for the new CO_2 capture solvents in APEA, several economic parameters were assumed (Table 28.) In the NETL report, project contingency costs were assumed to be 0% for pc power plant analyses since they are an established technology. However, with the implementation of a novel CO_2 capture solvent, a project contingency of 5% of the project capital cost was assumed.

To estimate the COE, a simplified equation that was a function of total overnight capital (TOC), fixed and variable operating and maintenance costs, capacity factor, and net output was given by the NETL report. All factors in the COE equation were expressed in base year dollars. The base year was the first year of capital expenditure, 2010.

$$COE = \frac{\substack{first\ year \\ capital\ charge} + \substack{first\ year \\ fixed\ operating \\ costs} + \substack{first\ year \\ variable\ operating \\ costs}}{\substack{annual\ net\ megawatt\ hours \\ of\ power\ generated}} \qquad \text{[Eq. 10]}$$

Table 4. APEA Economic Evaluation Parameters

Item	Units	Value
Capital Cost Evaluation Basis		
Project Type		New plant
Plant Location		North America
User Currency Name		Dollars
Time Period		
Period Description		Year
Operating Hours per Period	hours/period	8000
Number of Weeks per Period	weeks/period	52
Number of Periods for Analysis	period	20
Schedule		
Duration of Engineering Procurement Construction Phase	weeks	42
Length of Start-Up Period	weeks	20
Duration of Construction Phase	weeks	15
Capital Cost Parameters		
Working Capital Percentage	percent/period	0
Operating Costs Parameters		
Operating Supplies, lump sum	cost/period	0
Laboratory Charges, lump sum	cost/period	0
User-Entered Operating Charges, as percentage	percent/period	25
Operating Charges, % of operating labor costs	percent/period	25
Plant Overhead, % of operating labor and maintenance costs	percent/period	50
G and A Expenses, % of subtotal operating costs	percent/period	8
General Investment Parameters		
Tax Rate	percent/period	38
Interest Rate	percent/period	7
Economic Life of Project	period	35
Salvage Value, fraction of initial capital cost	percent	20
Depreciation Method		Straight line
Escalation		
Project Capital Escalation	percent/period	3.6
Products Escalation	percent/period	3
Raw Material Escalation	percent/period	3
Operating and Maintenance Labor Escalation	percent/period	3
Utilities Escalation	percent/period	3

$$COE = \frac{(CCF)(TOC)+OC_{FIX}+(CF)(OC_{VAR})}{(CF)(MWH)} \qquad \text{[Eq. 11]}$$

Where:

COE = revenue received by the generator (US$/MWh) during the power plant's first year of operation (expressed in base-year dollars)

CCF = capital charge factor

TOC = total overnight capital, expressed in base-year dollars

OC_{FIX} = the sum of all fixed annual operating costs

OC_{VAR} = the sum of all variable annual operating costs, including fuel at 100% capacity factor

CF = plant capacity factor (85%)

MWh = annual net megawatt-hours of power generated at 100% capacity factor

Other details for the cost-estimating methodology can be found in Section 2.7 of the NETL report.

9.3 Major Equipment List

Cost estimates were provided for each section of the power plant and categorized by account code (Table 29). Details for the major equipment in each account can be referenced in the NETL report. A major equipment list is provided for the CO_2 capture plant (Table 30).

9.4 Economic Results

The cost-estimating methodology described in Section 9.2 was used to calculate the total plant capital costs for the base case with MEA solvent, which was compared to three advanced solvents: Cansolv, Huntsman, and ION. Table 31 shows the total plant cost (TPC) results, which is organized by cost account. The costs for the advanced solvent cases were less expensive than the base MEA case since the CO_2 capture systems were more efficient. Less steam and electricity were required to operate the CO_2 capture plants; therefore, lesser amounts of fuel were required to produce 550 MW of electricity. The overall plant size and equipment costs were correspondingly less. Figure 76 shows the TPC results in graphical form in order to highlight the differences in cost between cases by account code for the four solvents tested.

Table 5. Plant Sections by Account Number

Account No.	Section Description
1	Coal and sorbent handling
2	Coal and sorbent preparation and feed
3	Feedwater and miscellaneous systems and equipment
4	Boiler and accessories
5	Flue gas cleanup
5B	CO_2 recovery
6	Combustion turbine/accessories
7	HRSG, ducting, and stack
8	Steam turbine generator and auxiliaries
9	Cooling water system
10	Ash/spent sorbent recovery and handling
11	Accessory electric plant
12	Instrumentation and control
13	Improvement to site
14	Building structures

Table 6. Account 5B Major Equipment List – CO_2 Recovery

Equipment No.	Description	Type	Design Condition	Operating Quality
1	Absorber tower	Packed		5
2	Cross heat exchanger	Floating head	350°F, 100 psig	5
3	Stripper tower	Packed		5
4	CO_2 compressor	Integrally geared, multistage centrifugal	2000 acfm at 2215 psia	2

Table 7. TPC Results for Each Case Organized by Account Code, costs in US$1000

Acct. No.	Description	MEA	Cansolv	Huntsman	ION
1	Coal and sorbent handling	50,748	48,659	49,135	46,649
2	Coal and sorbent preparation and feed	24,274	23,208	23,451	22,183
3	Feedwater and miscellaneous systems and equipment	100,947	95,572	96,796	90,399
4	Boiler and accessories	346,476	330,834	334,397	315,783
5	Flue gas cleanup	177,456	169,034	170,953	160,929
5B	CO_2 recovery	400,255	318,300	381,492	350,750
6	Combustion turbine/accessories	0	0	0	0
7	HRSG, ducting, and stack	43,526	42,952	43,083	42,401
8	Steam turbine generator and auxiliaries	133,295	130,087	130,817	126,999
9	Cooling water system	65,069	59,550	60,807	54,240
10	Ash/spent sorbent recovery and handling	16,252	15,658	15,794	15,086
11	Accessory electric plant	83,512	76,647	78,211	70,041
12	Instrumentation and control	26,363	25,431	25,644	24,535
13	Improvements to site	16,399	16,018	16,104	15,651
14	Buildings and structures	66,129	65,991	66,023	65,859
	TPC	1,500,701	1,417,943	1,492,707	1,401,505
	TOC	1,909,524	1,773,801	1,849,339	1,757,935

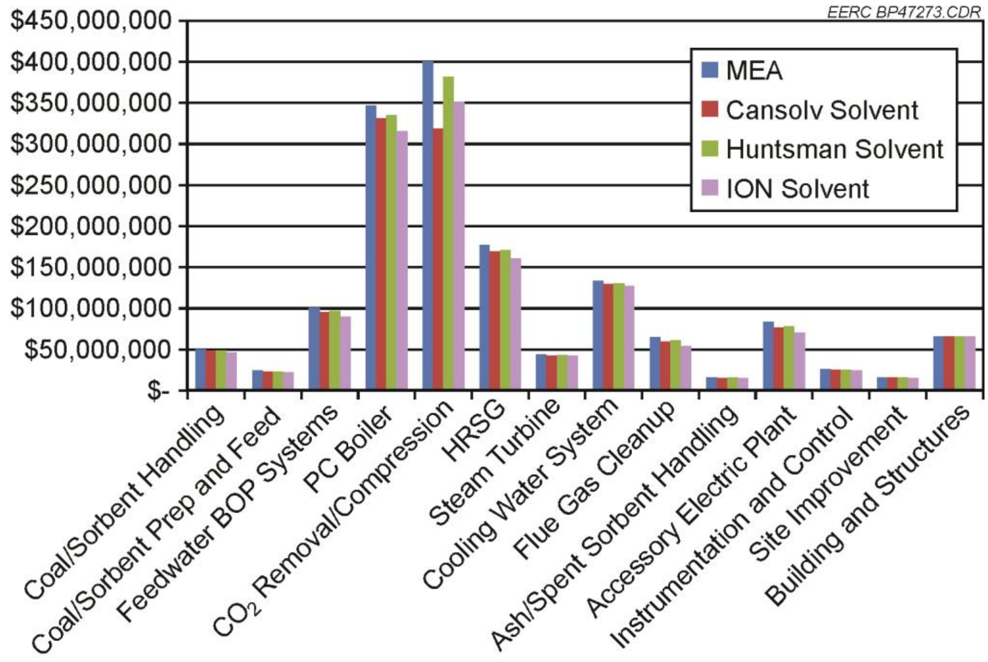

Figure 26. TPC results organized by account code.

The equipment cost of the major components of the CO_2 capture system is given in Table 32. The difference in cost between each case was largely because of the L/G ratio. If less solvent were required per unit volume of gas, then the towers, pumps, and heat exchangers were smaller in size, which reduced equipment cost. The L/G ratios for the advanced solvents were significantly lower than that of MEA. This result was based on the pilot-scale data results and was determined by comparing the capture efficiency at varying solvent flow rates in a fixed-height absorber. Faster kinetics and larger working capacities of these solvents lead to an overall reduction in L/G ratios.

Table 33 lists the estimates for annual operating and maintenance costs for each case, along with the result for COE calculation in US$/MWh. The fixed operating costs included operating, maintenance, and administrative labor along with annual property taxes and insurance costs. Variable operating costs included annual costs for maintenance materials, chemicals, catalysts, and disposal of waste. Fuel was the annual cost of coal, which was assumed to be Illinois No. 6 at a cost of US$47.80 per ton.

Table 8. Amine CO_2 Absorption System Equipment Costs

Item	MEA	Cansolv	Huntsman	ION
Absorber Towers	US$109,849	US$86,330	US$106,942	US$99,742
Pumps	US$6,983	US$3,488	US$5,920	US$4,542
Heat Exchangers	US$41,786	US$21,813	US$36,293	US$28,127
Stripper Towers	US$30,329	US$29,712	US$29,795	US$27,067
CO_2 Compressor	US$33,373	US$33,373	US$33,373	US$33,373
Amine Reclaimer	US$25,000	US$23,000	US$23,000	US$23,000

Table 9. Annual Operating and Maintenance Costs

	Base Plant Case 9	MEA Case 10	MEA EERC	Cansolv	Huntsman	ION
TOC	US$1,155,225	US$2,088,676	US$1,913,839	US$1,746,500	US$1,829,142	US$1,696,785
OC_{FIX}	US$33,724	US$56,240	US$53,153	US$48,489	US$49,551	US$44,000
OC_{VAR}	US$22,174	US$39,445	US$37,077	US$33,499	US$34,314	US$30,056
Fuel	US$77,828	US$109,445	US$105,100	US$98,562	US$100,054	US$92,261
COE, US$/ MWh	US$64	US$108	US$100	US$92	US$95	US$88
ICOE[1], %	NA[2]	69%	57%	44%	49%	37%
US$/ton CO_2 Captured	NA	US$45	US$39	US$32	US$34	US$27

[1] Increase in the cost of the electricity

[2] Not applicable.

The economic modeling included an analysis of DOE’s MEA Case 10, which is based on a basic 30 wt% MEA, which does not include any upgrades to the system based on current technology. The MEA EERC case is based on the EERC’s model, which was calibrated based on the pilot-scale data, showing the improvements from intercolumn cooling and advanced structured packing. The difference between these two cases is shown in Table 33, which shows an overall reduction in COE of US$8/MWh leading to an overall COE for MEA of 57% (based on 2010 US$). This MEA EERC model was then modified based on the pilot-scale data for the remaining solvents. Reductions of both steam and L/G ratio were modified in the model to mimic the pilot-scale results. Table 34 shows the factors that were used for each solvent as based on the pilot-scale data. The factors are based on MEA capture at 90% in the EERC pilot plant.

A wide variety of conditions existed within the pilot-scale results; therefore, it can become challenging to determine an accurate performance factor. This calls for a conservative approach when it comes to deriving such a factor, in order to not overestimate the solvent’s performance. Based on the current results, it is clear that a range of advancements has been shown over that of MEA. Capture costs can be seen to have an overall ICOE as low as 37% to 49%, which is getting close to the DOE’s target of 35%. The results show a cost range of US$27 to US$34/ton of CO_2 captured. Although these cost projections are for a generic plant case, the overall trends should be similar on a specific plant analysis. Several other factors will come into play when these technologies are considered as a retrofit option, such as space requirements and the efficiency of the existing steam turbine. These factors can result in significant increases to the projected costs shown here.

Table 10. Pilot-Scale Derived Performance Factors for Use in Adjusting the Aspen-Based Model

Solvent	MEA EERC	Cansolv	Huntsman	ION
L/G Ratio	1	0.62	1	0.75
Regeneration Energy	1	0.79	0.85	0.57