BENCH-SCALE DEVELOPMENT OF A NON-AQUEOUS SOLVENT (NAS) CO_2 CAPTURE PROCESS FOR COAL-FIRED POWER PLANTS

FINAL SCIENTIFIC/TECHNICAL REPORT

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Dr. Marty Lail, Senior Research Chemist

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Research Triangle Institute

Post Office Box 12194
Research Triangle Park, NC 27709-2194

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Abstract

The project aimed to advance RTI's non-aqueous amine solvent technology by improving the solvent to reduce volatility, demonstrating long-term continuous operation at lab- (0.5 liters solvent) and bench-scale (~120 liters solvent), showing low reboiler heat duty measured during bench-scale testing, evaluating degradation products, building a rate-based process model, and evaluating the techno-economic performance of the process. The project team (RTI, SINTEF, Linde Engineering) and the technology performed well in each area of advancement. The modifications incorporated throughout the project enabled the attainment of target absorber and regenerator conditions for the process. Reboiler duties below 2,000 kJ_t/kg CO_2 were observed in a bench-scale test unit operated at RTI.

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1. Executive Summary

The project aimed to advance RTI's non-aqueous amine solvent technology by improving the solvent to reduce volatility, demonstrating long-term continuous operation at lab- (0.5 liters solvent) and bench-scale (~120 liters solvent), showing low reboiler heat duty measured during bench-scale testing, evaluating degradation products, building a rate-based process model, and evaluating the techno-economic performance of the process. The project team (RTI, SINTEF, Linde Engineering) and the technology performed well in each area of advancement. The modifications incorporated throughout the project enabled the attainment of target absorber and regenerator conditions for the process. Reboiler duties below 2,000 $kJ_t/kg\ CO_2$ were observed in a bench-scale test unit operated at RTI.

Solvent volatility was reduced by modifying the solvent formulation in the first year of the project. A component was added to the formulation to replace an existing component which had a high vapor pressure. The new component has a much lower vapor pressure and has low viscosity. The component switch reduced the volatility of the solvent to below the targeted level of 1 kilopascal.

The solvent was demonstrated continuously for approximately one-hundred hours in a small lab-scale reactor system using simulated flue gas composed of carbon dioxide, oxygen, water, sulfur dioxide and nitrogen. The lab-scale system utilized approximately 0.5 liters of solvent circulated continuously. The demonstration showed that water levels could be balanced by several methods, demonstrated that the solvent was not majorly impacted by exposure to sulfur dioxide, and indicated that the heat duty would be low compared to other state of the art aqueous systems.

Thermal and oxidative degradation testing was performed in the first year of the project by SINTEF in Trondheim, Norway to show that the solvent was stable under typical process conditions. Two solvent formulations and each of their individual components were tested for five weeks to show that the thermal degradation of the non-aqueous solvent was much less than the degradation observed in aqueous systems. Oxidative testing revealed that the amine component of one of the solvents was impacted substantially by oxidative degradation, and this component was removed from further development. Long-term degradation testing (five weeks) was performed by SINTEF in the second year of the project using flue gas which included NO_x, and showed that the overall degradation was lower than the degradation observed in aqueous systems. Long-term testing also indicated that the non-aqueous solvent was less corrosive than aqueous solvent.

A rate-based process model was developed after first building an equilibrium-based model and acquiring the thermodynamic and physical properties of the solvent. The rate-based process model was used to predict process parameters and reboiler heat duties with close correlation to experimental results.

At the end of the project the rate-based model was used to direct bench-scale testing of the solvent system to reach low reboiler heat duties.

Bench-scale testing of the non-aqueous solvent system was performed at RTI and compared to the performance of the aqueous solvent consisting of 30 wt% monoethanolamine. The solvent was demonstrated in conventional process configuration modes as well as modified process configurations designed to optimize the performance of non-aqueous solvents. The demonstration indicated at small scale (approximately 125 liters solvent circulation) that the non-aqueous solvent benefits from inter-stage cooling in the absorber and inter-stage heating in the regenerator. Bench-scale testing at this level indicated that targeted reboiler heat duties of 2 GJ/ ton CO_2 and lower could be obtained using non-aqueous solvents.

A techno-economic analysis was completed using inputs from bench-scale testing and rate-based modeling and shows the non-aqueous solvent process to be competitive over existing state-of-the art aqueous amine processes.

2. Accomplishments

Project Goals and Objectives

The overall objective of this bench-scale project is to continue the advancement of the Non-Aqueous Solvent (NAS) CO_2 Capture Process by addressing and overcoming specific challenges facing the technical and economic potential of this process. The ultimate goal is to demonstrate the feasibility of the NAS CO_2 capture process at the bench-scale and evaluate its potential to substantially reduce the thermal regeneration energy associated with the capture of CO_2 from flue gas — a key criterion for achieving DOE's Carbon Capture Program's goal of >90% CO_2 capture with a 95% CO_2 product purity at a cost of < \$40/ton CO_2 captured by 2025. The following objectives by Budget Period have been identified in order to achieve the above performance goals.

Budget Period 1:

- Minimize solvent losses and make-up costs by
  - advancing the solvent formulation with respect to solvent cost and vapor pressure while maintaining critical performance criteria, including a high CO_2 working capacity at process conditions and
  - demonstrating that the NASs are not susceptible to severe degradation with exposure to common flue gas contaminants (i.e., H_2O, O_2, SO_2, NO_x) at envisioned process conditions and develop a characterization method to speciate and quantify the degradation products.
- Collect key experimental data for the best-candidate NAS(s), including CO_2 isotherms and heat of CO_2 absorption measurements spanning the operating range of the full-scale process and physical properties, including viscosity and foaming tendency.
- Develop framework and collect equilibrium data to support the development of a process model for the NAS process.
- Improve the fidelity of the process design specifically by developing a NAS Recovery/ Wash Section and developing a regenerator design specifically for NASs.
- Revise and maintain the Project Management Plan (PMP).
- Conduct overall project management reporting.
- Prepare and submit Budget Period 2 (BP2) Continuation Application.

Budget Period 2:

- Bench-scale evaluation of the NAS CO_2 Capture Process to

  - experimentally demonstrate that the NASs are capable of achieving 90% CO_2 capture and generating a high-purity CO_2 product (>95% CO_2) at an “optimal” L/G ratio as determined from process modeling with a 30%–50% reduction in the thermal regeneration energy compared to aqueous-amine processes;
  - evaluate the effectiveness of the process improvements/modifications, including the addition of an NAS Recovery/Wash section and a novel Solvent Regenerator design specific for NASs; and
  - develop a detailed understanding of the operational and performance differences between the NAS and conventional aqueous-amine CO_2 capture processes.
- Perform a rigorous solvent degradation study to estimate the rates of solvent degradation and determine the degradation pathways. Information will provide data to estimate the rate of solvent degradation for the commercial-scale process [kg solvent/1,000 kg CO_2 captured] and assist in determining the allowable contaminant levels in the flue gas and thus define the necessary flue gas cleanup requirements upstream of the CO_2 capture process.
- Conduct a detailed Techno-Economic Analysis (TEA) to understand the process’s potential to integrate with and substantially reduce the cost associated with CO_2 capture from coal-fired power plants.
- Prepare a Technology Environmental Health & Safety (EH&S) Risk Assessment to understand the potential risks associated with the process and novel solvents.
- Revise and maintain the Project Management Plan (PMP).
- Conduct overall project management reporting.

The Project Milestone Status Report, Table 1, was developed to monitor technical progress toward these objectives. A summary of the progress toward each active milestone is reported in the ‘Comments’ section of the table and more detailed descriptions of activities and accomplishments towards each of the active tasks is provided in the following section. All milestones were achieved by the end of the project and the NAS solvent technology appears promising for larger scale demonstrations in the future.

Table 1. Milestone Status Report

Milestone Description	Planned Completion Date	Actual Completion Date	Verification Method	Comments
A. Updated Project Management Plan	10/31/2013	10/31/2013	Project Management Plan file	PMP was completed and agreed to by Recipient and NETL. File was provided to Project Officer and is used as the ACTIVE PMP.
B. Kick-off Meeting	01/31/2014	01/31/2014	Presentation file	On-site Kick-off Meeting occurred on 01/10/2014. Presentation for public release was provided to Project Officer on 01/31/2014.
C. Finalize selection of NAS formulations based on the following performance criteria: ***Minimum Thermal Regeneration Energy:*** *<2,100 kJt/kg CO_2 as predicted by the “short-cut” method* ***NAS Vapor Pressure:*** *<1 kPa at 40°C* ***NAS Cost:*** *<\$50/kg* ***Viscosity:*** *<40 cP* ***Foaming Tendency:*** *Low* Health Rating: 3(≤MEA)	09/30/2014	12/31/2014	Quarterly Report #5	Milestone achieved in Q5. A NAS formulation was finalized which meets/exceeds all performance criteria except cost. Currently the cost of the solvent is ~\$90 kg. ***Minimum Thermal Regeneration Energy:*** *2,000 kJt/kg CO_2* ***NAS Vapor Pressure:*** *~0.3kPa at 40°C (abs. conditions)* ***NAS Cost:*** *~\$90/kg* ***Viscosity:*** *26.2 cP* ***Foaming Tendency:*** *Low* Health Rating: 2
D. Lab-scale demonstration that NAS Recovery System achieves: - NAS emissions < 10 ppm in treated gas - Separable NAS stream from wash section to be recycled to process	12/31/2014	02/15/2015	Quarterly Report #6	Lab-scale testing of the refined NAS solvent was completed in Q6. Emissions of NAS were shown to be less than 10 ppm.
E. Design package and cost estimate for the Bench-scale system modifications complete.	12/31/2014	03/31/2015	Quarterly Report #6	The design package for an absorber wash section was completed based on lab-scale testing results.
F. Complete installation/integration of new process units into bench-scale system. Verification: Initiation of bench-scale system commissioning.	06/30/2015	06/30/2015	Quarterly Report #7	Process upgrades were added to the bench-scale test unit in Q7. The bench-scale test unit was commissioned using aqueous and non-aqueous solvents.
G. Effectiveness of Bench-scale system modifications verified.	09/30/2015	09/30/2015	Quarterly Report #8	The BsTU was operated with NAS and demonstrated 90% capture of CO_2 from simulated flue gas.
H. Experimental data from bench-scale testing confirming that the NAS process is capable of achieving target regeneration energy [< 2,000 kJ_t / kg CO_2 at 90°C and > 200 kPa CO_2]	06/30/2016	06/30/2016	Quarterly Report #11	More than 100 hours of bench-scale testing was completed in Q11 using wet flue gas. Water balancing in the BsTU using NAS solvent was successful. Reboiler heat-duties <2,000 kJ_t/kg CO_2 were observed at >200 kPa CO_2 pressure in the regenerator.
I. Completed technical, economic, and EH&S assessments	06/30/2016	06/30/2016	Topical report	A techno-economic evaluation based on an experimentally-verified, rate-based, Aspen model was performed showing increase in cost of electricity (excluding TS&M) of \$46.97/ ton CO_2. An EH&S assessment was performed in collaboration with Linde for the NAS solvent.

3. Major Activities, Results, Discussion, and Conclusions

Budget period 1 activities include:

Task 1: Project Management and Planning

Task 2: Refining Solvent Formulation to Minimize Make-up Costs

Task 3: NAS Model Development

Task 4: NAS CO_2 Capture Process Development

Budget Period 2 activities include:

Task 5: Construction and Testing of Upgraded Bench-Scale System

Task 6: Solvent Degradation Studies

Task 7: Process Modeling

Task 8: TEA and Technology EH&S Assessment of a Commercial NAS CO_2 Capture Process

A summary of progress made in each of these areas is given below.

Task 1.0 – Project Management and Planning

This task addressed activities for the Recipient to coordinate, manage and plan project activities that included monitoring and controlling of project scope, technical, budgetary and scheduling activities, project and task planning, asset management, cost tracking, progress reporting and updating National Environmental Policy Act (NEPA) documentation throughout the project period of the award as necessary. Coordination and planning has been conducted with DOE and project team members. RTI revised and maintained the Project Management Plan (PMP) over the course of the project in order to reflect changes in the schedule, risk, resources, key technical drivers, technical approach, risk, etc. as needed throughout the project.

During BP1 the project kickoff meeting, drafting and updating the project management plan, and presenting at conferences were accomplished. The project meeting was held in January 2014 after contracting was completed with project team members. The project management plan was drafted and agreed upon by the project team early in BP1. The project management plan was updated twice during BP1 for the requests of two three-month no-cost extensions. No cost extensions were requested during BP1 for the following reasons.

1) a longer than anticipated sub-award negotiation with our industrial partner, Linde
2) a longer than anticipated time to refine the solvent formulation
3) unexpected issues related to an analytical instrument which was planned for use in a lab-scale demonstration
4) the addition of SINTEF as a team member to perform a solvent degradation study

As a result of the delays, the completion of BP1 work was delayed by six months. The no cost extension requests were discussed with DOE and carefully administered to insure that all the work was being done and that sufficient technical progress was being made. In December of 2014 a presentation was given to NETL updating the team on the progress of the project in preparation for evaluation of the continuation application. The project met all the technical milestones which were set at the beginning of BP1 and was on budget. A continuation application for BP2 was submitted in February of 2015 during the second no cost extension period and was approved. In April of 2015 BP2 commenced with no delay in project activities or progress.

In February of 2016 a third three-month no-cost extension was requested to extend the period of performance through June 30, 2016. The no-cost extension was needed to complete large-scale testing of the NAS process in the bench-scale test unit at RTI with project partner Linde. Bench-scale testing and all remaining project tasks were completed by June 30th in accordance with the third extension.

RTI presented at three NETL CO_2 Capture Technology conferences during the project and a Gordon Research Conference in the spring of 2015. One manuscript was published in Energy Procedia in 2013.

Task 2 - Refining Solvent Formulation to Minimize Make-up Costs

Task 2.1 – NAS Component Selection Refinement

The main objective of this task was to drive down the cost of the NASs (make-up costs) by identifying suitable organic diluents with low-cost, low-vapor pressure, and low rates of solvent degradation. The formulations must maintain the critical performance characteristics of high working capacity at process conditions, low heat of absorption, low water solubility, low heat capacity, low viscosity, and low health rating. The overall goal was to refine the NAS formulations such that the following criteria are met:

- Minimum Thermal Regeneration Energy: <2,000 kJt/kg CO_2 as predicted by the “short-cut” method
- NAS Vapor Pressure: <1 kPa at 40°C (abs. conditions)
- NAS Cost: <\$50/kg
- Viscosity: <40 cP

- Foaming Tendency: Low
- Health Rating: 3(≤MEA)

All the objectives were successfully achieved in BP1 except for the cost target. However, in BP2 the cost of the solvent decreased further as quotations for larger quantities were received from manufacturers. Currently the costs of the NAS refined formulations are approximately \$36.50/kg. The main contributor to the cost is currently one of the diluent components, which contributes ~\$22/kg to the cost of the solvent. The other components (diluent and amine) amount to ~\$14.50/kg towards the cost. We anticipate the cost of the amine to decrease further as larger volumes are purchased for future scale-up. The properties of the refined solvents are given in **Table 2** below.

Table 2. Properties of refined NAS solvents.

Criteria	**Target**	**NAS**
Vapor Pressure [kPa] @ 40°C	< 1	0.3 (Estimated)
Water Content [wt%]	<10	7.26
Viscosity [cP] CO_2-rich at 40°C	< 40	< 30
Foaming Tendency	Low	Low
Cost [\$/kg]	< 50	36.50
Health Rating	≤ 3 (≤MEA)	2
Min. thermal regeneration energy* [kJt/kg CO_2]	<2,000	2,000

In BP1 we completed solvent refinement and arrived at a solvent formulation which has all of the physical properties needed to meet the performance requirements of a NAS process. This was accomplished after insights about the heat of reaction became evident in calorimetry data which was obtained during Q5.

At the beginning of BP1 the major challenge was to reduce the volatility of one of the solvent components from our earlier work with ARPA-E. In doing so we identified a substitute for the volatile component, which had a much lower vapor pressure, well below the vapor pressure of the amine itself. Use of the diluent component was satisfactory in terms of viscosity, hydrophobicity, cost, and commercial availability.

Additional studies on the formulation while varying water content revealed that water increases the heat of absorption of the refined non-aqueous solvent formulation and will probably need to be kept below 10 wt% in the process, but in Q6 we have observed that the water content of the solvent can be managed by process conditions and has some beneficial effects with respect to CO_2 loading during regeneration. The solubility of the CO_2 product (carbamate) does not pose a problem for the new refined solvent nor does volatility. Hence, we believe the solvent formulation is sufficiently refined to move forward to demonstration at larger scales.

Task 2.2 NAS Lab-scale Evaluation

The lab-scale gas absorber system was completed in BP1 and was used to demonstrate promising solvent formulations and prove process modifications at the lab-scale (0.5 liters). A photo of the LsGAS is shown in Figure 1.

Figure 1. LsGAS equipped with regenerator feed splitting section.

An aqueous solvent composed of 30%wt MEA-H_2O was used to collect baseline operational data for the LsGAS. Simulated flue gas containing 13.3% CO_2, 8% H_2O, and balance N_2 was fed at 3 SLPM to the absorber column. The solvent was circulated at 23-24 g/min, corresponding to an L/G ratio of 5.7-6. Selected measurements during MEA-H_2O commissioning run are shown in Figure 2 and Figure 3. The pressure drop across absorber column, shown in Figure 2, gradually increased as the CO_2 loading of the solvent increased and stabilized once steady state was reached. At steady state, the CO_2 concentration at the absorber outlet was found to be 2-2.3%, corresponding to about 83-85% capture efficiency. Temperature profiles (see Figure 3) for the absorber and regenerator sumps, regenerator column, solvent returning to absorber and gas leaving absorber were all relatively stable during the commissioning run. In summary, the commissioning run using MEA solution was completed without issue.

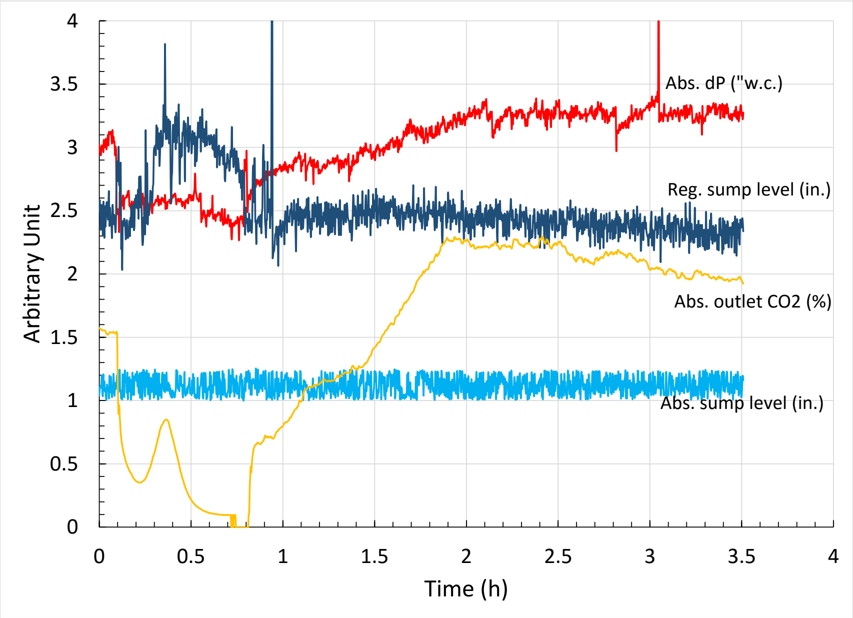


Figure 2. CO_2 concentration profile, lump levels, and pressure drop across absorber during MEA-H_2O commissioning run.

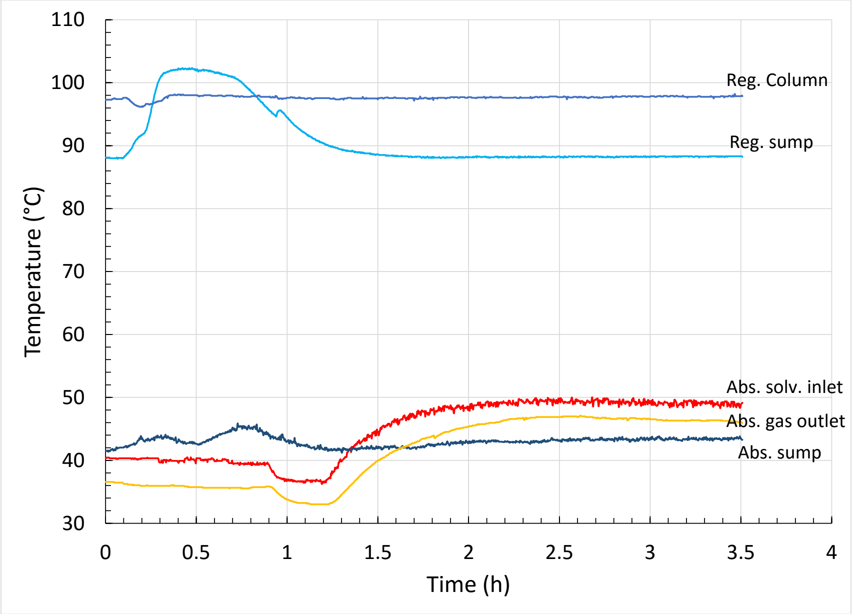


Figure 3. Temperature profiles at various process locations during MEA-H_2O commissioning run.

In Q5 we completed several tasks with NAS using the LSGAS. One was demonstrating the stable operation of a non-aqueous solvent at 90% capture efficiency, water balanced, and stable process measurements for 100 h. The data for this is shown below in Figure 4. As is shown, the system was operated for approximately 100 hours with stable CO_2 capture efficiency. The system was able to maintain the CO_2 capture efficiency between 88-90%. The gradual decrease in CO_2 efficiency was due to the evaporative loss of amine component through both absorber and regenerator off-gases. Fresh amine was added on a daily basis (i.e., at 26, 44, 68, and 91 h) to the system to increase the amine content and maintain the capture performance. This indicates the importance of a solvent recovery/wash section. With the installation of the wash section, we expect that the evaporative loss of amine will be substantially reduced, hence, improving the system stability and reducing the operation cost for solvent makeup.

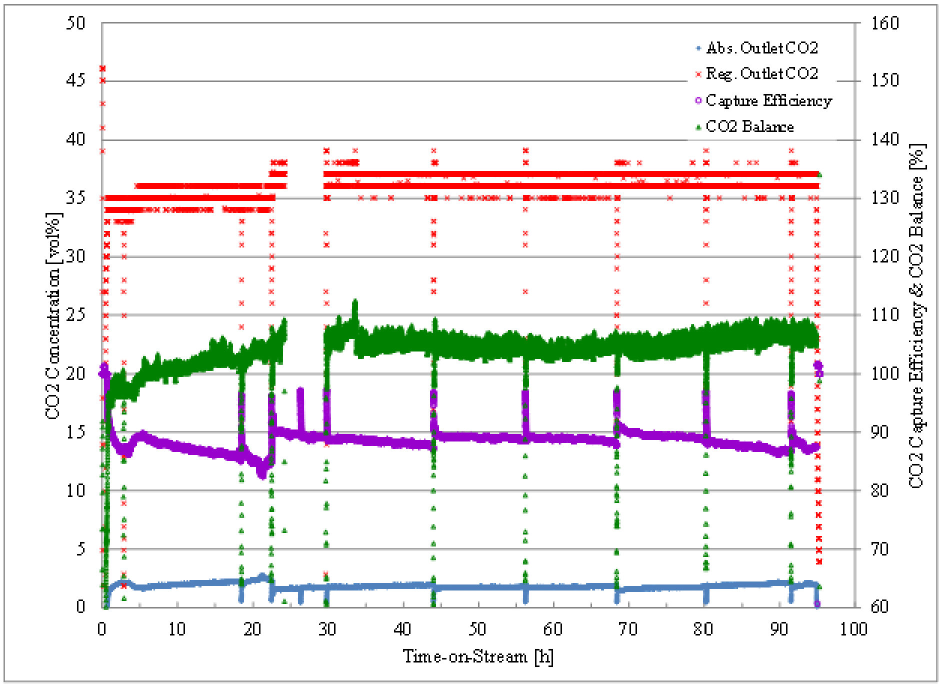


Figure 4. *CO_2 concentration profiles at the absorber and regenerator outlets, capture efficiency and CO_2 balance during 100 h of operation.*

The water balance of the system was monitored throughout the demonstration and is shown in Figure 5. CO_2-rich solvent from the absorber sump showed 5-6 wt% of water while CO_2-lean solvent from the regenerator consistently showed a higher water content in the 6-8 wt% range. The higher water content observed in the CO_2-lean solvent from the regenerator is most likely due to the change in molecular weight between the rich and lean solvent. It should be noted that upon the visual inspection of the regenerator sump (maintained at 105-110 °C) during the long-term testing, the water phase was formed as a small globule at the bottom of the sump while the absorber sump showed only a homogenous NAS phase. Overall, the water balance of the system agrees well and a detailed discussion was given in the Q5 report.

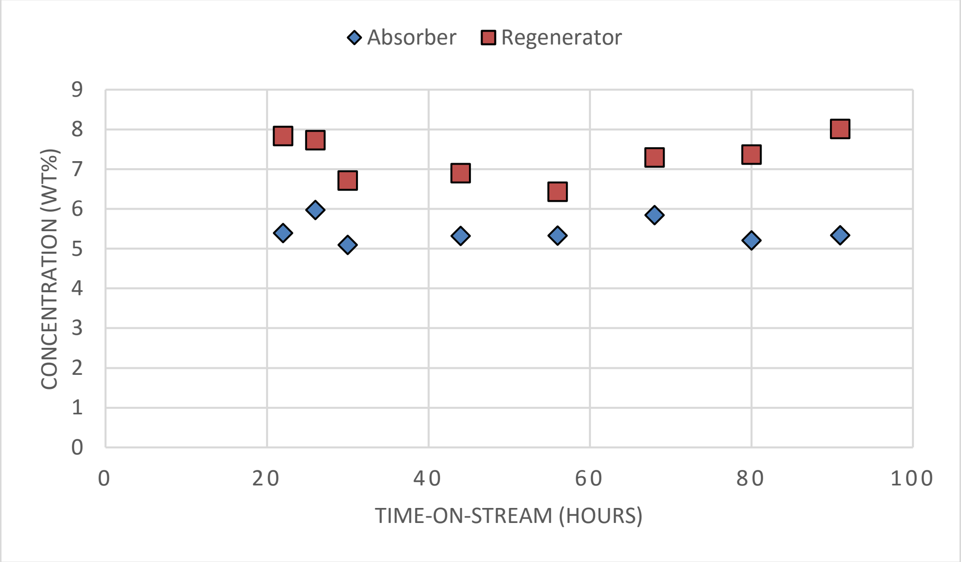


Figure 5. *H_2O content in NAS solvent from absorber and regenerator sumps during 100 h operation.*

A water wash section was incorporated into the LsGAS in Q5 to treat the absorber outlet off-gas which contains solvent volatiles. Though the evaporative loss of the solvent is not expected to be significant due to its low vapor pressure, the solvent loss through the high gas volumetric flow from the absorber side will require some solvent make up. In addition, the emission of the solvent cannot exceed environmental limits. It is a common practice in gas separation industries to install a scrubber unit to reduce emissions and recuperate some of the operating cost via solvent recovery.

A schematic of the wash section is shown in Figure 6 below along with a photo showing the incorporation into the LsGas. The absorber off-gas is temperature controlled and fed through a wash column, CL-400, at the bottom and leaves the wash section at the top of CL-400. The wash column consists of a standard borosilicate glass packed-bed gas absorption column 4 feet in length and 19 mm in diameter positioned on top of a 250 mL borosilicate, tapered wall flask. The absorption column was packed with approximately 200 grams of 0.16 in.^{2} Pro-Pak® protruded metal packing; a high-efficiency, lab packing material. Water is circulated from the wash section sump V-400, located at the bottom of CL-400, through a manually controlled pump P-400 and sprayed down from the top of CL-400. The temperature of the scrubbing water is also controlled. CL-400 is also equipped with heat rope in the case of operating the wash column at elevated temperature is required. The sample gases from the absorber off-gas prior to entering and leaving the wash section can be selected and fed to the GC via 3-way solenoid valve to determine the solvent concentration in these gas streams.

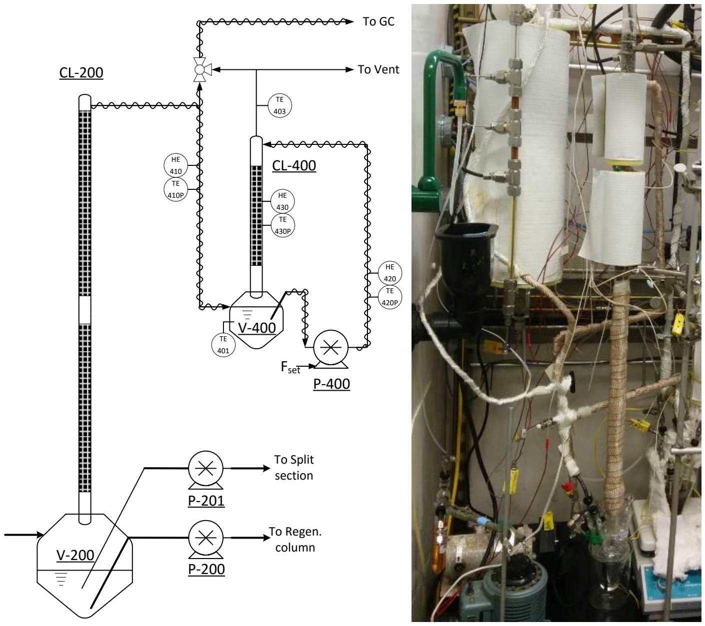


Figure 6. Simplified process diagram of LsGAS absorber wash section (Left) and actual installation on the system (right).

When the wash section was operated in Q5, RTI was not able to achieve amine emissions below 10 ppm. However, scrubbing water samples were collected every 2 h to determine the amine content in the liquid phase during the run and it was noted that the A1 concentration in the scrubbing water was far from the saturation point at 40 °C. This indicated that the scrubbing efficiency could be improved by increasing the contact time between the off-gas and scrubbing water to achieve the target emission of lower than 10 ppm. As a result, an additional 30 cm section of packing was installed in the wash section to increase the gas-liquid contact time.

A parallel development in the solvent formulation also led to an improved version of the solvent in which a weak acid component was added to lower the heat of absorption. The weak acid is hypothesized to participate in the CO_2 absorption mechanism in conjunction with the amine component with advantages of lowering the heat of absorption together with a reduction in the amine loss. The improved solvent was loaded into the LsGAS and the system was run under the standard operating conditions. The scrubbing water circulation rate was increased from 30-31 to 35-36 g/min during this test run. The GC sampling lines from the wash section were also rearranged to reduce the artifact in the concentration reading caused by the liquid droplets. Figure 7 shows the concentration of amine in the gas entering and leaving the wash section during the run. Under equivalent temperature (40 °C) and gas flow rate in the absorber, the average amine concentration entering wash section was at 20 ppm, significantly lower than that observed previously. The amine concentration rapidly dropped while passing through the wash section and remained in nondetectable range at the wash section exit after 1 h of switching the sampling valve to monitor the wash section outlet gas. This suggests that the current configuration of the wash section is effective for scrubbing NAS amine components in the absorber off-gas to low levels.

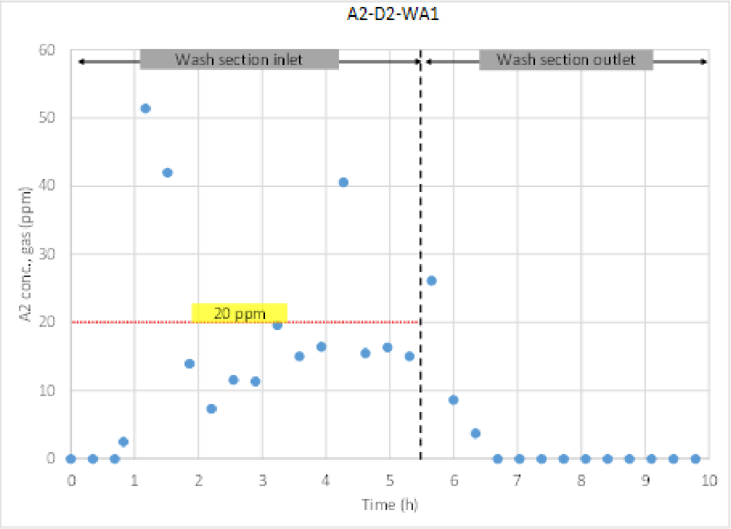


Figure 7. Concentration profile of amine in the wash section inlet and outlet during LsGAS run.

Task 2.3 – Initial Degradation Study

Thermal Degradation

The goal of this task is to observe thermal and oxidative degradation of the non-aqueous solvent formulations. The thermal and oxidative degradation studies were conducted by SINTEF Materials and Chemistry Department in Trondheim, Norway. In Q5 SINTEF started the study and completed it in Q6. Findings from the study are discussed below.

Solvent components consisting of amines A1 and A2, diluents D2 and WA-1, and monoethanolamine (MEA) have been used to make solvent formulations A1-D2, A2-D2, and A2-D2-WA-1 for thermal degradation study. The study of five total systems was conducted consisting of studies of each individual component (A1, A2, and MEA) and the formulations themselves (A1-D2, A2-D2, and A2-D2-WA1). Results are given in Figure 8 below.

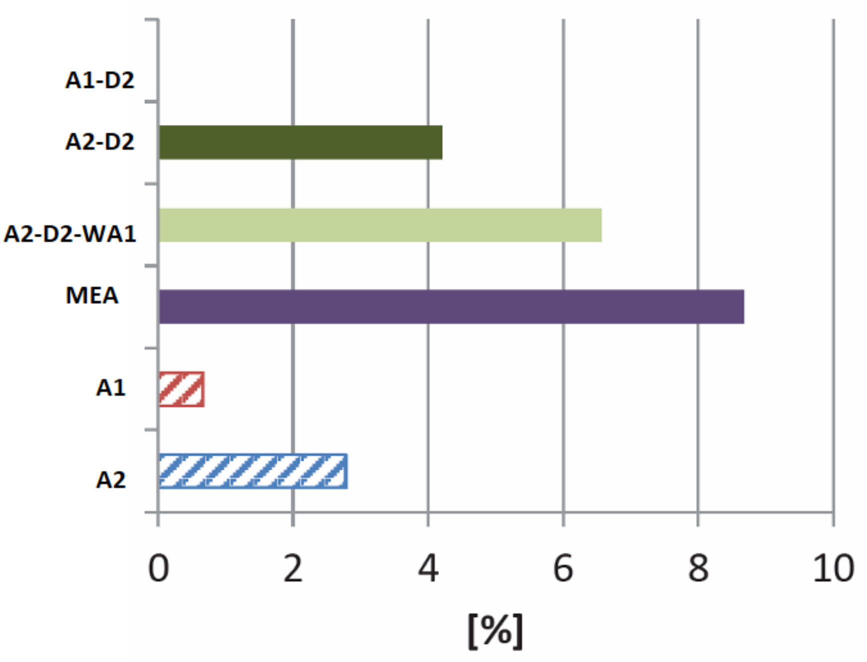


Figure 8. Thermal degradation results based on LC-MS comparing NAS formulation and NAS amine components to MEA.

The thermal degradation experiments were conducted in stainless steel cells of total volume approximately 27 mL. Each cell is first purged with nitrogen, then loaded with approximately 15 mL rich amine solution or solvent component. After additional nitrogen flush the cells are sealed then placed in a forced convection oven at 110°C for five weeks. The solutions were analyzed weekly by LC-MS. In addition the density, CO_2 content, alkalinity, and metals content (by ICP-MS) were also measured.

The results show that all three of the NAS formulations undergo low degradation under these conditions. A1-D2 showed notably low thermal degradation, which was somewhat better than A2-D2 or A2-D2-WA1. Neat A1 was more stable than neat A2, and all compared favorably to pure MEA. Ureas were identified as one of the degradation products found in the NAS solvents. The most prevalent degradation product observed in aqueous amine systems is carbamate cyclization to oxazolidone and this was not observed for NAS solvents.

Metals Content

Metals content (iron, nickel, and chromium) of the solutions was also measured during the course of the five week thermal experiments. Metals content was measured by ICP-MS, and results showing the iron content at the end of five weeks for all six solutions are shown in Figure 9. Measurements of chromium and nickel followed the trend shown in Figure 9 but were over the range of 0-50 mg/L rather than 0-500 mg/L. A promising trend is observed for solvents which incorporate diluent D2, all of which show iron concentrations which are more than an order of magnitude lower than MEA. In the case of A2, which as a pure component without dilution shows a relatively high final concentration (~335 mg/L), the concentration of iron is substantially reduced when A2 is diluted with D2 (~10 mg/L). A promising trend is also observed for the NAS amine component A1, which even as a pure amine component, showed a low iron content of ~30 mg/L.

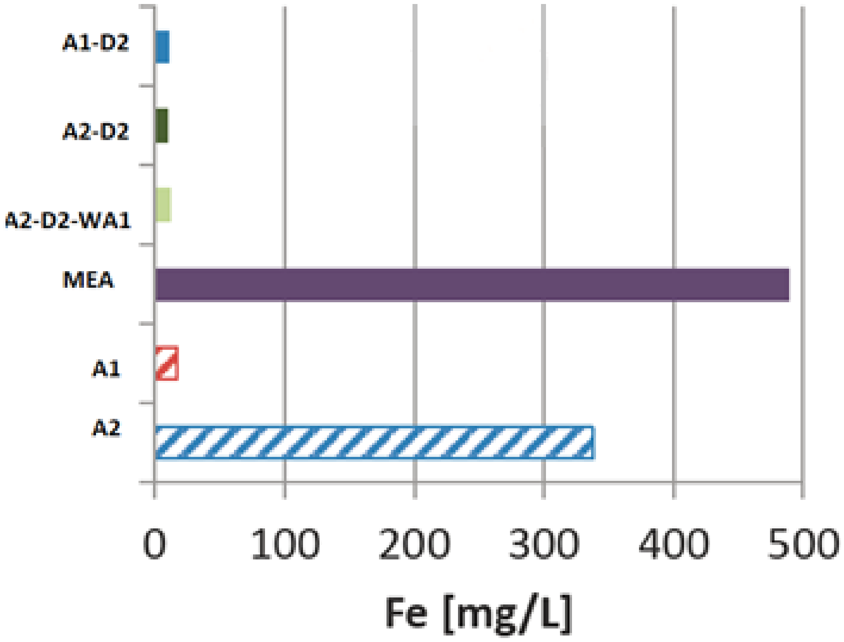


Figure 9. Comparison of iron content of NAS solvents, pure NAS amine components, and MEA.

Oxidative Degradation

Oxidative degradation testing was conducted on NAS solvents A1-D2 and A2-D2-WA1. The testing was performed using an apparatus shown in Figure 10 below. Reaction gas consisting of humidified air with 2 vol% CO_2 was purged continuously through the reactor at a flow rate of approximately 250 mL/min. The main reaction vessel has a thermostatic jacket which was connected to a water bath maintained at 50°C. All solvents were preloaded with CO_2 to a loading of 0.3 mol CO_2/mol amine prior to the experiments.

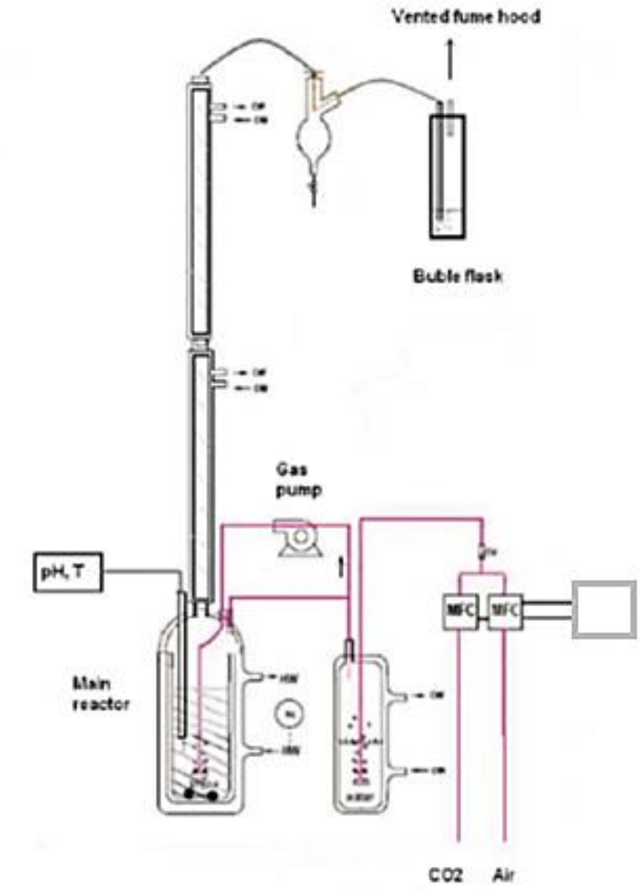


Figure 10. Diagram of apparatus used for oxidative degradation of NAS solvents.

The solvent system consisting of A1-D2 performed well under accelerated oxidizing conditions. A small amount of degradation was observed, both visually by a color change of the sulfuric acid solution in the bubble flask above the main reactor as well as by monitoring the concentration of all formulation components by LC-MS over the course of the experiment. The degradation of the amine component A1 is shown in Figure 11 below. The overall loss as measured by LC-MS is ~10%. This is comparable to losses observed for MEA. In addition to measuring amine concentration by LC-MS, the concentration of CO_2, density, alkalinity, and nitrogen content of the system was measured at the start and at the end of the experiment and were consistent with LC-MS results.

At the beginning of the experiment the CO_2 loading was measured to be 0.62 moles CO_2/ kg or approximately 0.27 mol CO_2/ mol A1. This is a little more than half of the total working capacity of the solvent, and represents a loading that is likely to be found in the absorber as the solvent flows down through the packing. The density of the solvent was measured to be 0.97 g/mL and the concentration of the amine by alkalinity was 2.31 mol/kg.

At the end of the experiment (after 500 hours continuous testing) the parameters were checked again. The amount of CO_2 was 0.16 mol CO_2/ kg, much lower than the initial loading despite having 2 vol% CO_2 in the purge gas. This is the equivalent of approximately 0.08 moles CO_2 per mole amine by the end of the experiment, and could be explained by the vapor liquid equilibrium loading of the solvent at 50°C. Though the vapor liquid equilibrium for A1-D2 has not been measured at 50°C, its capacity at CO_2 partial pressure of ~2 kPa is anticipated to be slightly higher than this result would indicate. There could some error associated in applying an aqueous CO_2 titration method to NAS. The concentration of the amine at the end of testing was 2.04 mol/kg, and the density was approximately 0.96 g/mL.

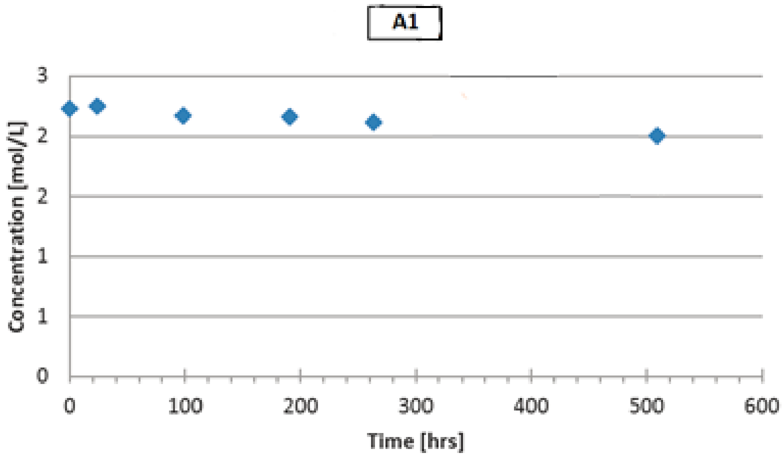


Figure 11. Concentration of NAS amine component A1 as a function of time under accelerated oxidizing conditions.

The nature of the components leaving the system and causing the color change observed in the sulfuric acid trap and downstream water-bubbler were investigated by LC-MS. The sulfuric acid trap contained approximately 26 mmol A1/L while the second bubbler containing water only contained only .009 mmol Al/ L. The pH of the sulfuric acid bottle remained below 1 for the entire experiment. This finding was used to specify the conditions for the wash section used when the solvent was run in the solvent degradation rig (SDR) in Q7. The amount of A1 collected in the acid trap was only 3-4 mmol over the entire experiment while almost 0.32 mol A1 left the reactor. Additional work is needed in order to fully understand the A1 losses from this solvent system.

Solvent system A2-D2-WA1 was tested in the same manner. Figure 12 below shows that within the first 100 hours of testing that almost 20% of A2 was degraded. By the end of the 500 hours the solvent contained less than 10% A2 relative to the initial concentration. Component WA1 was relatively unaffected by the accelerated oxidative conditions. Component D2, which was present in both solvents, showed little evidence of oxidative degradation.

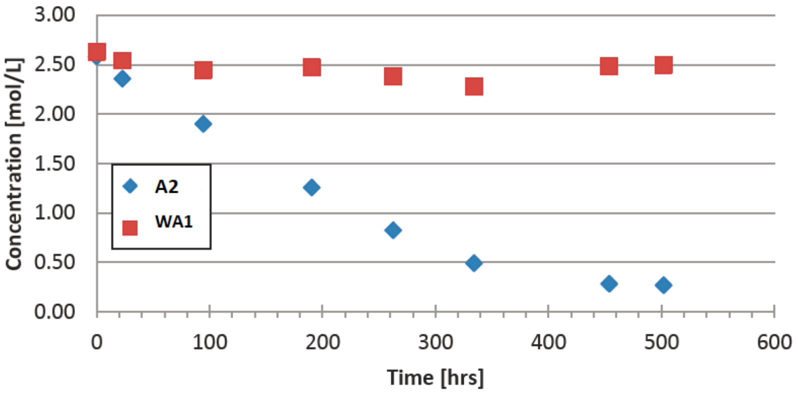


Figure 12. Oxidative degradation of NAS amine components A2 and WA1.

The degradation of A2 was probed further to learn more details about the products of A2 decomposition. As mentioned above and shown in Figure 10, a gas bubble flask with 0.25M H_2SO_4 as medium was used to trap volatile amine emissions which were anticipated to be either vapor phase A2 or volatile amine degradation products. The pH of the bubble flask was monitored during the experiment. After 334 hours the pH of the H_2SO_4 flask was 8, indicating that all of the acid had been consumed by neutralization with volatile amine. At 502 hours the pH was checked again and found to be <1.5. The content of the bubble flask was also examined by LC-MS. Overall, the acidic medium in the gas bubble flask collected only around 0.32 mmol A2 over the entire 500 hour experiment. This small amount of A2 does not explain the high pH observed at hour 334 of the experiment. The total loss of A2 from the reactor is close to 2.14 moles, which indicates that less than 0.1% of the lost A2 is collected in the H_2SO_4 solution. Apparently when A2 is degraded the product formed is a highly volatile amine which escapes the reactor and the acid throughout the experiment. The use of A2 as a solvent component could be investigated more in the future with the addition of an oxidation inhibitor to the solution, however the conclusion of the oxidative degradation study was to discontinue the use of A2 and continue instead with A1.

Summary of Initial Degradation Study

The results of the initial degradation studies indicate that NAS solvents continue to show promise as viable next generation solvents. Solvent components consisting of two amines, a diluent, and a weak acid were tested individually and/or as solvent mixtures for thermal degradation and corrosion. Comparisons were made to MEA. The NAS solvents and components across the board showed lower percentages of thermal degradation (0.1-6.5%) compared to MEA (8.5%). The NAS solvents also dissolved lower amounts of metals commonly found in steel compared to MEA. Oxidative degradation testing was performed on two NAS solvent formulations. One of the solvent formulations contained an amine component which was rapidly degraded under the enhanced oxidizing conditions and will likely need an oxidation inhibitor to enable long-term solvent stability. The second NAS solvent formulation underwent a smaller amount of oxidative degradation during the testing resulting in loss of approximately 20% of the amine over the course of 500 hours.

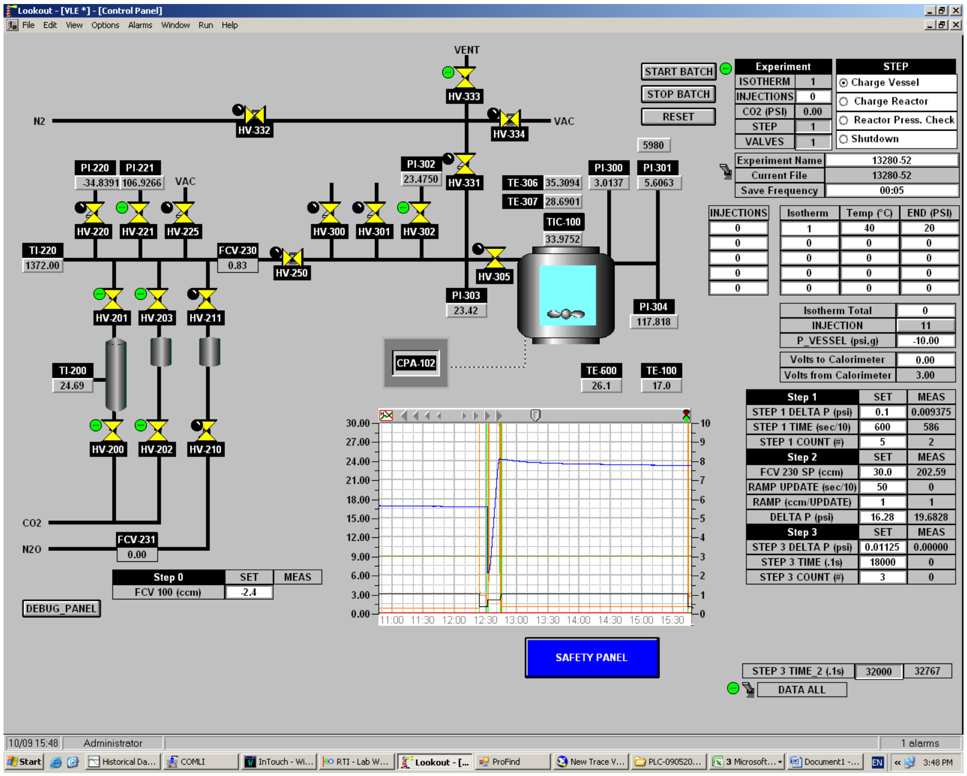
Task 3 - NAS Model Development

The goal of this task is to set the groundwork for the development of a model for our best-candidate NAS. In this task, we upgraded our existing capabilities to support this effort, developed the model framework, and collected equilibrium and reaction rate data for the best-candidate NAS. Progress on these activities are reported in the following sections.

Task 3.1 – Upgrading of Automated VLE and Reaction Calorimetry System

Construction, calibration, and commissioning of our automated VLE/ΔHr system was completed in Q4. A picture of the complete unit (Figure 13) and a screen shot of the user-control interface (Figure 14) are provided below.

Figure 13. RTI's Automated VLE – ΔHr System.



PI-220 -34.8391
PI-221 106.9266
PI-302 23.4750
PI-303 23.42
PI-300 3.0137
PI-301 5.6063
PI-304 117.818
TI-220 1372.00
TI-200 24.69
TE-306 35.3094
TE-307 28.6901
TIC-100 33.9752
TE-600 26.1
TE-100 17.0
FCV-230 0.83
FCV-231 0.00
5980

Experiment	
ISOTHERM	1
INJECTIONS	0
CO2 (PSI)	0.00
STEP	1
VALVES	1

STEP
- ● Charge Vessel
- ○ Charge Reactor
- ○ Reactor Press. Check
- ○ Shutdown

Experiment Name	13280-52
Current File	13280-52
Save Frequency	00:05

INJECTIONS
0
0
0
0
0

Isotherm	Temp (°C)	END (PSI)
1	40	20
0	0	0
0	0	0
0	0	0
0	0	0

Isotherm Total	0
INJECTION	11
P_VESSEL (psi,g)	-10.00
Volts to Calorimeter	0.00
Volts from Calorimeter	3.00

Step 0	SET	MEAS
FCV 100 (ccm)	-2.4	

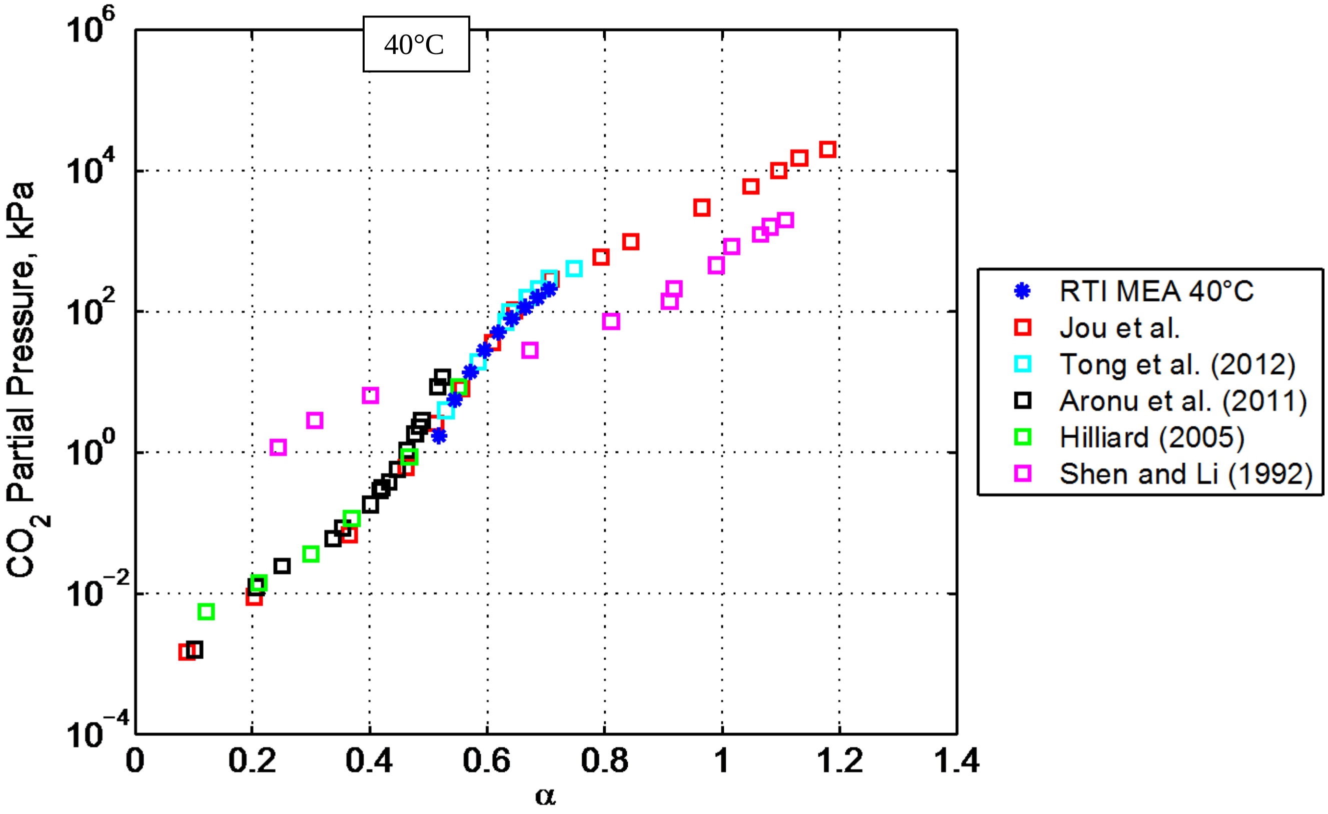
Step 1	SET	MEAS
STEP 1 DELTA P (psi)	0.1	0.009375
STEP 1 TIME (sec/10)	600	586
STEP 1 COUNT (#)	5	2
Step 2	**SET**	**MEAS**
FCV 230 SP (ccm)	30.0	202.59
RAMP UPDATE (sec/10)	50	0
RAMP (ccm/UPDATE)	1	1
DELTA P (psi)	16.28	19.6828
Step 3	**SET**	**MEAS**
STEP 3 DELTA P (psi)	0.01125	0.00000
STEP 3 TIME (.1s)	18000	0
STEP 3 COUNT (#)	3	0

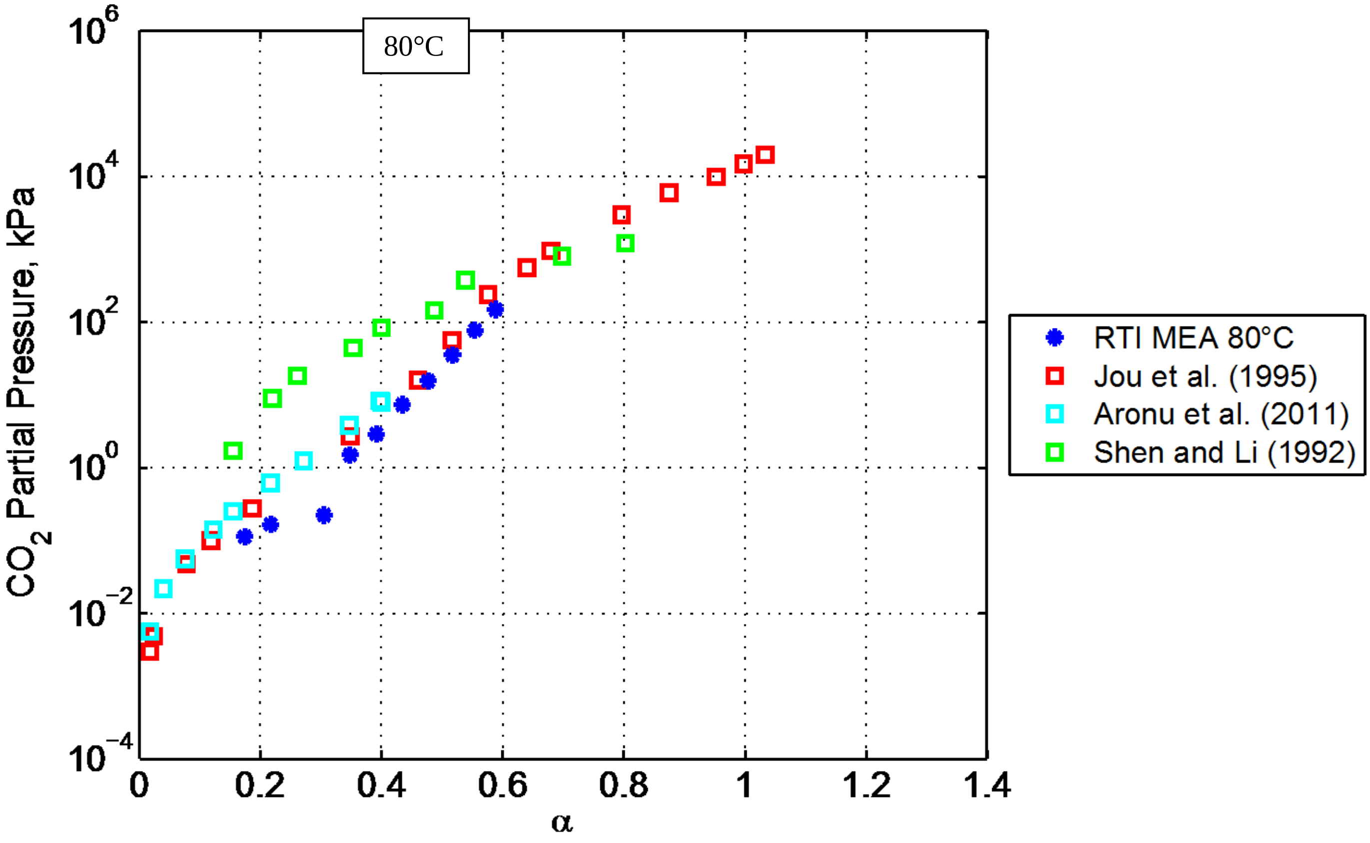
STEP 3 TIME_2 (.1s)	32000	32767

10/09 15:48 Administrator 1 alarms

Figure 14. Screenshot of User-Control Interface for RTI's Automated VLE – ΔHr System.

Commissioning experiments to measure CO_2 isotherms via vapor-liquid equilibrium (VLE) and heat of CO_2 absorption were performed using a 30 wt% MEA-water solvent with the results generated compared to those reported in the literature. CO_2 isotherm measurements – CO_2 partial pressure vs. CO_2 loading (α) – were collected for the CO_2 - 30 wt% MEA-water system at 40°C, 80°C, and 120°C (Figure 15) with a comparison for measurements reported in the literature. CO_2 isotherm measurements collected using our system agree very well with those reported in the literature for 30 wt% MEA-water. Similarly, heat of CO_2 absorption measurements were collected for the CO_2 - 30 wt% MEA-water system at 40°C and 80°C (Figure 16) with a comparison for measurements reported in the literature. ΔHr measurements collected using our system agree very well with those reported in the literature for 30 wt% MEA-water. Overall, these results indicate that our VLE/ΔHr system is well calibrated and capable of collecting high-quality thermodynamic data on par with, or better than that, reported in the literature.


40°C
10^6
10^4
10^2
10^0
10^{-2}
10^{-4}
CO_2 Partial Pressure, kPa
0
0.2
0.4
0.6
0.8
1
1.2
1.4
α
RTI MEA 40°C
Jou et al.
Tong et al. (2012)
Aronu et al. (2011)
Hilliard (2005)
Shen and Li (1992)


80°C
10^6
10^4
10^2
10^0
10^{-2}
10^{-4}
CO_2 Partial Pressure, kPa
0
0.2
0.4
0.6
0.8
1
1.2
1.4
α
RTI MEA 80°C
Jou et al. (1995)
Aronu et al. (2011)
Shen and Li (1992)

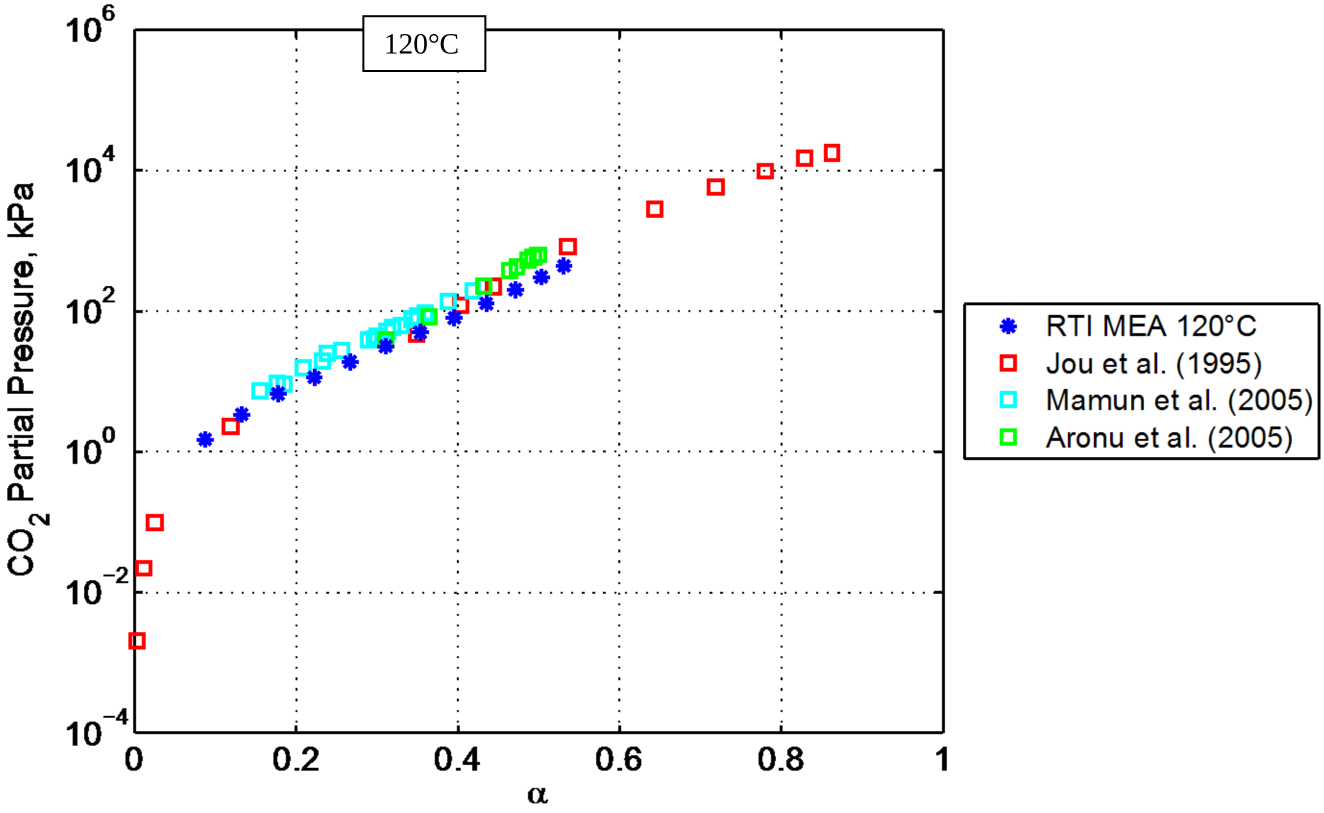


Figure 15. CO_2 Isotherm Measurements for 30 wt% MEA-water at a) 40°C, b) 80°C, and c) 120°C.

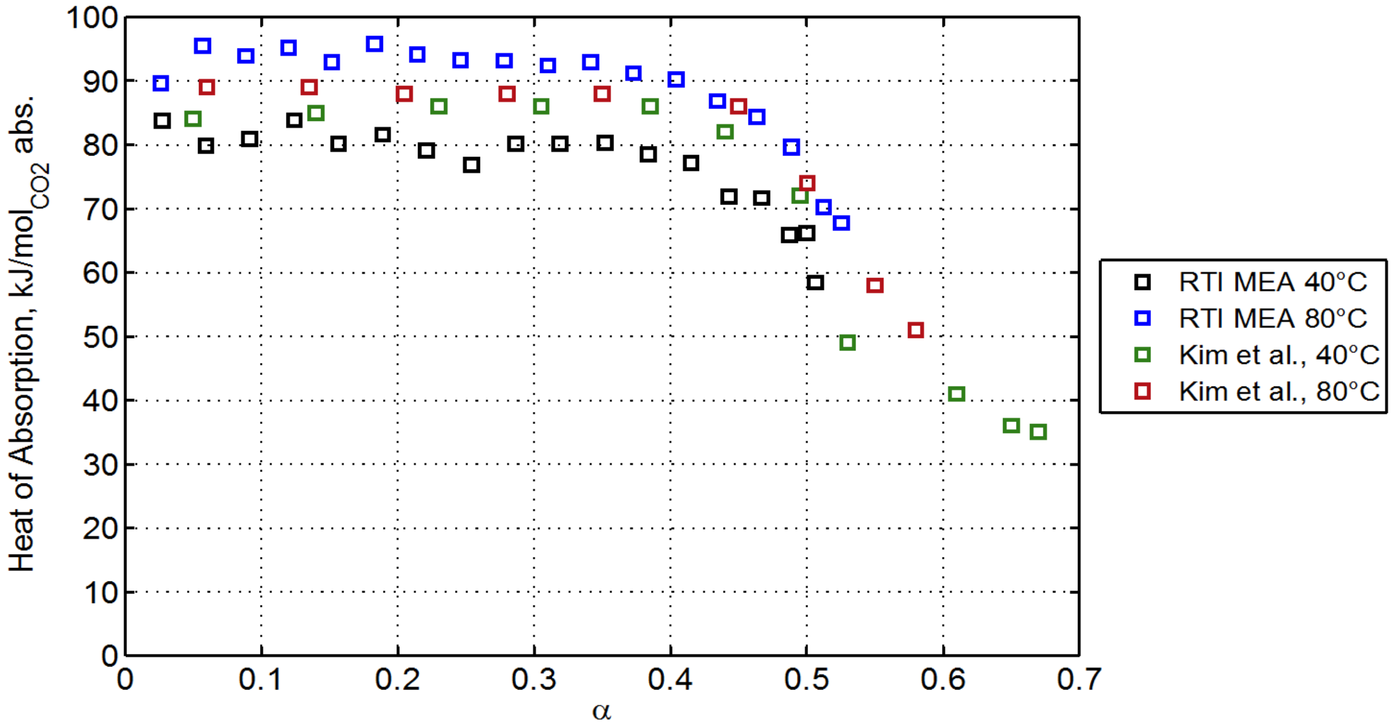


Figure 16. Heat of CO_2 Absorption (ΔHr) for 30 wt% MEA-water at a) 40°C, and b) 80°C.

Task 3.2 Development of Model Framework

This task is focused on the development of a mechanistic-based, thermodynamically-consistent model of the interaction of CO_2 with the NAS solvents. Given the absence of fundamental, thermodynamic data for the non-aqueous solvents, we developed empirical based models to describe equilibrium and reaction rates for the NASs. In Q5, we further developed the empirical model framework and initiated data analysis and regression (Task 3.5).

The model framework is given below, Equation 1 and Equation 2. A polynomial of fourth order with respect to CO_2 loading (mol_{CO2}/mol_{amine}) and of first order with respect to the reciprocal temperature was applied to achieve a good fit to the experimentally determined CO_2 partial pressure (Pa) and loadings (moles CO_2/ mole amine) at different temperatures (K).

$$\ln P_{CO_2}(Pa) = C0 + \frac{C1}{T} + C2\alpha + C3\frac{\alpha}{T} + C4\alpha^2 + C5\frac{\alpha^2}{T} + C6\alpha^3 + C7\frac{\alpha^3}{T} + C8\alpha^4 \qquad \text{(Equation 1)}$$

$$\Delta H_{abs}\left(\frac{kJ}{molCO2}\right) = -R(C1 + C3\alpha + C5\alpha^2 + C7\alpha^3) \qquad \text{(Equation 2)}$$

The constant, R, is 0.008314 kJ/mol/K. The proposed correlation was fit for experimental loadings and heats of adsorption of 30wt% MEA to verify predictability and accuracy (Figures 10 and 11 below). The model data agrees well with experimental findings. This model was used to fit the VLE and heat of absorption measurements acquired for NASs in Q6.

Task 3.3 Measurement of Equilibrium Data

The goal of this task is the collection of equilibrium data including CO_2 isotherms, vapor pressure and Henry's law constant for the best-candidate non-aqueous solvents at conditions spanning the absorption and desorption regions. With the VLE/calorimeter system being fully operational and commissioned, equilibrium measurements were collected for best-candidate NAS formulations. In Q5, we completed an assessment of the equilibrium parameters for a NAS formulation. The vapor-liquid equilibrium data for the NAS formulation is shown in Figure 19 below. Isotherms were determined at three different temperatures and indicate promising working capacities. The isotherms show that at 40°C the solvent can be loaded to 0.38 moles CO_2/ mole amine at a CO_2 partial pressure of approximately 1.8 KPa, conditions which are anticipated at the top of the absorber. As the solvent flows down the column to higher concentrations it will absorb up to ~0.5 moles CO_2/ mole amine. The measured heat of absorption data for the NAS is shown in Figure 22. The heat of adsorption was measured at 80°C and agrees well with the model prediction.

In addition, we evaluated the effect that the water fraction dissolved in the non-aqueous solvent formulation has on the CO_2 isotherm and the heat of CO_2 absorption of a non-aqueous solvent. We speculate that there is a mechanistic phenomenon that is important in realizing lower heats of adsorption, but a discussion is not given in this report due to a lack of comprehensive evidence to prove the hypothesis. It has been observed that the water content in the non-aqueous solvents has an impact on the heat of absorption as shown in Figure 17. We measured the heats of absorption with water content in NAS solvent at 0, 5, and 10 wt% and observe that the heat of adsorption changes little when the concentration of water is at 5 wt% or below, but increases roughly about 12% when there is approximately 10wt% water in the solvent. This will be a parameter to monitor and control in the process to keep the energy penalty as low as possible, but this observation shows that with respect to heat of absorption, the solvent will be able to tolerate some water in the process while maintaining a low heat of absorption.

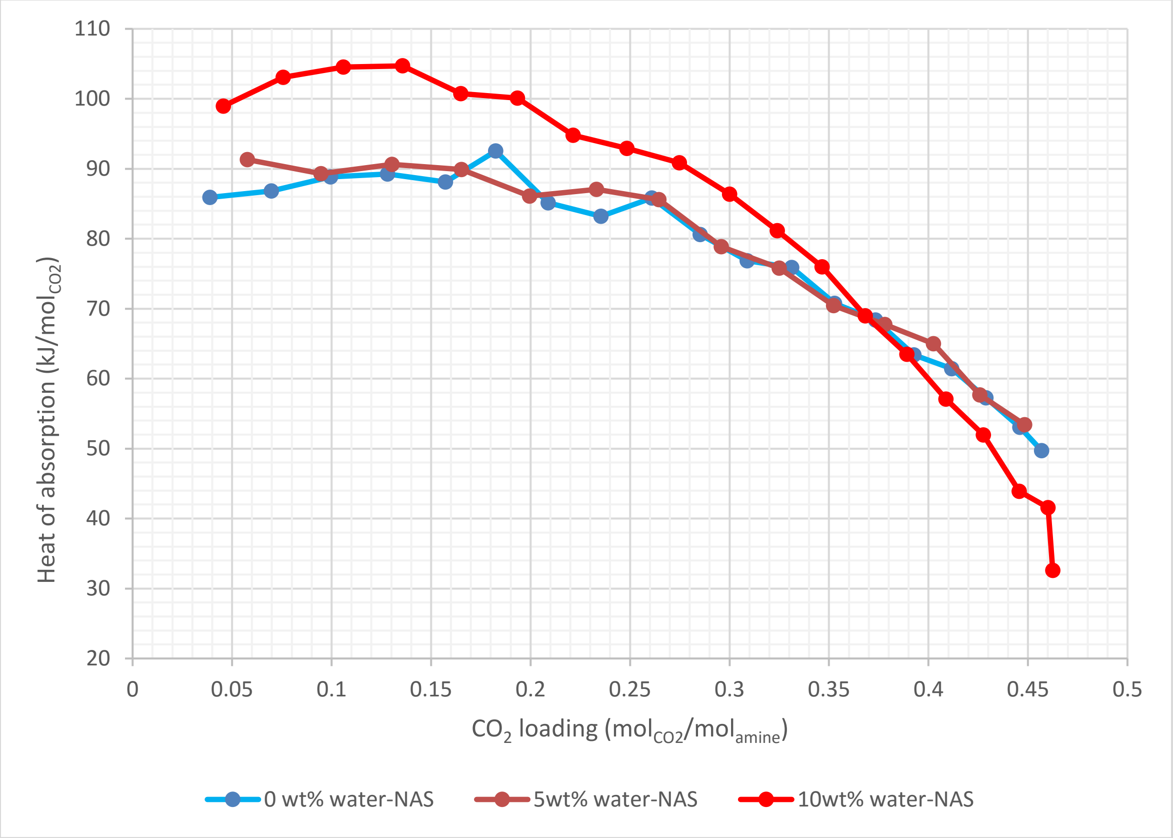


Figure 17. Heat of adsorption data (80°C) for non-aqueous solvent with 0,5, and 10 wt% water content

Task 3.4 – Measurement of Reaction Data

The goal of this subtask was the collection of CO_2 absorption and desorption rate data for the best-candidate NASs at conditions spanning the absorption and desorption regions. This task was moved into Task 7, completed during BP2, and discussed in the Task 7 section below.

Task 3.5 – Data Analysis and Regression

Equilibrium Model for Non-aqueous Solvent (NAS)

The absorption of CO_2 into an amine solution involves phase and chemical equilibria. The amount of CO_2 absorbed in aqueous amine solutions is determined by both its physical solubility of CO_2 in the aqueous phase and the chemical equilibrium for the aqueous phase reactions (among CO_2, water and amine). Whereas, in a non-aqueous solvent system, chemical equilibrium for the non-aqueous phase reactions (among CO_2, water, amine, weak acid and a physical solvent (Genosorb)) governs the total solubility of CO_2 in the NAS solvent along with physical solubility of CO_2 in the amine, weak acid and a physical solvent. The main difference between these systems was observed to be the formation of bicarbonates and carbonates with respect to the carbamate formation. Based on our NMR studies we concluded that there is no bicarbonate and carbonate formation in the NAS system, while this does occur in aqueous systems.

Aqueous phase chemical reactions involved in the MEA-H_2O-CO_2 system (Table 3) and NAS system (Table 4) can be expressed as below:

Table 3. Equilibrium reactions considered for MEA-H_2O system used in this work

Reaction	Type	Stoichiometry
1	Equilibrium	$2H_2O \leftrightarrow H_3O^+ + OH^-$
2	Equilibrium	$CO_2 + 2H_2O \leftrightarrow HCO_3- + H_3O^+$
3	Equilibrium	$HCO_3^- + H_2O \leftrightarrow CO_3^{--} + H_3O^+$
4	Equilibrium	$MEA^+ + H_2O \leftrightarrow MEA + H_3O^+$
5	Equilibrium	$MEACOO^- + H_2O \leftrightarrow MEA + HCO_3^-$

Table 4. Equilibrium reactions considered for NAS system used in this work

Reaction	Type	Stoichiometry
6	Equilibrium	$2NMBA + H^+ \leftrightarrow 2NMBAH^+$
7	Equilibrium	$2(NMBA) + CO_2 \leftrightarrow 2MNBACO- + 2NMBAH+$
8	Equilibrium	$H_2O \leftrightarrow H^+ + OH^-$
9	Equilibrium	MEPHOH <--> MEPHO- + H+

The equilibrium constants (K_{eq}) for the above chemical reactions are defined as follows:

$$K_{eq} = \frac{mole\ fraction\ of\ products}{mole\ fraction\ of\ reactants} \times \frac{activity\ coefficients\ of\ products}{activity\ coefficients\ of\ reactants} \quad \text{Equation 1}$$

$$\ln K_{eq} = A + B/T + C^*\ln T + D^*T \text{ (mole fraction basis)} \quad \text{Equation 2}$$

The vapor-liquid equilibria for CO_2 can be described by an extended Henry's law:

$$\varphi_{CO_2} P_{CO_2} = \gamma_{co_2} x_{co_2} H_{CO_2} exp^{\left(\frac{v_{CO_2}^{\infty}(P-P_{solvent}^{S})}{RT}\right)} \qquad \text{Equation 3}$$

H_{CO_2} is the Henry's constant of CO_2 in the solvent (for MEA system: MEA and water; for NAS system: NMBA, MEPHOH, Genosorb and Water). φ_{CO_2} is the fugacity coefficient of CO_2 calculated using a SRK (Soave-Redlich-Kwong) equation of state. x_{CO_2} is the mole fraction of CO_2 in the solvent. P and $P_{solvent}^{s}$ are the total pressure and saturated solvent vapor pressure. $v_{CO_2}^{\infty}$ $(cm^3 mol^{-1})$ is the partial molar volume at infinite dilution. Therefore, parameters required to determine the absorption of CO_2 are equilibrium constants for all reactions, Henry's law constants, fugacity coefficient and activity coefficients of molecular species (for MEA system: H_2O, CO_2, MEA; for NAS: H_2O, CO_2, NMBA, MEPHOH) and ionic species (for MEA: H_3O^+, OH^-, HCO_3^-, MEA^+, $MEACOO^-$, OH^-, CO_3^-; for NAS: H^+, OH^-, $NMBAH^+$, $NMBACO^-$, $MEPHO^-$).

Modeling approaches:

In the modeling work, we used two activity coefficient models to calculate the equilibrium constants. The reasons to choose them are listed below:

1. Modified Kent-Eisenberg Model
2. Electrolyte-Non-Random Two Liquid Model with Symmetric Reference State Model

Modified Kent-Eisenberg model (MATLAB)

1. This model is widely used and easy to develop with little consideration for the non-ideality of the solvent (Tong, Trusler, Maitland, Gibbins, & Fennell, 2012).
2. Fewer physical properties are needed for this model compared to other activity coefficient models.
3. In order to regress large numbers of parameters in more rigorous models, such as Electrolyte-NRTL model, initial guesses and trend in carbamate formation reaction can be obtained using this non-rigorous model.
4. This model may be used to interpolate and extrapolate data which could be used in more rigorous models to get more accurate interaction parameters required in the model.

Figure 18 and Figure 19 show the predicted VLE and the equilibrium constants obtained in both MEA-H_2O-CO_2 and NAS-H_2O-CO_2 systems. It was found that the change in equilibrium constant for aqueous system does not change substantially with temperatures and CO_2 loadings, whereas for non-aqueous system it was found to change with respect to both temperatures and CO_2 loadings. Therefore, the equation to represent the equilibrium constant was changed as a function of both temperature and CO_2 loading. This shows that the role of other components in the NAS solvent such as the weak acid and physical solvent plays significant role in absorbing CO_2 and the need of non-ideality in the solvent phase for the NAS-H_2O-CO_2 system is substantial and have to be improved in the equilibrium model to predict the VLE of the system. This enforces the need of a more rigorous model such as Electrolyte-Non-Random Two Liquid (E-NRTL) model for NAS- H_2O-CO_2 system.

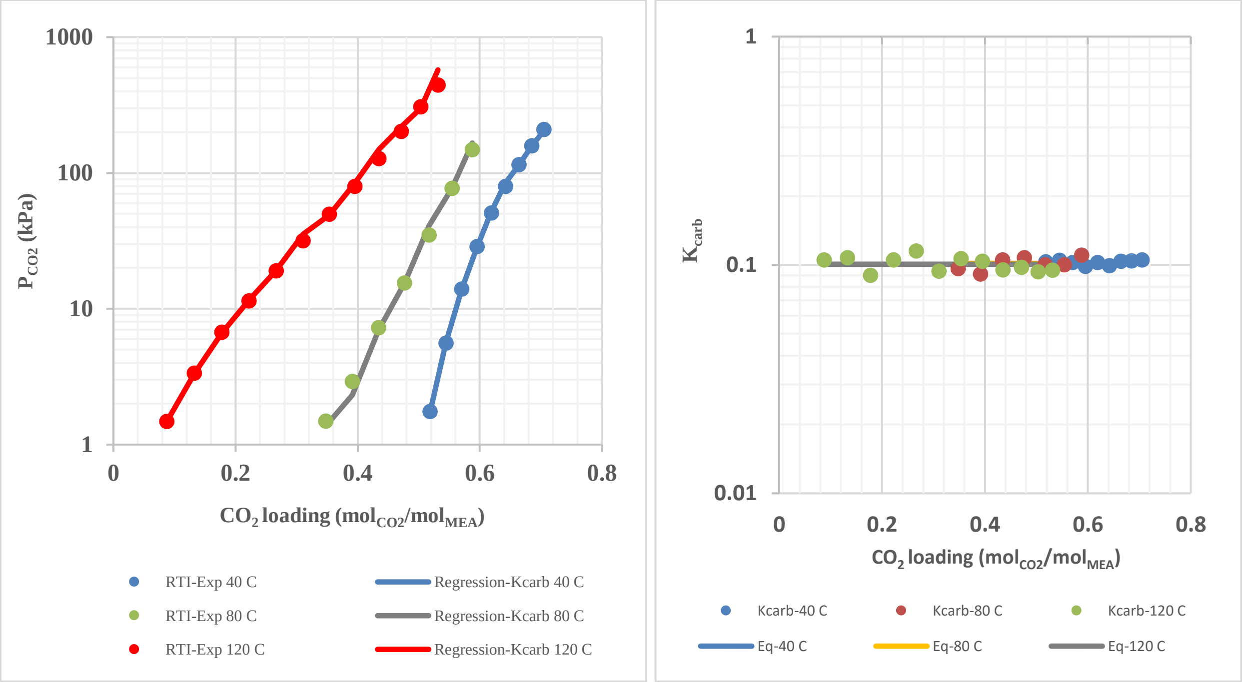


Figure 18. VLE of CO_2 in 30 wt% MEA (left) and carbamate equilibrium constant at different temperatures for CO_2 in 30 wt% MEA(right)

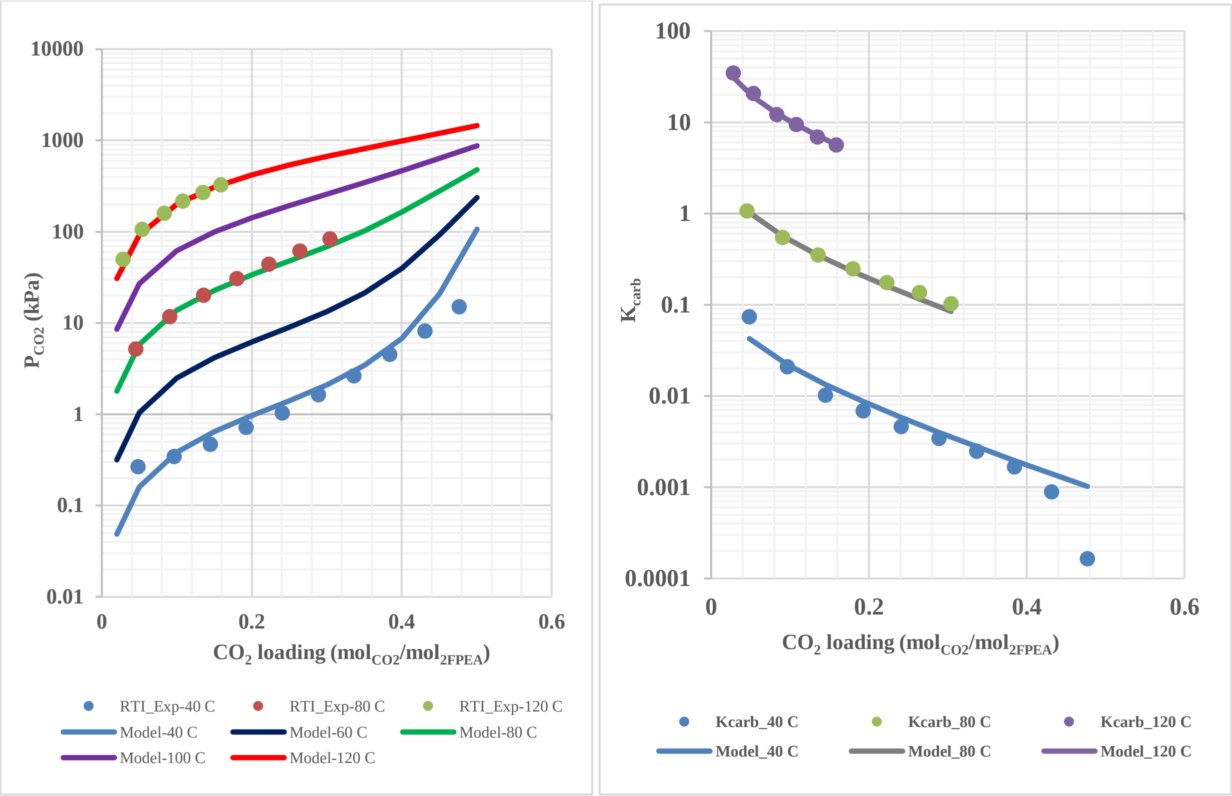


Figure 19. VLE of CO_2 in the NAS system (left) and carbamate equilibrium constant at different temperatures for CO_2 in the NAS system (right)

Electrolyte-Non Random Two Liquid Model with Symmetric Reference State (ASPEN PLUS)

1. This model option available in Aspen Plus commercial software is more rigorous and considers the full extent of non-ideality of the solvent. Developing a thermodynamic system model in the Aspen Plus software using this property model is possible.
2. Symmetric reference state which considers the reference state for ions as pure fused salts, rather than infinite dilution in aqueous solution is more suitable to develop the equilibrium model for the NAS solvent. This basis is easier to use for non-aqueous and mixed solvent systems and eliminates the need to introduce water into otherwise water-free systems.
3. The model will reduce to the standard NRTL model when there are no electrolytes in the system. Chemical constants, enthalpy and Gibbs free energy are calculated with respect to a symmetric ionic reference state. This model could be adjusted for zwitterions also.
4. Due to the large contribution of water in the MEA-H_2O-CO_2 system, the Unsymmetric Electrolyte NRTL activity coefficient model was used with the mixed solvent option for the activity coefficient basis for Henry's Law components (CO_2 in this work). By considering the lower contribution of

water, the symmetric Electrolyte NRTL activity coefficient model was used for NAS-H_2O-CO_2 system.

5. By modeling the MEA-H_2O-CO_2 system simultaneously using the VLE and Heat of absorption data obtained from the RTI VLE and ΔH_R measurement system, we found the sensitive parameters needed to regress and adjust to match the experimental data in the model for the NAS-H_2O-CO_2 system. Several group contribution methods were used to predict the unavailable experimental data for the NAS-H_2O-CO_2 system to predict VLE and ΔH_R such as specific heat capacity of liquids, heat of vaporization, heat of formation etc. The parameters needed to model the VLE of the NAS system in ENRTL-SR model can be summarized in the following Table 5. Literature used to determine these properties are given in Table 6.

Table 5. Properties required for ENRTL-SR model (Aspen Technology, 2010)

Property	**Experiment or Estimation method**
Temperature	Experiment set point
Equilibrium constants	Regressed from VLE
Vapor pressures	VLE with no acid gas
Henry's constants	N_2O analogy, Low press VLE
Critical temperature	Molecular structure [Estimate/Aspen]
Critical pressure	Molecular structure [Estimate/Aspen]
Critical volume	Molecular structure [Estimate/Aspen]
Compressibility factor	Estimate using Aspen
Acentric factor	Estimate using Aspen
Density	Gravimetric determination
Molecular weight	Molecular formula
Characteristic volume	Estimate using Aspen
Saturation volume	Estimate using Aspen
Isothermal compressibility	Estimate using Aspen
Closest approach parameter	Estimated at 14.9
Ionic Radius	Estimate at 3 Angstrom
Binary interaction parameters	Regressed from VLE
Non-randomness factors	Regressed from VLE

Table 6. Literature used to determine properties for the NAS system

Properties	Literature
pK_a	(Armstrong & Barlow, 1976), (Richner, et al., 2015), (Liptak, 2002)
Dielectric constants	(Electro-Acoustics, 2001), (Smallwood, 1996)
Standard State Properties	(Zhang, 2011)
Vapor pressures	(Aspen Technology, 2010), (Mokbel, 2009), (Yaws, 2008)
Thermophysical properties	(Yaws, 2008)
Henry's constants	(Lee M. C.-W., 1999),(Sciamanna, 1988), (Clariant GmbH Report, 2002)
VLE data	(Lee M. C.-W., 1999), (Klauck, 2008), (Rayer, 2012), (NIST-data, 2015), (Chiavone-Filho, 1993), (Dow-Chemical, 2001), (Lee H. , 1996), (Cox, 1926), (Fredenslund, 1975), (Dhal, 1991)

Figure 20 shows the fitted and predicted VLE for aqueous MEA and the NAS system. Using the parameters regressed to predict the VLE, one could also predict the heat of absorption of CO_2 in the solvent. Figure 21 shows the obtained heat of absorption of 30 wt% MEA from the fitted VLE parameters. Based on the calculations suggested by Hilliard (Hilliard, 2008), after introducing the coefficients to predict the aqueous infinte dilution heat capacity for the unknown ionic speices at different temperatures ($MEAH^+$ and $MEACOO^-$) in Aspen Plus, the variation of predicted heat of CO_2 absorption was improved as shown in Figure 21. Based on this study, we concluded that the following parameters are necessary for predicting the heat of absorption of CO_2 in NAS solvent:

(i) ideal gas heat capacity of molecular compoents in NAS

(ii) reference state properties such as heat of formation, Gibbs free energy of formation, entropy of formation

(iii) aqueous infinte dilution heat capacity of ionic components. All of these properties for the NAS solvent were predicted using various group contribution methods.

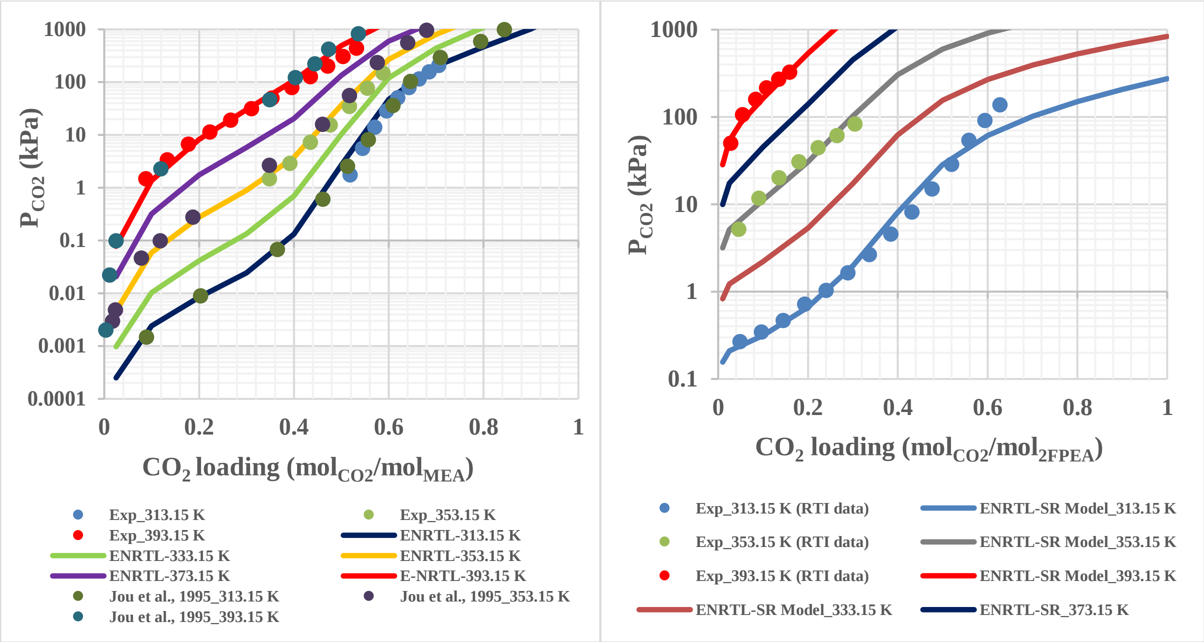


Figure 20. Fitted and predicted VLE for aqueous MEA (left) and the NAS system (right)

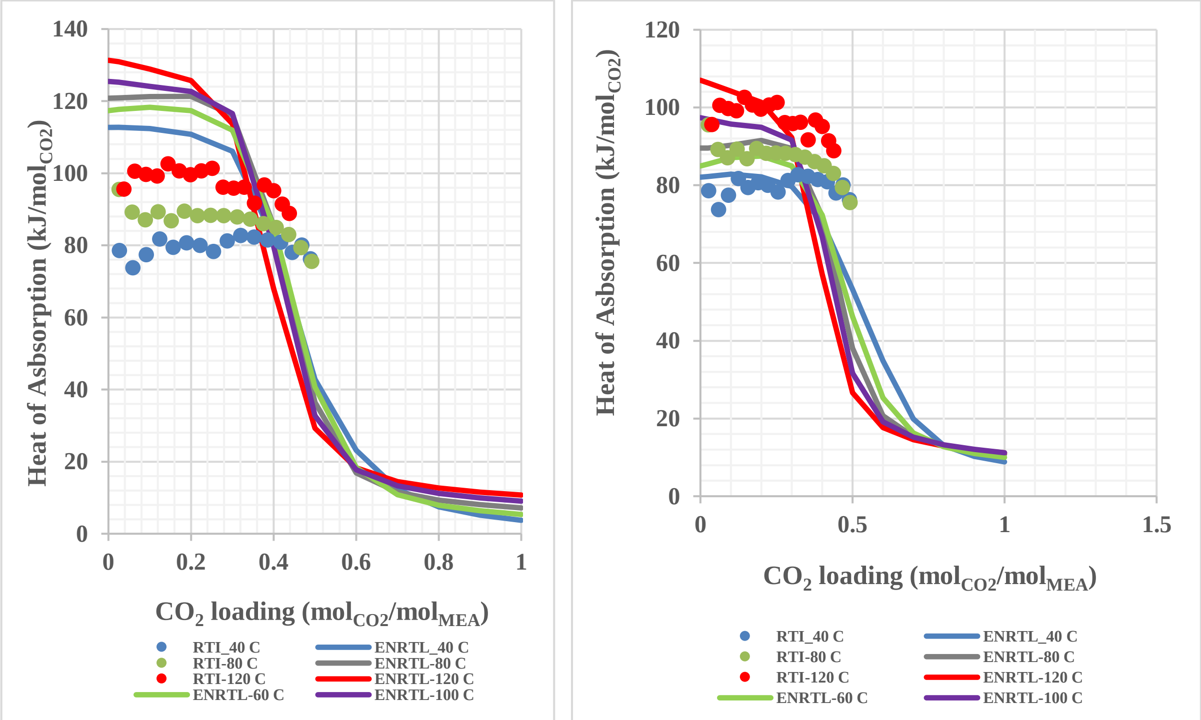


Figure 21. Predicted Heat of absorption for MEA-H$_2$O-CO$_2$ system (Before and After calorimetric correction)

Figure 22 shows the predicted heat of absorption for the NAS system using the ENRTL-SR model developed in this work using the flash column procedure as suggested by (Hilliard, 2008). In order to show the difference between the calorific prediction and VLE prediction, the heat of absorption calculated by Gibbs-Helmhotz equation were shown in Figure 22:

$$\frac{-\Delta H_{abs}}{R} = \left[\frac{df^{v}_{CO_2}}{d\frac{1}{T}}\right]_{x_{CO_2}} \qquad \text{Equation 4}$$

$f^{v}_{CO_2}$ is the fugacity of CO_2 predicted by VLE parameters for ENRTL-SR model developed in this work. ENRTL-SR model predictions can be improved in the future by adding more accurate reference state properties and non-ideality properties estimated from more VLE measurements for NAS molecules and their interactions with CO_2 in the RTI VLE measurement system. More experimental data for VLE and heat of absorption of CO_2 in the NAS system at different temperatures and CO_2 loadings have to be measured in the future to verify and to adjust the coefficients for calculating the aqueous infinite dilution heat capacities for ionic components in the NAS system.

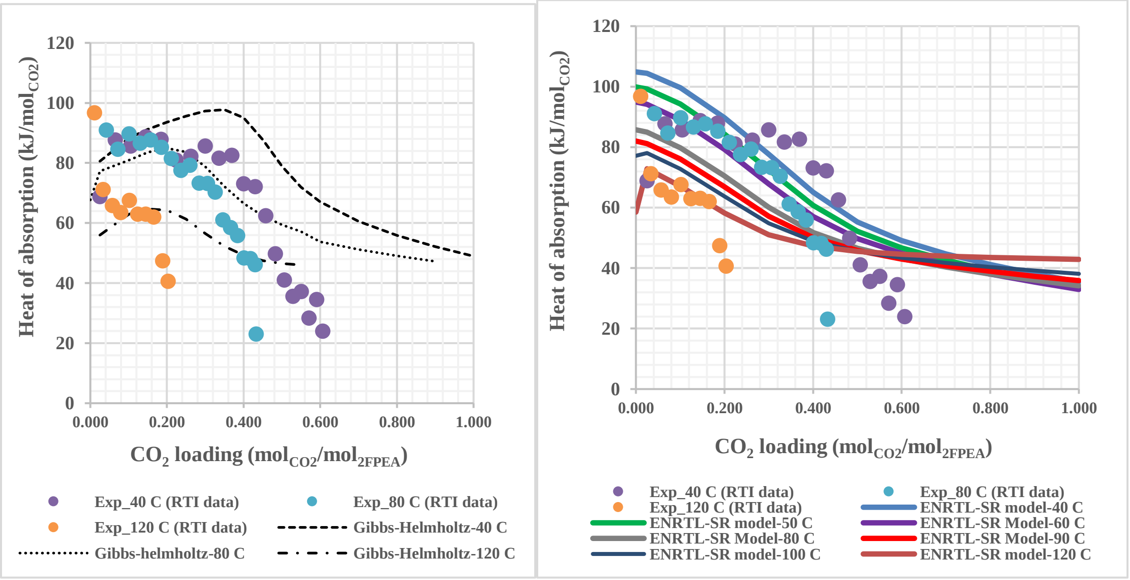


Figure 22. Heat of absorption of CO_2 in NAS solvent and their prediction using Gibbs-Helmholtz equation (top) and ENRTL-SR model (bottom)

The developed ENTRL-SR model was implemented into an Aspen Plus Simulation using a flow sheet with an absorber and a desorber with packing configurations and desired running conditions similar to the process configuration shown in Figure 23. It was used to estimate the optimal operating conditions of the RTI bench-scale test unit and to develop a rate-based model based reaction kinetics for CO_2 and the NAS system.

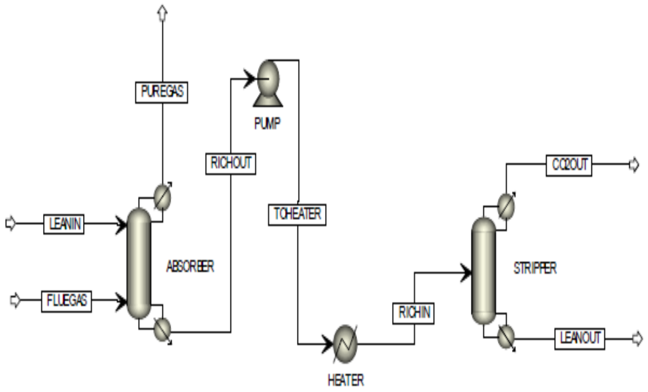


Figure 23. Flow sheet for thermodynamic model with ENTRL-SR model

Experiments with a wide range of temperatures, water concentrations, and CO_2 loadings have been conducted to gain VLE and heat of absorption data and incorporated into the ENRTL-SR model to improve and validate. This allowed for the role of water on the regenerator heat duty to be investigated.

Critical properties needed to improve the ENRTL-SR model and to develop a rate-based model are mentioned below in Table 7 and were measured or estimated accurately for the NAS molecules.

Table 7. Properties required to improve the ENRTL-SR model

Properties	Mixture	Molecules	Critical
Henry's constant of CO_2	Yes	Yes	Yes
Liquid Heat Capacity	Yes	Yes	Yes
Vapor Pressures	Maybe	Yes	Yes
Reference state properties	Yes	Yes	Not
Heat of Vaporization	Maybe	Yes	Not
Dissociation constant (pK_a) at different temperatures	Yes	Yes	Yes
VLE at different temperatures	Yes	Yes	Yes
Density at different temperatures	Yes	Yes	
Heat of absorption at different temperatures	Yes	No	Yes
Viscosity at different temperatures	Yes	Yes	Yes
Surface tension at different temperatures	Yes	Yes	Yes
Thermal conductivity at different temperatures	Yes	Yes	Yes
Dielectric constant at different temperatures	Yes	Yes	Yes
Diffusivity of CO_2	Yes	Yes	Yes

Task 4 - NAS CO_2 Capture Process Development (Task 4)

The objective of this task is to increase the fidelity of the process design such that all necessary process components are included and that each component's performance is adequately understood to support performing a detailed technical and economic assessment. At this stage of development, the two most significant uncertainties in the design of the NAS CO_2 Capture Process are:

1. the design and performance of a wash section to recover/eliminate solvent from the treated gas stream,
   - without this unit, the operating costs of the process would become insurmountably large and hydrocarbon emissions may exceed permissible levels
2. the design and performance of a suitable regenerator.
   - currently no commercial embodiments are known that are suitable for regenerating chemisorption-based NASs that do not have low boiling point components

Task 4.1 – Lab-scale Development and Evaluation of Solvent Recovery and Regenerator Systems

NAS Recovery/Wash Section

The goal of this lab-scale effort is to develop a recovery/wash section for reducing NAS emissions in the treated gas to <10 ppm,v and for producing a separate NAS phase that can be continuously separated from the wash water and returned to the process. In Q2, progress was made in defining the critical design criteria for the wash-recovery section (i.e., Process Design Considerations document completed) and the necessary analytic instruments were identified as planned. In Q5 the wash section was incorporated with the outlet of the absorber column on the lab-scale system. A GC method was developed to measure the amine emissions from the absorber column and experiments were performed and show that it will be an effective method for preventing amine emissions. Based on Q6 findings, a NAS Recovery/Wash Section (C-250) was designed for the outlet of the bench-scale CO_2 Absorber and is described below. This system could be used in the future to demonstrate the ability to reduce solvent makeup costs at larger scales. Testing with a water wash at the lab scale showed that the wash section substantially reduced the amine content in the treated flue gas from ~20 ppm to below 10 ppm.

System Design

Key System Components

- P-250 – The water recirculation pump operates at a continuous speed during operation of the bench-scale process, for a calculated L/G ratio at the current operating conditions.
- HX-250 – A water-wash cooler lowers the temperature of the recycled water to achieve a gas outlet temperature from the wash section of 40°C. The reduced temperature increases the absorption of NAS components in the water wash.
- P-255 – A recovery pump is used intermittently to remove a NAS-rich second liquid phase from the bottom of C-250.
- C-250 – The NAS Recover/Wash Section column is constructed of SS316, with a sump capacity of 10L. The column is packed with Mellapak 350X with a 90° shift in orientation between each packing section. A spray nozzle is incorporated at the recirculated water inlet to the top of the column to ensure an even distribution of solvent across the column. The temperature of the sump, gas inlet and outlet, and recirculated water are all monitored. A gas sampling port is included near the gas outlet of the column. A demister is section is included in the gas outlet to prevent wash-water carryover from the column.

Costing

In a similar-scale, but separate, bench-scale CO_2 capture project using an advanced solid sorbent, RTI is using a water-wash section for flue-gas pretreatment to lower SO_2 and NO_x concentrations in the flue gas before it is contacted with a solid sorbent. The wash section is very similar to what has been described for the water wash section for the NAS bench-scale unit. In the design of the wash section for flue gas pretreatment, the estimated cost of fabrication is $50,000. By replacing corrosion resistant parts and vessels, which are applicable to flue gas treatment containing acidic species such as SO_2 and NO_x, with the reduction in gas volume being treated in our NAS bench-scale system, we have projected that the total fabrication and installation cost of the water wash section will be under $35,000.

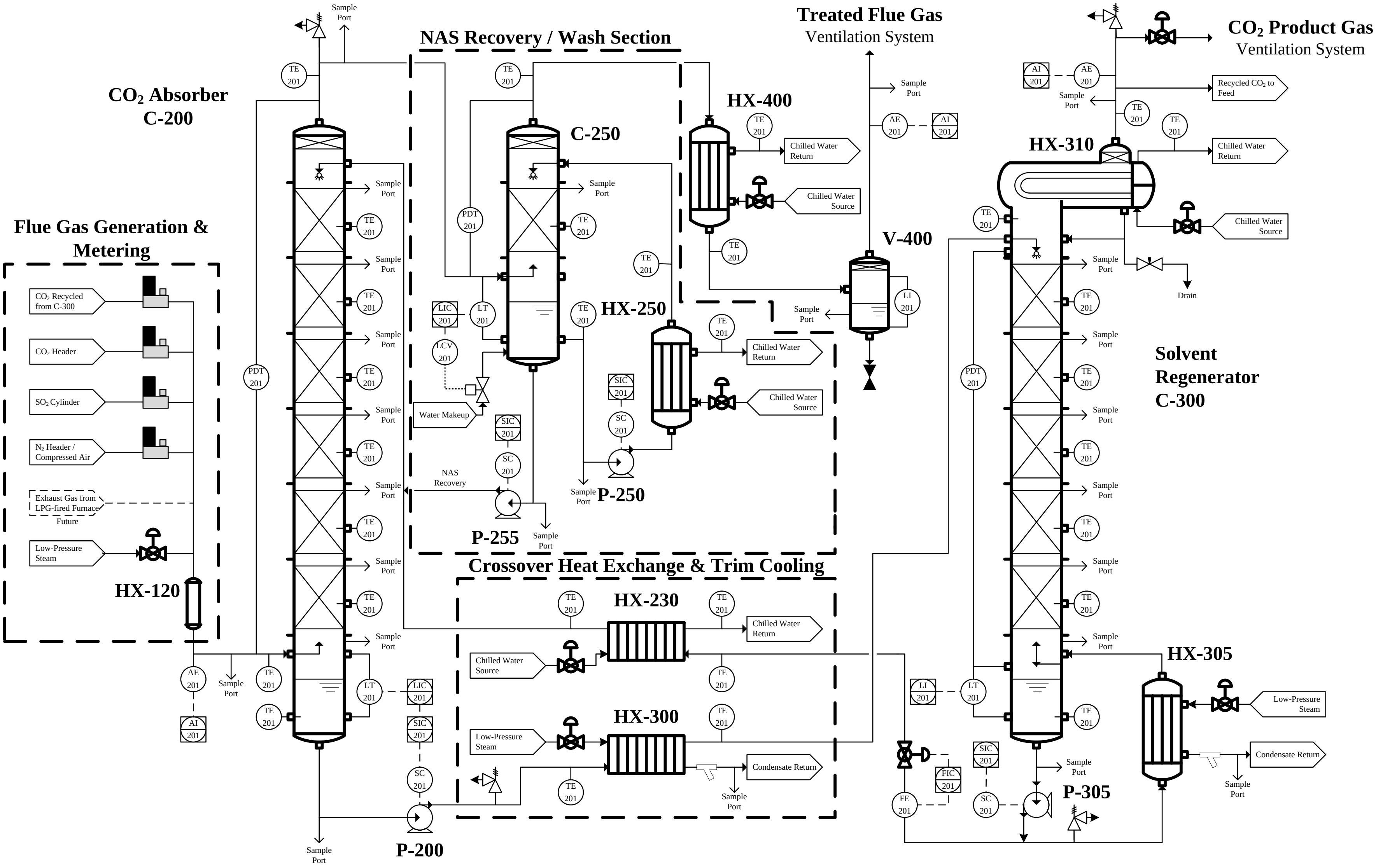


Figure 24: Updated Bench-scale Test Unit with NAS Recovery/Wash Section

NAS Regenerator

The goal of this effort is to identify at least one promising regenerator design that is capable of achieving the desired degree of solvent regeneration at the desired low regeneration temperature of 90°C. In Q4 it was reported that RTI and Linde have proposed to evaluate conventional stripper-reboiler regenerators to determine the suitability for utilization in NAS processes with minor process and operational modifications. Although the LsGAS is too small (system volume < 400 mL) to evaluate representative prototype regenerators, it is suitable for demonstrating critical process concepts. The LsGAS was modified to have a conventional stripper-reboiler arrangement with a rich feed split as discussed earlier, and successfully demonstrated that the non-aqueous solvent formulation could be operated using a conventional stripper-reboiler. This regenerator arrangement performs several key roles including: i) recovering heat from the column gas which can have a substantial water vapor content, ii) integrating higher quality heat in the cross-over heat exchanger, and iii) scrubbing water and trace amine from the column gas prior to entering the overhead condenser. This regenerator arrangement was shown to be capable of achieving deep solvent regeneration and that the water fraction dissolved in the NAS. In fact, the rich feed section was added to the top of the stripping column as a means of recovering heat in the boil-up steam despite the relatively small boil-up fraction in the non-aqueous solvent. Given this observation, RTI and Linde will further assess the potential to use a conventional regenerator for an initial assessment of the performance of the non-aqueous solvent in the bench-scale system.

Task 4.2 – Design and Engineering of Process Modification to Bench-scale System

The goal of this task was to prepare a complete engineering design package for the Bench-Scale System modifications, including the bench-scale NAS Recovery/Wash Section and NAS Solvent Regenerator sections. This effort was probed in Q6 to discern whether or not a process modification should be implemented before evaluation of the non-aqueous solvent in the bench-scale system in BP2. Initial findings showed that the solvent could be operated in the existing bench-scale system configuration to achieve 90% CO_2 removal from the simulated flue gas. A high L/G ratio was required to accomplish this level of CO_2 reduction. Given this result, the project team performed additional testing to measure the energy penalty using a conventional configuration and reported the results from this testing in Q7. The results indicated that the process can be performed in a conventional configuration but with less significant improvement in the energy penalty compared to alternative regenerator configurations which were operated in Q8 and later.

Task 5 – Construction and Testing of Upgraded Bench-Scale System

The project team has identified two levels of upgrades to the bench-scale test unit. A simplified process diagram of the bench-scale test unit is shown in Figure 26 below for reference. The first level of upgrades are referred to as baseline level upgrades and are executed on the bench-scale test unit using the existing conventional configuration which has a stripper regenerator optimized for aqueous solvent systems. These upgrades improve process measurements or impart better control on the bench-scale test unit while still being operated in the conventional configuration. The second level of upgrade is a configurational upgrade, in which a major process unit, such as the regenerator, is changed to improve the overall performance of the carbon capture system.

At the end of BP1 the project team agreed that an evaluation of NAS in a conventional configuration should be performed to see if it could be operated successfully to achieve 90% capture and to see how the process steam consumption compared with the steam consumption measured in baseline MEA testing. To achieve this effort, baseline level upgrades were made to the system prior to testing a NAS. A description of the upgrades are given in the Subtask 5.1 description below.

Initially the performance of the bench-scale test unit was verified using a 30% aqueous MEA solution. This was done during week-long operation of the unit in collaboration with Linde. A description of this is given in the Subtask 5.2 description below. In addition, baseline modifications which were made after testing with MEA, were confirmed to operate as designed by conducting tests with NAS in the bench-scale test unit to remove CO_2 from a simulated flue gas stream. Parametric testing with NAS in the conventional configuration was completed and reported in Q8.

Bench-scale Testing Unit Process Description:

The BsTU, Figure 25, has a conventional gas scrubbing process arrangement and was designed to be a highly instrumented and controlled experimental system capable of performing detailed evaluations of solvents for the removal of CO_2 from simulated flue gas streams and to operate for extended periods to support long-term performance evaluation efforts. System specifications are provided in Table 8. The unit has been designed with many process measurement devices, thoroughly insulated, and exclusively uses low-pressure steam at a constant temperature to allow for accurate and reliable mass and energy balances to support the measurement of the thermal energy consumed by the unit. The unit was also comprehensively equipped with process control devices to ensure the quality of experimental data collected and the safe and proper control of the unit during extended operation test campaigns. An analytical technique has been developed to determine the CO_2 loading, amine, and water content, providing insight into the working capacity of the NAS under different process conditions. A block flow diagram of the bench-scale unit in a conventional configuration with all process vessels and key process measurements and controls is provided in Figure 26 and a detailed description is provided below.

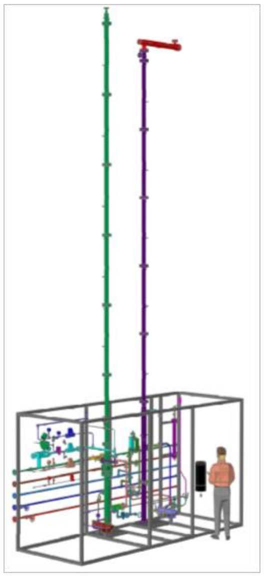


Figure 25. 3D drawing of bench-scale test unit.

Table 8. Bench-Scale Unit Specifications

Simulated Flue Gas		CO₂ Absorber (C-200)		Solvent Regenerator (C-300)	
FG Flow Rate:	100 to 485 SLPM	**Diameter:**	3” Sch. 10 SS316	**Diameter:**	3” Sch. 10 SS316
CO_2 Feed Rate:	1.8 to 8.6 kg/h	**Height:**	8.5 m (28’)	**Height:**	7.1 m (23’-4”)
Feed Temp.:	30 to 50°C	**Packing:**	8.05 m (26’-4”) Mellapak 350.X	**Packing:**	6.7 m (22’) Mellapak 350.X
Target Comp:	CO_2: 13.3%; H_2O: 6.1%; O_2: 2.35%; N_2: bal.	**Temp.:**	30 to 55°C	**Temp.:**	up to 150°C
CO_2 Content:	up to 15 %vol	**Pressure:**	ambient to 200 kPa	**Pressure:**	ambient to 1 MPa(g)
Water Content:	~0 to 12.3%vol	**Gas Vel.:**	0.33 to 1.5 m/s		
SO_2 Content:	up to 20 ppmv	**L:**	15 – 75 kg/h		

Simulated flue gas (Sim. FG), generated by blending compressed air, CO_2, SO_2, and LP steam, is preheated by HX-120 to avoid condensation prior to entering the CO_2 Absorber (C-200). The humidified simulated FG is fed to the C-200 sump and flows upward. C-200 is a conventional packed-column equipped with six K-type thermocouples to monitor the column temperature profile and six gas/liquid sample ports. As the Sim. FG flows through the packing and contacts the CO_2-absorbing liquid, the CO_2 content of the gas decreases. The gas exits C-200 after passing through a mist eliminator and is cooled to ~15°C (HX-400) to knock out water and trace solvent. The two-phase fluid stream is fed to a knockout pot (V-400) to separate and collect the condensed liquids. The cooled, CO_2-lean gas is then vented through the ETDF ventilation system. Warm, CO_2-lean solvent is transferred from the pressurized Solvent Regenerator (C-300), passes through a solvent cooler (HX-230)—reducing the temperature to ~40°C, and is then fed to the top of the CO_2 Absorber and column packing. The solvent flows downward, scrubbing CO_2 from the Sim. FG. The solvent, now rich in $CO_{2,}$ drips from the bottom packing into the column sump. P-200 transfers the CO_2-rich solvent from C-200 to the Solvent Heater (HX-300)—heating the solvent to 80-120°C by indirect contact with LP steam—prior to entering C-300. The Regenerator—analogous to C-200 – is also equipped with K-type thermocouples and gas/liquid sample ports. The warm, CO_2-rich solvent is distributed on top of the packing and flows downward, releasing CO_2. The hot, CO_2-lean solvent is transferred from the C-300 sump by means of the pressurized C-300 and a flow control valve, which returns the hot solvent to HX-230. The HX-305 reboiler is a standard shell-and-tube heat exchanger that heats the solvent indirectly by condensing LP steam. The boil-up from HX-305 are fed to the bottom of C-300 (to the sump) by thermo-syphoning process. The boil-up, primarily steam, rises through C-300, and condenses on the packing and walls, providing regeneration heat to the downward flowing solvent. Excess boil-up steam and CO_2 exit C-300 and enter a water-cooled, on-column overhead condenser (HX-310). Condensate is returned to the top of C-300 as reflux and to maintain desired water concentration (and may also be extracted for compositional analysis). CO_2 product gas exits HX-310 and is sent to the ventilation system. Prior to venting, the CO_2 can be recycled and blended with the Sim. FG via FCV-310 as a way to reduce operating costs (but is not required). C-300 pressure is maintained by PV-310.

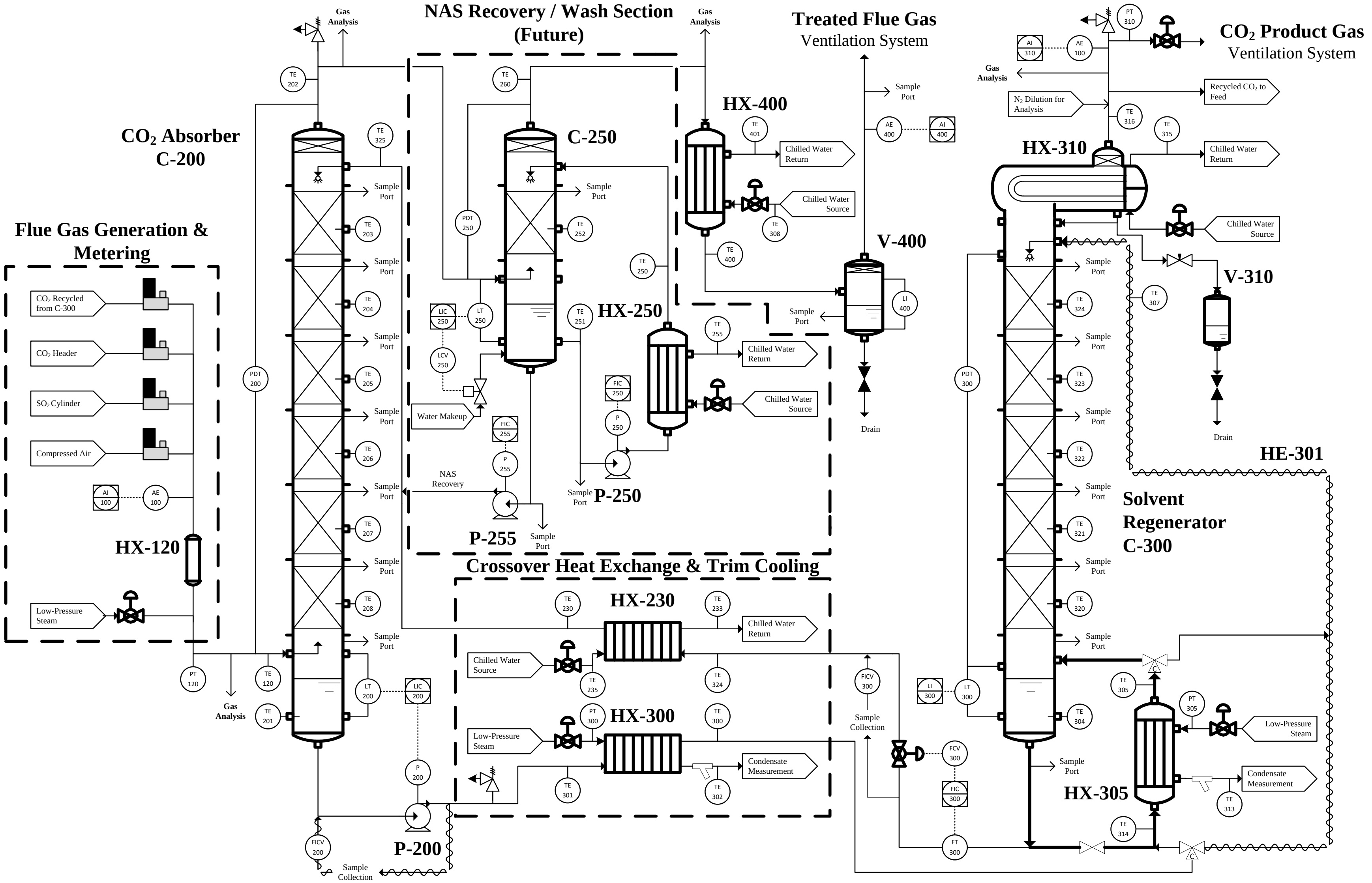


Figure 26. Block Flow Diagram of the Bench-Scale Unit with the conventional configuration reboiler flow path bolded.

Subtask 5.1-Bench-scale System Upgrade and Definition of Operating and Safety Protocols

In Q7 several baseline level upgrades were made to the bench scale test unit. The upgrades were surmised to remedy certain issues which were perceived by the project team to limit operational control and accuracy of the NAS process during testing. The areas which needed improvement were general system operation and stability, steam injection, heat exchanger operation and measurement, and gas and liquid analysis. The upgrades are explained in the following section. In addition, a full Operating Manual was established for the system.

System Operation and Stability

The first area of upgrades were made to improve the overall system operation and stability. First, the nitrogen supply to the system is used in the control of many critical process valves and subsystems. Nitrogen is supplied to the system from a dewar that is filled approximately once a week, requiring that the supply be turned off during filling. In order to ensure that long-term operation of the system is uninterrupted, a secondary nitrogen supply, shown in Figure 28, was installed. The secondary supply is configured with a gas pressure regulator set to open just below the standard nitrogen supply pressure, so it will open to maintain the nitrogen pressure at a suitable point during a refilling event. In addition, the process for solvent addition to the system was altered to limit any exposure of personnel to solvent vapors. The original method included pouring solvent into a vessel, shown in Figure 27, that was then pressurized to pass solvent into the regenerator sump outlet. The new method utilizes an air-powered diaphragm pump to pump solvent directly from the solvent carrier vessel to the absorber sump, as shown below in Figure 29.

Figure 28. Secondary nitrogen supply

Figure 27. Original solvent addition vessel

Figure 29: Solvent addition system with diaphragm pump, left, and absorber sump, right.

Steam Injection

Steam is injected into the feed gas for humidification to desired operating conditions. The original injection method used a flow control valve with a coriolis flow meter. The desired level of control on the flow rate was not able to be achieved and the setup was replaced with an orifice plate. The steam flow rate through the orifice is controlled by regulating the upstream pressure with a needle valve. The pressure is monitored through a pressure gage and through the HMI with a pressure transducer, and the complete setup is shown in Figure 30. The calculated steam flow rate through the orifice plate was verified with humidity sensors in the humidified flue gas.

Figure 30: Steam injection system for humidifying feed gas through an orifice plate, right, and HX-120, left.

Heat Exchangers

HX-120

The feed gas is heated to the desired operating conditions by an in-line electric heater. The heater was installed at the same level as the feed gas entrance to the absorber sump. As a result, solvent may reach the electric heater if a system disruption led to a high liquid level in the absorber. The piping and orientation of the heater was changed to raise it approximately two feet above the absorber sump to remove this potential hazard, as depicted above in Figure 30.

Figure 31. HX-230 air vent

HX-230

The lean solvent returning to the absorber from the regenerator is cooled in HX-230, acting as both the crossover heat exchanger and a trim cooler. It was found that entrained air in the process cooling water supply caused irregular and insufficient cooling in HX-230. An automatic air vent, shown in Figure 31, was added to the system just before the process cooling water entered HX-230, and the performance of the heat exchanger improved dramatically.

HX-300

The steam traps installed on the heat exchangers on the bench-scale system were found to operate poorly at the operating conditions of the system. The traps were replaced with more appropriately-sized thermostatic traps that operated much more reliably.

HX-305 and HX-306

The bench-scale system was designed with a pump (P-305) to provide the head to feed both a forced reboiler loop and the solvent circulation to the top of the absorber column. HX-306 operated upstream of P-305 to cool the liquid to an acceptable temperature for the pump gears. The control of this heat exchanger was difficult attempting to maintain a small temperature drop of the solvent with the two inlet streams approximately 100°C apart. In addition, this heat removed from the solvent would have to be added back into the solvent in HX-305 and compensated for in the heat balance of the system. HX-306 and P-305 were removed from the system to alleviate these issues, and the regenerator was pressurized to provide the necessary head to circulate solvent to the top of the absorber. HX-305 was set up as a thermo-syphon reboiler and verified to be able to deliver the necessary heat input to regenerate the solvent.

Figure 32. HX-305 setup as a thermo-syphon reboiler

The steam trap on HX-305 was also replaced with a thermostatic trap that greatly increased the functioning of the heat exchanger. An air vent was added to the top of the heat exchanger to prevent any dissolved gases from the boiler from collecting in the top of the shell and tube heat exchanger, decreasing performance. Finally, the control of the solvent temperature exiting HX-305 was found to be most stable by controlling the steam pressure on the shell side of HX-305. The PID controller was able to respond much faster using this mode of operation as opposed to controlling the outlet solvent temperature.

HX-310

Condensate formed in HX-310 is returned to the top of the regenerator, and a rotameter was added to this line to measure the amount of condensate formed, as shown in Figure 33. This flow measurement allows for improved heat and mass balances regarding HX-310. In addition, a collection vessel was added to this line to allow for condensate collection for analysis and investigating different water balancing techniques.

Figure 33. HX-310 condensate collection vessel.

Heat Balance

Determining the heat balance of the entire system is paramount to successful demonstration of the NAS solvents in the BsTU. Several upgrades were made to the system to ensure the most accurate measurement and analysis. HE-301 was added to the solvent transfer line from the absorber to the top of the regenerator. The tubing from the exit of HE-300 to the top of the regenerator is approximately 50 ft. and, while insulated, was experiencing a significant heat loss and temperature drop. Heat tracing was added to the line and controlled to maintain the temperature following the exit of HX-300.

Multiple sensors were added to the steam system on HX-300 and HX-305 to provide the most accurate measurement of the steam demand of the system, as shown in Figure 34. Pressure transducers were added to both heat exchangers to monitor the regulated pressure of the steam. Thermocouples were also added to measure the condensate temperature at the exit of each heat exchanger. As a result, both the heat of vaporization at the steam pressure and any subcooling of the condensed steam are accounted for.

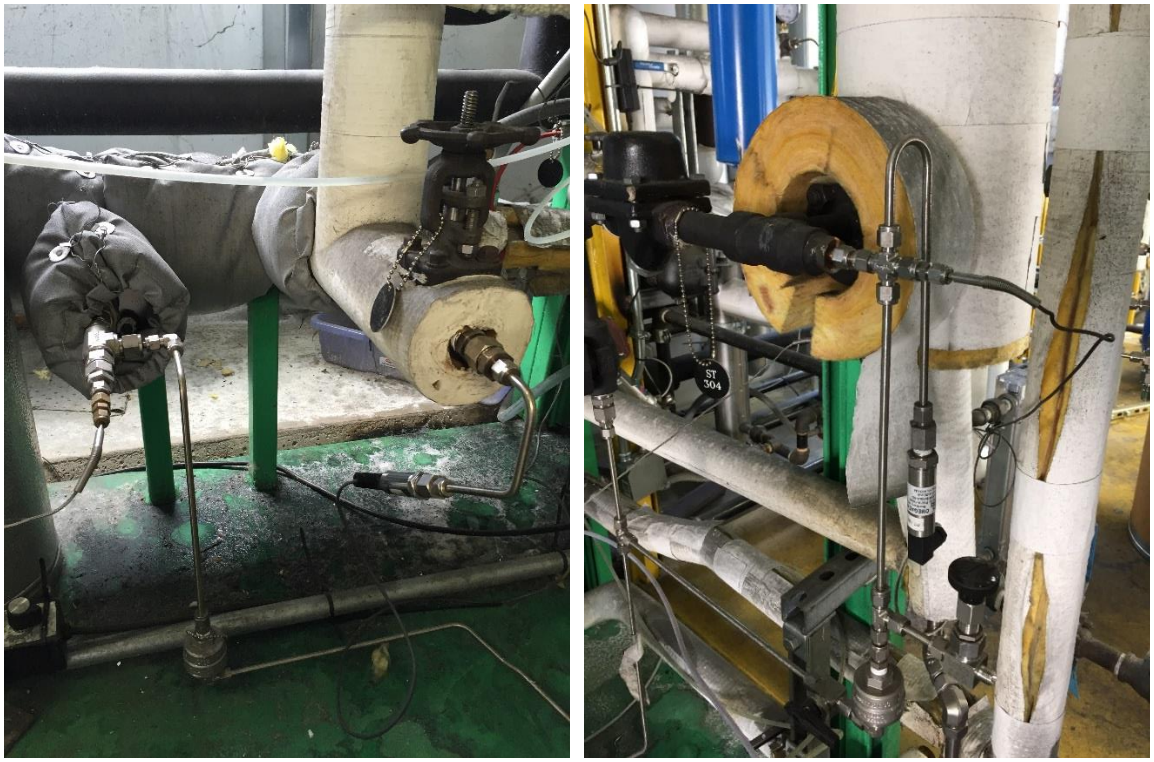


Figure 34: Additional pressure and temperature sensors on HX-300, left, and HX-305, right.

Finally, coolers were added to the collected condensate from HX-300 and HX-305 to allow for accurate measurement of the condensate and prevent any flashing once the condensate is dropped to a lower pressure, as shown in Figure 35. These coolers were installed with rotameters on the cooling water and condensate lines for visual measurement of the flow rates. Initially, this condensate was collected for a specified time period and weighed to record the steam demand. However, it was found that this intermittent measurement did not capture all of the dynamics of the system. A condensate collection tank was outfitted with a pump to automatically drain when full. The collection tank was placed on a balance with continuous weight measurement and recording. This arrangement, shown below, has allowed for continuous, accurate analysis of the steam demand of the system.

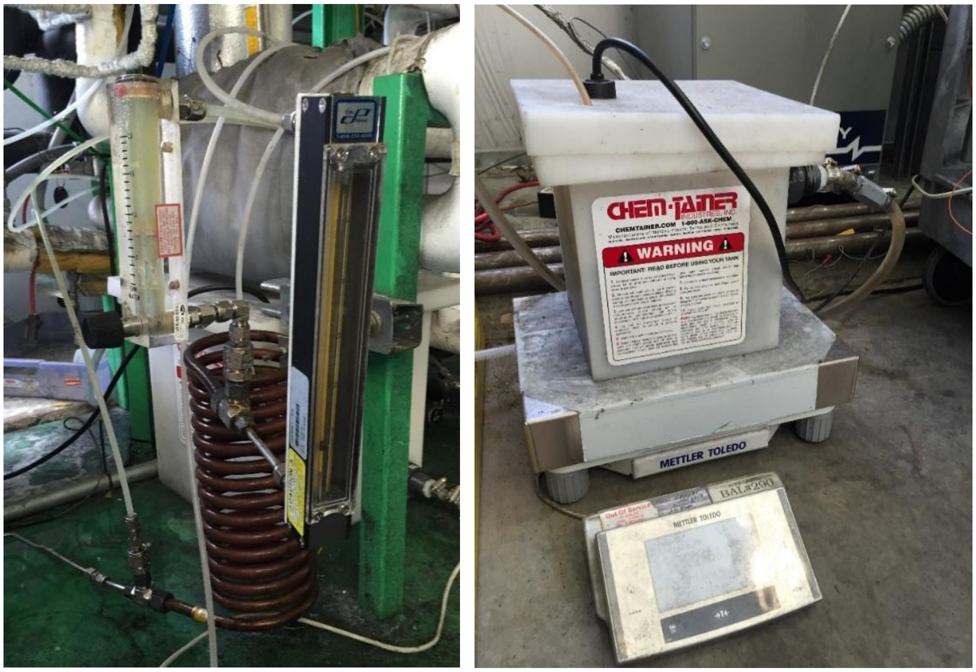


Figure 35. Steam condensate cooler with cooling water and condensate rotameters, left, and continuous condensate weight measurement setup, right.

Liquid Analysis

The liquid flow rate in the system is measured by FT-300, which was calibrated with water during the system commissioning. However, as discussed above, this coriolis flow meter needs the ability to be calibrated during operation of the system. A diverting 3-way valve was added to the solvent circulation loop at the entrance to the top of the absorber. The solvent flow is able to be diverted to a collection vessel for a short time and the collected liquid weighed to calibrate the flow meter during operation.

Liquid samples from BsTU are extracted from the absorber and regenerator sumps and safely fill sample vials via two liquid sampling systems by Texas Instruments. The liquid transfer lines between the absorber sump and sampling box are now heat-traced and insulated to prevent any potential issue of solid formation in the sample line due to a high CO_2 loading in the liquid. The heat-traced line temperature is controlled at 40-50°C via a AC voltage controller. Sample lines running between the regenerator sump and sample box are also insulated, but not heat-traced as liquid from regenerator sump is hot and contains low CO_2, i.e., CO_2-lean solvent.

Figure 37. Heat-traced sample lines running to and from liquid sampling box.

Figure 36: 3-way valve for online calibration of FT-300

Gas Analysis

Inline relative humidity sensors were installed at the absorber gas inlet, absorber gas outlet, and regenerator gas outlet in an attempt to determine the water content in these gas streams. However, the functionality and reading accuracy of the sensors were compromised due to the high temperature and tendency of water condensation in the sensor probe at these locations. These sensors were removed and water content is currently determined by an MKS online analyzer instead.

In the early stage of solvent screening and testing at the Lab-scale Gas Absorber System (LsGAS), we encountered a handful of solvent formulations that induce the formation of solid carbamate salt, a product between CO_2 and amine species in NAS solvent, which hinders the stability and operability of the LsGAS. Level and pressure transmitters used in the LsGAS are installed with N_2 purge taps to prevent plugging caused by the carbamate salt within these transmitters' probes. A small

Figure 38. Flow control panel for N_2 purge taps (Left) and example of N_2 purge tap installation on one of the pressure transmitter (Right). N_2 enters through the horizontal tube at the tee.

amount of N_2 continuously flows through these taps, enters the process, and leaves with the effluent gases from both the absorber and regenerator. Level and pressure transmitters installed in the BsTU adopted a similar setup to prevent any plugging from occurring. However, our recent runs in the BsTU have suggested that N_2 purges were not required and that it created a performance artifact (see Subtask 5.2 for detail). N_2 purge taps are currently disconnected from the system and can be reconnected if needed.


Figure 39. DETCON CO_2 analyzer added to the regenerator effluent

A DETCON CO_2 analyzer was added to a slipstream of the regenerator effluent to provide a secondary measurement of the amount of CO_2 captured and regenerated from the solvent. This slipstream is then diluted with a similar amount of N_2 to fall within the range of the CO_2 analyzer. Without a diluting N_2 flow rate in the regenerator effluent, the CO_2 concentration would be ~100%. The mass flow rate of CO_2 regenerated from the solvent can be calculated from the concentration of CO_2 with the remainder from the known N_2 flow rate to the purge taps at the bottom of the regenerator. Once the N_2 purge taps were removed from the system, another N_2 dilution point was added to the regenerator effluent at the exit of HX-310. This measurement allows for a cross-check of the CO_2 capture rate from the absorber feed and effluent streams.

An online NDIR gas analyzer from MKS has been added to the BsTU to improve the accuracy of the CO_2 concentration measurement at key locations in the process which include (i) absorber gas inlet, (ii) absorber gas outlet, and (iii) regenerator gas outlet. The sample gases are drawn from these locations and fed to a gas sampling panel through heat-traced gas sampling lines. The manual gas sampling valves on the panel allow for a source to feed to the MKS one at a time for compositional analysis. The MKS reading is used for cross-checking the accuracy of the CO_2 concentration obtained from the in-line DETCON CO_2 analyzers at these locations. With this verification, the CO_2 balance of the system can then be accurately determined. The analyzer is also capable of measuring water content in these gas streams at the process conditions, which is one of critical control parameters for a non-


Figure 41. MKS online analyzer connected to BsTU with heat-traced line running from the sample panel.

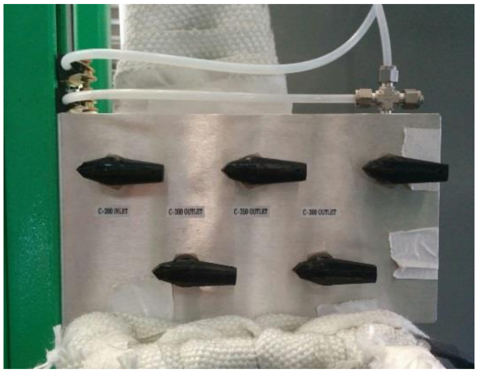


Figure 40. MKS gas sample panel.

aqueous solvent system. The ability to determine water content in a gas stream and circulating liquid allows for the observation of the effect of water content on the solvent's regeneration energy. With this monitoring, the operating conditions can be changed to create water-stripping or water-accumulating modes in order to tailor performance of the system Furthermore, the MKS analyzer is capable of determining organic constituents once proper calibrations for the interested species are established. A separate effort on establishing the method to determine trace amounts of NAS component in the gas streams leaving the system is currently being developed. This will allow for the evaluation of the solvent loss rate due to evaporation from the system, and estimate the economic impact from the solvent make-up as well as compare the emission of this solvent to other similar compounds.

Subtask 5.2 Evaluate Effectiveness of Bench-scale System Modifications

Benchmarking RTI's Bench-scale Testing Unit (BsTU) for CO_2 Capture Process

In this quarter, a set of experiments was performed in the BsTU after the system was fully validated and commissioned. The objective of these experiments was to characterize the operating and regeneration energy windows for the MEA/H_2O CO_2 capture process to establish baseline performance of the system and benchmarking the energy consumption of the system with the data available in literature. Experiments were performed to measure the thermal regeneration energy at specific process conditions as a function of L/G ratios (i.e., working capacity) while maintaining 90% CO_2 capture with more than 95% CO_2 purity. The thermal regeneration energy [kg-steam/kg CO_2] was estimated by performing an accurate mass and energy balance around the BsTU and, more specifically, the Solvent Regenerator (C-300). Since low-pressure steam is used exclusively in the system to provide heat, the amount of heat delivered to the system can be determined by collecting the steam condensate from the respective heat exchangers over a period of time while the system is operating at a steady state at the desired operating conditions and measuring the steam conditions. This approach measures the total heat load of the regenerator, including not only the solvent regeneration energy but also the heat lost to the environment, which can be significant for small experimental systems. Proactive measures have been taken to minimize heat losses, including thoroughly insulating the entire system, and additional measures have been taken, including the addition of thermocouples on external surfaces to improve estimating/ characterizing the rate of heat loss. Accurately determining heat losses is not a trivial task. Our approach to estimate the heat losses was operating the system at different total gas and liquid flows conditions while maintaining a constant L/G ratio. The total amount of energy consumption via condensate collection (E_{total}) in each case was compared assuming the heat loss is constant, and the increase in energy consumption at higher total flow is only attributed by the increase in regeneration energy. Hence, the heat loss can be determined by the following simple set of equations:

At low total flow condition:

$$E_{regen,low} + E_{loss} = E_{total,low} \tag{1}$$

High total flow condition, assuming flow rates are doubled:

$$E_{regen,high} + E_{loss} = E_{total,high} \text{ where } E_{regen,high} = 2E_{regen,low} \tag{2}$$

Although this approach provides a single point of measurement and heat loss can vary due to changes in ambient temperature, it improves the quality of the energy consumption data significantly. Once the amount of heat lost to the environment was accurately accounted for, the remaining contributors to the mass and energy balance were quantified by process measurements including flow rates, temperatures, pressures, and composition, all of which are included in the BsTU design.

The long-term testing of the BsTU was performed by operating the system to achieve a steady state at a targeted L/G for at least 1 hour prior to evaluating the steam consumption around the regenerator. The test spanned over 5 days with 3 operators on day-shift and 2 operators on night-shift to maintain the continuous operation of the system. Analytical techniques were developed to determine amine content, water content, and CO_2 loading for MEA/H_2O samples. Liquid samples collected from absorber and regenerator were refrigerated until the time of analysis to minimize CO_2 desorption from the samples. The testing sequence and operating condition run during the long-term test is present in Table 9:

Table 9. Operating parameters of BsTU during long-term testing of MEA/H_2O for CO_2 capture.

		L/G						
	unit	**3.20**	**3.17**	**3.20**	**2.18**	**1.92**	**1.71**	**1.54**
Liquid Flow Rate (L)	kg/min	1.50	1.13	0.75	0.51	0.45	0.40	0.36
Gas Flow Rate (G)	SLPM	350	265	175	175	175	175	175
Feed Gas Composition		13-15% CO2, 5-8% H_2O, bal. air						
Feed Test Temp.	°C	60						
Abs. Temp.	°C	40-75						
Regen. Temp.	°C	100-130						
Regen. Press.	bar, g	1.50						

The steam consumption at different L/G ratios extracted from the long-term run and predictions from a Promax® simulation are present in Figure 42. This V-shape characteristic curve of the energy consumption for regeneration of MEA/H_2O system has been well-established and reported in the literature[1]. The high steam consumption at low L/G ratio is due to the fact that the separation in the regenerator becomes difficult. Steam consumption shows a linear increase as L/G increases due to the excess water vapor that is generated during CO_2 desorption. The low deviation observed on steam consumption at L/G of 2.4-3.4 indicates that the results are highly reproducible. The results obtained from the run show that the V-shape trend has shifted left relative to the simulated result which is due to a reading deviation from the liquid flow meter, as the meter was calibrated using pure water rather than the mixture of 30% MEA in water. The steam consumption values, once compensated for heat losses show good agreement with the Promax® simulation.

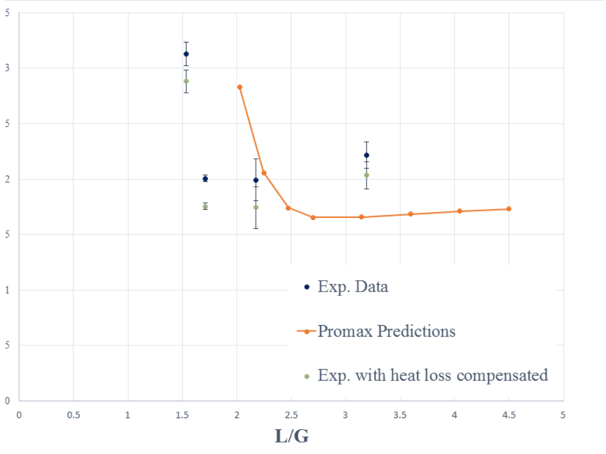


Figure 42. Steam consumption at different L/G ratio for MEA/H_2O system from long-term testing and the projected result from Promax® simulation.

Initial runs of non-aqueous solvent (NAS) in the BsTU

Effect of Process Configuration

After the completion of benchmarking and characterizing RTI's BsTU with conventional MEA/H_2O, MEA/H_2O was removed from BsTU and the in-house developed NAS solvent was loaded into the process. The initial testing of the NAS was performed under the same process configuration as that was tested during MEA/H_2O benchmark. The L/G ratio for NAS run was significantly larger than that of MEA/H_2O in order to achieve 90% capture based on our test using Lab-scale Gas Absorption System (LsGAS, see Q6 report). However, the system was not able to achieve 90% capture efficiency due to the lack of a CO_2 stripping agent and a reduction in the temperature of the regenerator column during the operation. In the MEA/H_2O system, the abundant water component (70 wt%) in the solution produces a sufficient amount of steam, which acts as a stripping agent during the solvent regeneration. In the case of NAS solvent, the water only attributed up to 5 wt% and does not produce a sufficient amount of steam to be used as a stripping agent as in MEA/H_2O scenario. The reduction in regenerator temperature was also due to the lack of steam rising through the column and condensing to maintain a proper regeneration temperature in the NAS run. As a result, the colder regenerator led to the re-absorption of regenerated CO_2 by NAS that was fed at the top of the column and reduced the overall capture efficiency of the process.

To circumvent the lack of a CO_2 stripping agent issue, the process configuration was altered such that the reboiler (HX-305) has become a secondary heater after the regenerator pre-heater (HX-300) as shown in Figure 43. The tube run from the outlet of HX-305 to the top of regenerator is heat-traced to prevent heat losses and the re-absorption of CO_2. This process configuration allows the solvent to be heated and maintain the temperature until the solvent enters the regenerator column. A two-phase flow of desorbed CO_2 and NAS is present after solvent is heated by HX-305. The CO_2 is then released at the top of regenerator while NAS solvent flows downward and continues desorbing CO_2, cooling down along the way to the bottom of C-300. This modified process configuration resulted in the system maintaining 90% capture efficiency during our brief session of testing shown in Figure 44. Note that the total gas flow during the NAS run was substantially lower than that of MEA/H_2O due to the limitation in liquid flow rate that the absorber transfer pump P-200 can produce. A replacement pump with larger flow capacity was later installed and operated to increase the liquid flow rate.

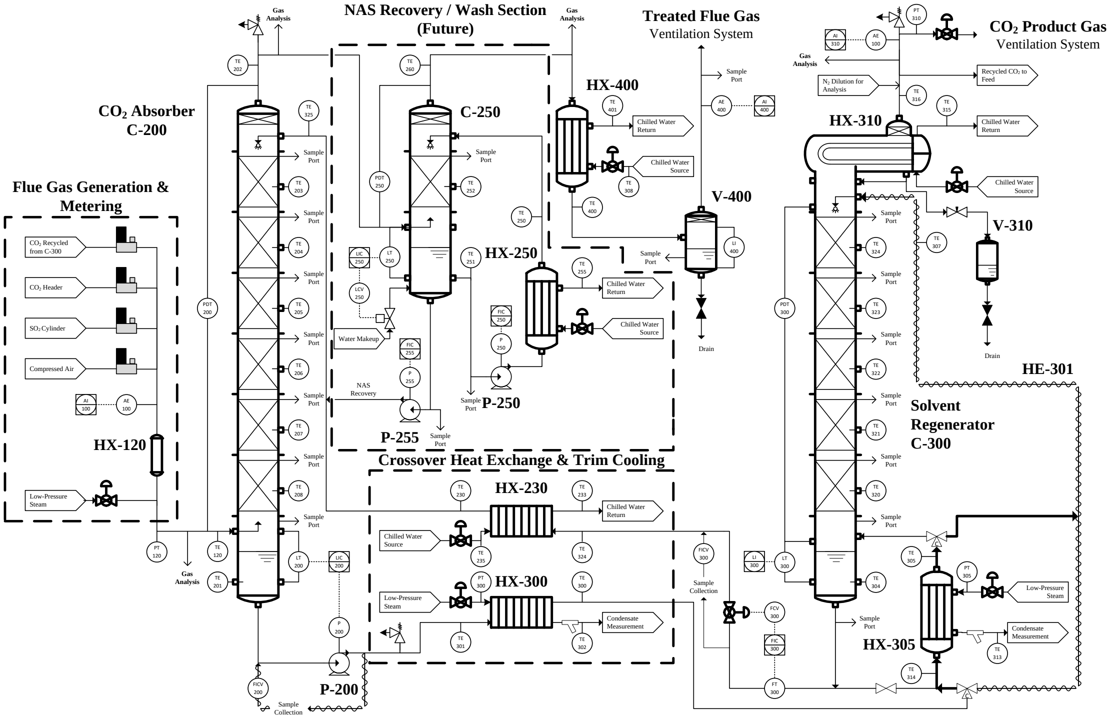
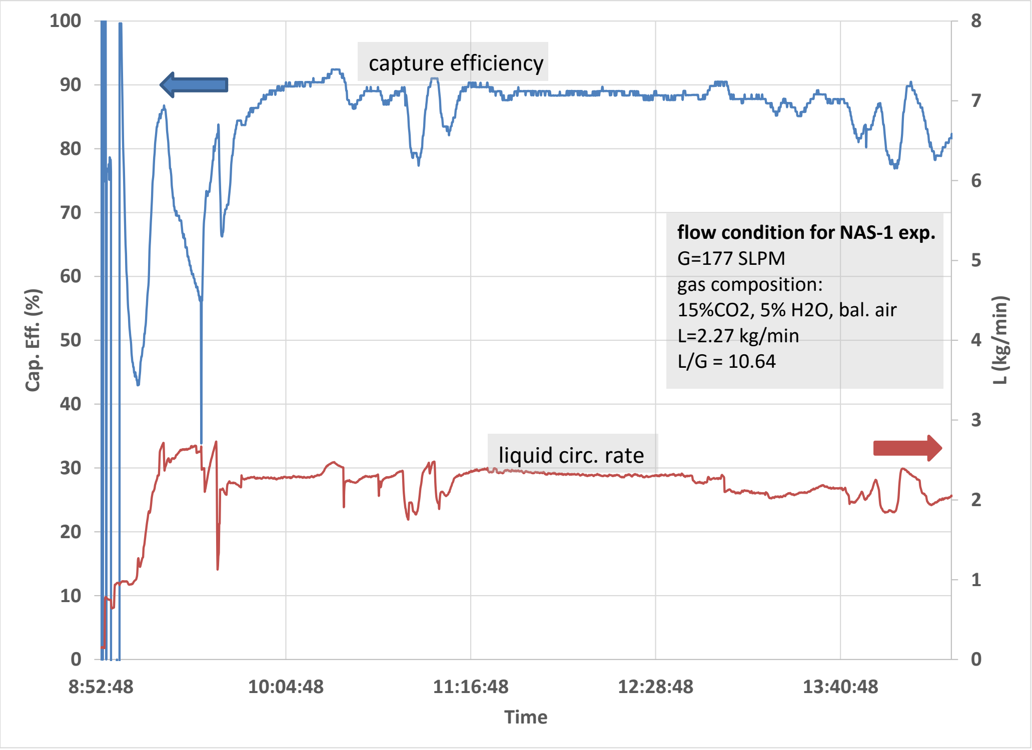


Figure 43. A BsTU with a modified process configuration to have a secondary heater after the solvent pre-heater (flow path bolded). The outlet of HX-305 is heat-traced and temperature controlled to prevent the re-absorption of CO_2 during the solvent transfer to regenerator.



flow condition for NAS-1 exp.
G=177 SLPM
gas composition:
15%CO2, 5% H2O, bal. air
L=2.27 kg/min
L/G = 10.64

Figure 44. CO_2 capture efficiency of NAS with the modified HX-305 as secondary heater.

Effect of N_2 Purges

The N_2 purges to the level and pressure differential transmitters at the base of each column were closed off during the NAS run. The combination of the N_2 purge among these transmitters are set to a total of 3 SLPM to each column during the MEA/H_2O benchmark run. The purpose of N_2 purging is to ensure reading accuracy by preventing the liquid backflow and being trapped in the transmission probes connected to the process. In addition, trapped solvent may precipitate solids depending on the process and ambient conditions and could plug the lines. The introduction of the N_2 purges to these devices causes dilution in the feed gas to the absorber and also the regenerated CO_2 in the regenerator. The effect of these purges does not cause a substantial deviation in process control and performance under high gas flow conditions such as those observed during the MEA/H_2O run (i.e., 175-350 SLPM of total absorber feed gas vs. 3 SLPM N_2 purge). However, the effect of N_2 dilution can create an artifact that complicates the performance evaluation under low gas flow conditions, especially in the regenerator column where CO_2 is the only gaseous species flowing out of the column (i.e., 15-22 SLPM regenerated CO_2 vs. 3 SLPM N_2 purge). The presence of N_2 purge in the regenerator could significantly dilute the regenerated CO_2 by 15-20% which is undesirable as the N_2 dilution causes the CO_2 partial pressure to reduce and artificially aides the CO_2 desorption from the solvent in the regenerator column.

A brief verification of the effect of N_2 purges on the regenerator was explored in a separate test with the result shown in Figure 45. We observed that NAS achieved 90% capture efficiency in the presence of N_2 purge of 3 SLPM to the regenerator column. Assuming 90% of the CO_2 being captured from absorber and released in the regenerator, we have roughly 20 SLPM of desorbed CO_2. The presence of the N_2 purges resulted in 20% dilution of the regenerated CO_2 stream. This dilution promotes the conversion of carbamate species in NAS to gas phase CO_2 based on the vapor-liquid equilibrium for this particular solvent. The N_2 purge taps were turned off in the second part of this experiment and NAS circulation rate was increased from 1.4 to 1.9 kg/min in anticipation of the reduction in capture efficiency. The efficiency dropped to 72% and the system was not able to regain the 90% capture efficiency despite the increase in liquid circulation rate.

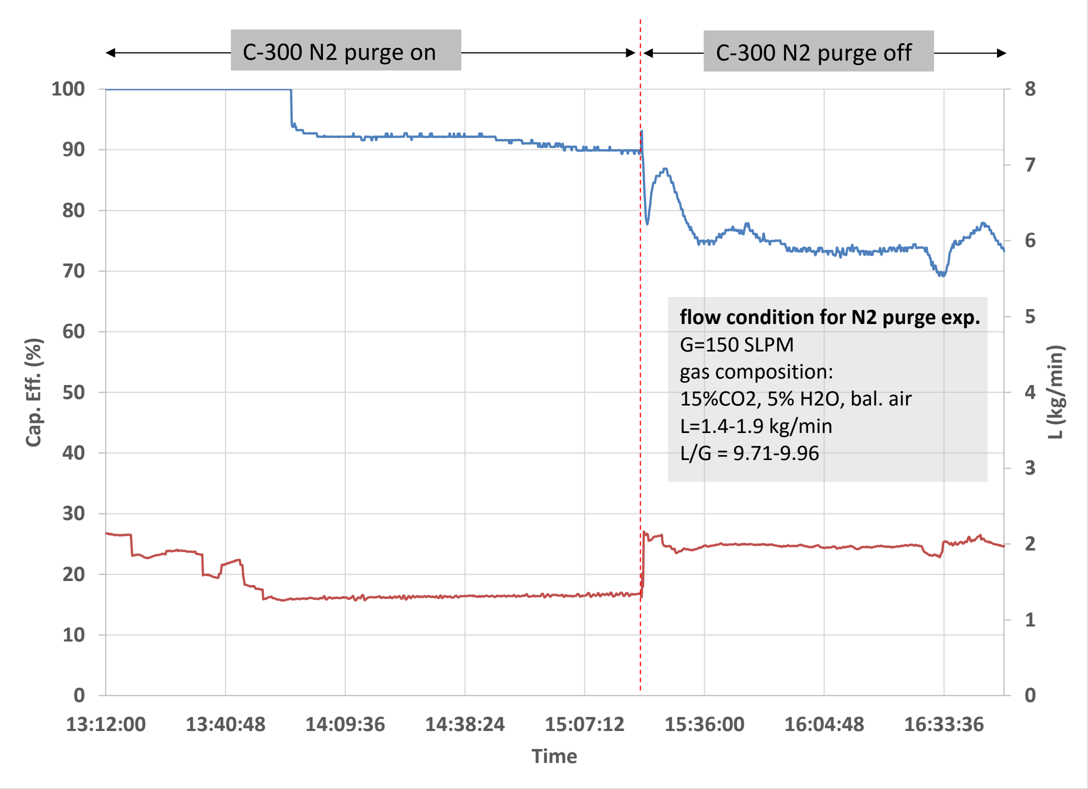


Figure 45. CO_2 capture efficiency under the presence and absence of N_2 purge at the regenerator (C-300).

The results from this initial evaluation of NAS solvent in the BsTU should not be judged too critically without knowing the context of the project and should not be interpreted as overly negative regarding NAS performance. As mentioned above, this round of NAS testing in the BsTU was performed using a NAS formulation which was simultaneously being shown to suffer from significant amine oxidative degradation could have been a contributing factor to the lower absorption capacity of the solvent because the solvent was loaded, stored, circulated, and operated in the BsTU for several months during the evaluation. Subsequent testing with a modified formulation was able to achieve 90% capture without the incorporation of nitrogen purges associated with the regenerator.

The performance of the NAS process during the start-up and initial operation of the bench-scale test unit shows the importance of having multiple solvent formulations if possible. Testing was conducted in Q8 using one of the other solvent formulations and which achieved the 90% capture efficiency goal. N_2 purges were removed from the BsTU to ensure that realistic performance of the solvent was acquired. To circumvent liquid backflow in these taps, the revised start-up procedure included inspecting and draining the transmitter taps as routine to ensure the proper reading for column sump levels and pressure drop across the columns. The start-up experience described above was a point of learning for the team and should not be taken outside of the context.

The BsTU demonstrated that stable operation without major upsets and on-target CO_2 capture could be achieved during the MEA/H_2O benchmark run. The energy consumptions obtained under various L/G ratios agree well with literature. NASwas initially tested to evaluate the performance and operability of the BsTU with the NAS solvent. The solvent was able to achieve 90% capture under the presence of N_2 purges. However, the capture performance dropped after the N_2 purges were turned off. This was likely due to degradation of the amine being utilized in the NAS formulation. The amine composition was changed and subsequent testing in Q8 showed that 90% capture could be achieved and maintained without process interruption with the revised NAS formulation.

Subtask 5.3 – Parametric Testing Campaign

During Q11 parametric testing in the bench-scale test unit (BsTU) using NAS solvent was completed. Testing was performed to evaluate the performance of the solvent at different L/G ratios. It was reported in quarterly reports that operation of the stripper in the bench-scale unit with NAS has used a flash configuration as opposed to a conventional configuration (i.e., utilizing a reboiler), as is used for the state of the art aqueous solvents. A block flow diagram depicting the system configuration is shown in Figure 46. The experimental results are described below.

In March of 2016, over 100 hours of “dry” testing was completed with the NAS process showing promising steam consumption rates. In April a subsequent 100 hours of CO_2 capture using NAS in the presence of water in the flue gas was performed. For the “wet” run, water was introduced to the simulated feed gas through the addition of steam through an orifice plate to mix with the preheated simulated flue gas. A series of testing conditions were evaluated to determine the effect of water to the regeneration heat duty and process control. The total gas flow was held constant at 100 SLPM with 15.4% $CO_{2,}$ 7% H_2O and a balance of air in runs 2-12. Dry feed gas was used in run 1 to establish the baseline for this series of testing before water was introduced. CO_2 capture in all testing conditions was controlled at 90 ±1%. The system was held stable at each condition for at least 2 hours to obtain steady state heat duty data.

The heat loss to the environment was determined in separate experiments by circulating the NAS in the system without feeding the CO_2 in the gas stream. The system was operated such that the solvent entered the absorber and was uniformly held at 100°C and 110°C throughout the regenerator until exiting. The heat loss to the environment is then subtracted from the total heat duty in each run.

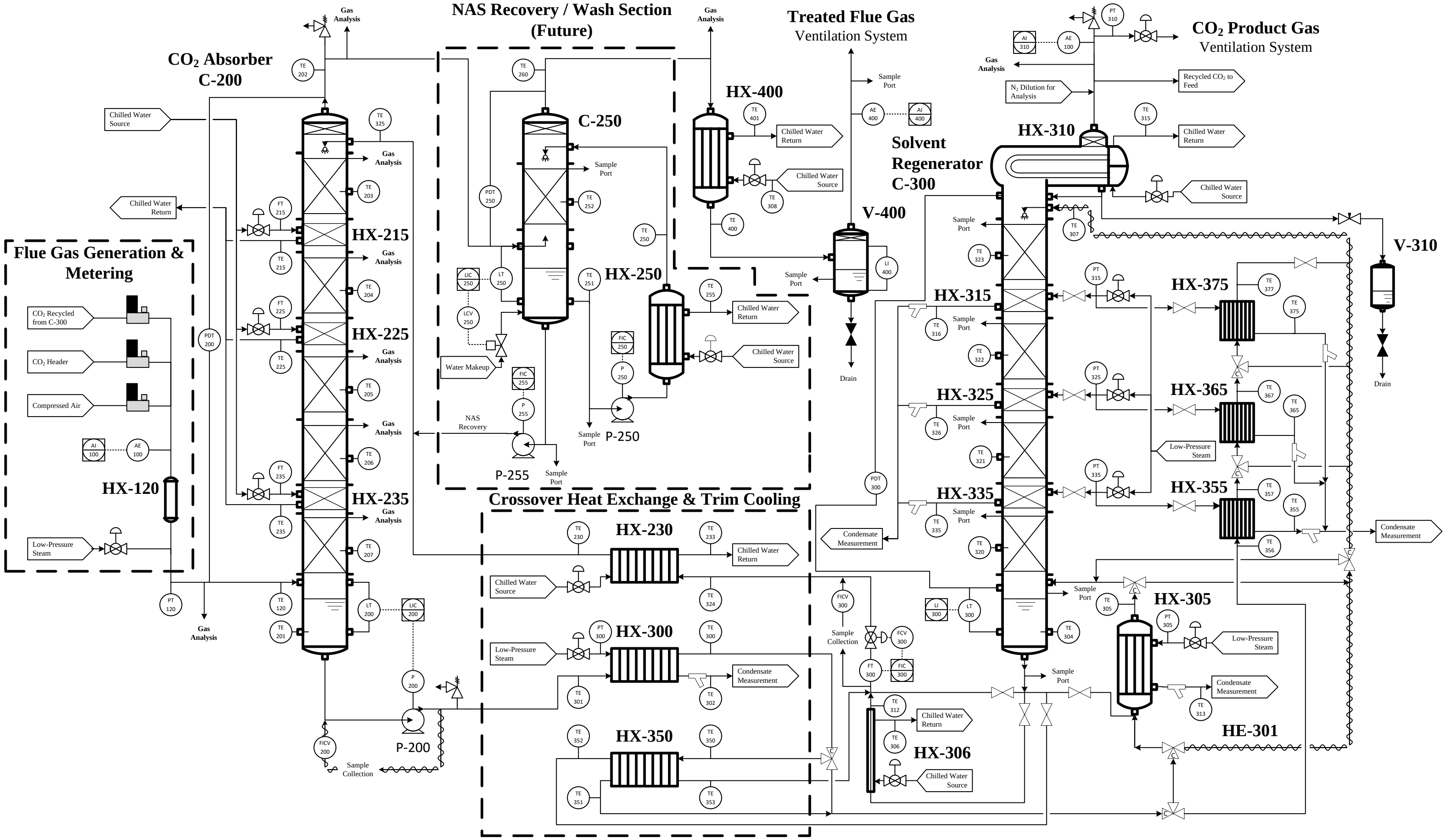


Figure 46. Block Flow Diagram of the Bench-Scale Unit with heat exchanger installations and interstage column heaters and coolers.

Effect of Water

Water was introduced to the feed gas during the transition from run 1 to run 2. The accumulation of water in the NAS can be seen in this period in Figure 47 from 5 hr to 35 hr. The NAS slowly absorbed water and showed relatively stable water content of 6-8 % throughout the rest of the 100 hour test. Once the water was introduced to the system, the water content in the NAS was controlled at approximately 7 wt% throughout the run, near the saturation point of the solvent.

Figure 47. Water content in NAS during the extended test run.

A portion of the gas analysis conducted on the BsTU testing is shown below in Figure 48. There are a number of online gas analyzers on the unit as well as one MKS FTIR Multigas Analyzer that is manually selected to which gas stream it analyzes. The background colors denote the stream that the MKS is analyzing. For instance, on the left side of the figure, the area with the yellow background is the feed gas into the absorber (C-200). The medium blue line near the top of the figure shows the measured CO_2 signal which is approximately 15.9%. The light blue line near the middle of the figure shows the measured H_2O signal, which is approximately 7%, and nearly on top of the dashed yellow line that denotes the saturation point of the feed gas. This indicates that the inlet relative humidity is maintained approximately between 95% and 100%. An indication that the system is water balanced is shown by a similar 7% H_2O contained in the absorber effluent shown in the right side of the figure with the purple background. The saturation point of the absorber effluent is indicated by the dotted red line which is near 8.5%. This figure shows that the outlet relative humidity is maintained near 80-85%. From throughout the tests, it became clear that the largest controller of the system water balance was the solvent temperature into the top of the absorber, and as a result the temperature of the gas out of the absorber. The amount of water in the solvent was able to be controlled effectively in the tests by raising or lowering the absorber outlet temperature to achieve the variations seen in the times greater than 50 hr in Figure 47.

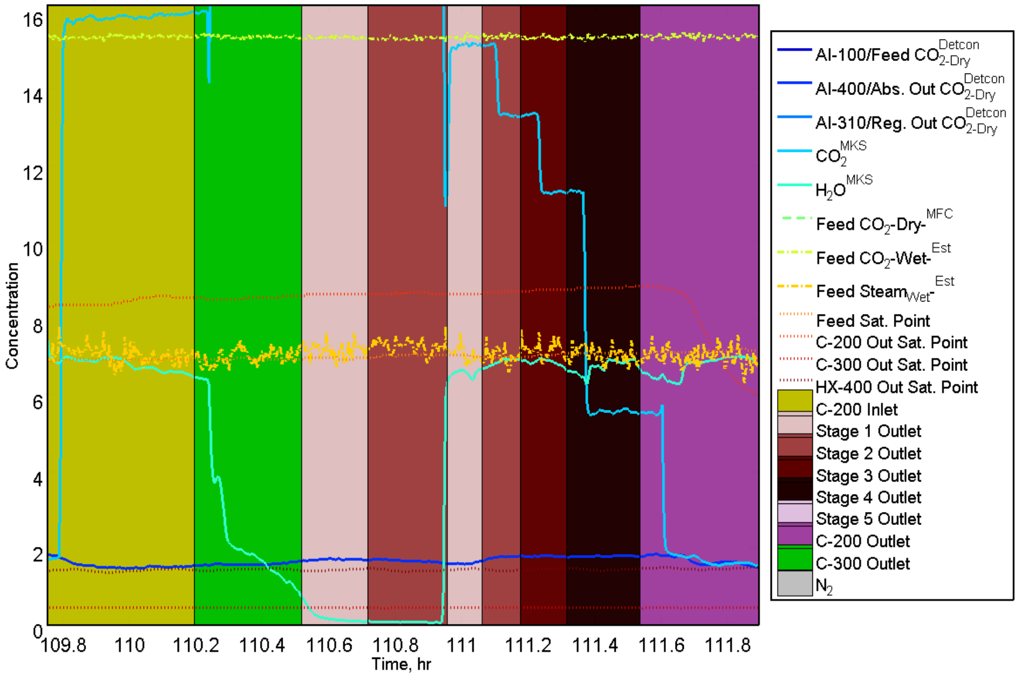


Figure 48. Gas analysis from various points in the BsTU system.

Reboiler Heat Duty

The regenerator heat duty is made up of three terms as shown below in Equation 1. The motivation for using NAS is to reduce the overall regenerator heat duty. The heat of vaporization term is reduced to near zero, and the heat of reaction of the NAS is significantly less than that of aqueous MEA solvents. In addition, the specific heat is significantly reduced from that of aqueous solvents.

$$\mathbf{q_R} = \left[\frac{\mathbf{C_P(T_R - T_F)}}{\boldsymbol{\Delta\alpha}} \cdot \frac{\mathbf{M_{sol}}}{\mathbf{M_{CO_2}}} \cdot \frac{\mathbf{1}}{\mathbf{x_{sol}}}\right] + \left[\boldsymbol{\Delta}\mathbf{H_{V,H_2O}} \cdot \frac{\mathbf{p_{H_2O}}}{\mathbf{p_{CO_2}}} \cdot \frac{\mathbf{1}}{\mathbf{M_{CO_2}}}\right] + \left[\frac{\boldsymbol{\Delta}\mathbf{H_{abs,CO_2}}}{\mathbf{M_{CO_2}}}\right] \quad (1)$$

Regenerator Heat **Sensible Heat** **Heat of Vaporization** **Heat of Reaction**

Table 10 shows the running conditions and the measured heat duty for CO2 regeneration at each condition. The energy required for regenerating CO2 under dry conditions (i.e., run 1) was determined to be 2.4 MJ/kg-CO2. This establishes the baseline performance for the dry running condition and further compares this value to the rest of the runs. This estimate matches previous measurements from the 100 hour test campaign performed in March 2016.

A number of observations could be made from the differences in the presence of water in Run 2 as compared to Run 1 with no water. The liquid circulation rate dropped significantly from 8 to 6.6 while the capture efficiency remained at 90%. This could suggest the positive impact water has on enhancing mass transfer of CO_2 in the bulk of the liquid due to the lower viscosity of the solution. In addition, the presence of water has indicated a potential increase in reaction kinetics, either through a potential change in the reaction pathway, or increased mass transfer rates in the solvent with a decreased viscosity. With the improved capture performance of the solvent in the presence of water, the regeneration temperature was maintained the same and the L/G reduced to maintain 90% capture. Run 3 was conducted at the same L/G as Run1 and indicated that the presence of water may shift the regeneration temperature required to a lower value. As a result, there was also a small reduction in the regeneration heat duty from 2.4 to 2.3 MJ/kg-CO_2 with the addition of water in the flue gas. A comparison of the measured heat duty required for regeneration is shown in Figure 49.

Run 1 and a previous dry run from earlier in April are shown in orange. Runs 2, 3, 4, and 6 were implemented to construct the correlation between the heat duty and L/G in the presence of water and are shown in light blue. The minimum point on the curve determines an optimum L/G ratio where the heat required for regeneration is lowest. Low L/G values will cause a high energy penalty because of the deep stripping of CO_2 from the solvent that is required in the regenerator (i.e., large increase in the third term of the eq. (1)). On the other hand, high L/G values will also increase in the regeneration energy due to the increase in sensible heat requirement, the first term of eq. (1). The addition of water to the flue gas appears to shift the NAS performance to lower L/G ratios and lower heat duty values as compared to the dry runs.

Table 10. Summary of experimental conditions tested during the extended test run of NAS under the presence of water in flue gas stream.

					absorber					regenerator				
run no.	parameters	Reg. Pressure (barg)	L/G Ratio	L (kg/min)	Inlet NAS Temp. at Abs. top	top interstage cooler	middle interstage cooler	bottom interstage cooler	Abs. Sump Temp	top interstage heater	middle interstage heater	bottom interstage heater	Reg. Sump Temp	Heat Duty (MJ/kg CO2)
1	determine optimal L/G - dry	1.5	8.0	0.97	33-35	37	37	37	40	105	110	115	115	2.4
2	effect of water - steam requirement	1.5	6.6	0.78	33-35	42	38	38	40	105	110	115	115	2.8
3	L/G = 8	1.5	8.0	0.97	33-35	42	38	38	40	97	101	104	105	2.3
4	L/G = 10.5	1.5	10.8	1.27	33-35	42	38	38	40	92	96	98	100	2.2
5	reg. pressure	2.75	10.8	1.27	33-35	42	38	38	40	110	115	120	120	2.7
6	L/G = 14	1.5	14.0	1.7	33-35	37	37	37	37	88	91	94	95	2.4
8	Abs. sump. At 36 C	1.5	9.5	1.12	37-39	42	38	36	36	92	96	98	100	2.08
9	Reg. sump at 105 C	1.5	7.6	0.9	37-39	40-42	38	36	36	93	98	100	105	2.18
10	38% amine	1.5	6.7	0.82	37-39	40	37	36	38	93	98	100	105	2
11	38% amine with Reg. sump at 100 C	1.5	8.4	1.01	37-39	39	37	36	38	90	95	98	100	2
12	38% amine - Abs. sump at 36 C	1.5	8.1	0.98	37-39	39	37	36	36	90	95	98	100	1.9

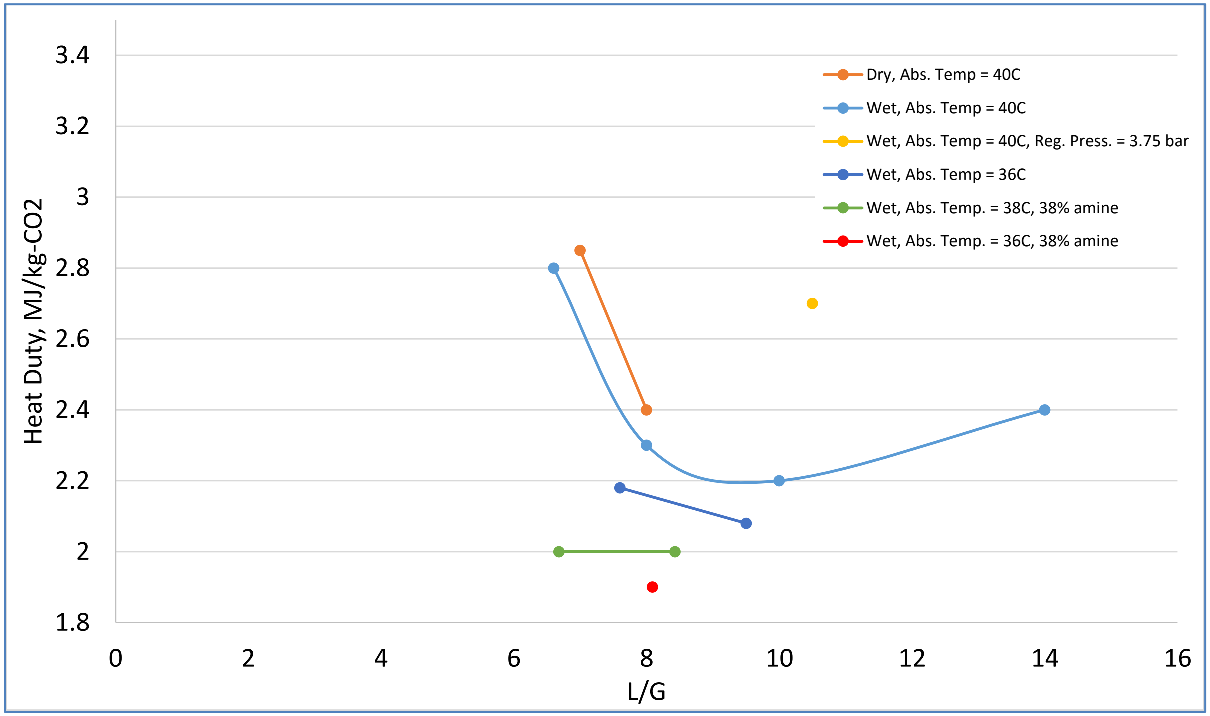


Figure 49. L/G vs. regenerator heat duty results from extended test run.

The performance curve produced by the NAS shifts to higher L/G values and lower heat duty values relative to a conventional aqueous MEA system. This suggests that although the NAS requires higher liquid circulation rates than that of MEA, NAS still exhibits an overall lower heat duty due to the substantially lower heat of absorption between CO_2 and amine component in its formulation.

In order to further lower the regeneration heat duty, the absorber sump temperature was lowered to 36°C in Runs 8 and 9. These runs are shown as dark blue in Figure 49. This change in absorber sump temperature appears to further shift the NAS performance curve to lower L/G ratios and lower heat duty values. To compensate for an increased amount of water condensing from the flue gas due to the colder section at the bottom of the absorber, the temperature of the solvent entering the top of the absorber was increased to raise the temperature out of the absorber to keep the system water balanced. This method was effective and the system maintained near 7 wt% water in the NAS during the tests.

The amine concentration in the NAS was then increased to 38% from 36% following Run 9. The absorber sump temperature was increased back to 40°C to ensure no solids were formed in the rich NAS, and two different L/G ratios were investigated in Runs 10 and 11. Each condition estimated a regenerator heat duty of approximately 2 MJ/kg-CO_2. Finally, the absorber sump temperature was lowered to 38°C and the regenerator heat duty was found to reach 1.9 MJ/kg-CO_2.

Temperature Profiles

Temperature profiles obtained from the Run 12 were plotted with those obtained from MEA/H_2O system for comparison in Figure 50 and Figure 51 for absorber and regenerator, respectively. Noted that the MEA/H_2O runs were performed at the near optimal L/G of 3.9 with the heat duty reported for both of these runs at 3.5-4 MJ/kg-CO_2. From these results, it is obvious that both columns were run at significant lower temperature compared to MEA/H_2O. The NAS rich loading is sensitive to the absorption temperature as the equilibrium loading changes rapidly in the lower temperature range between 30-60 °C. Operating the absorber at the lower temperature increases the rich loading and, subsequently, lowers the regenerator temperature as the solvent does not require deep stripping to maintain its working capacity. The low absorber temperature also limits the solvent loss via evaporation and carry-over which may reduce the solvent makeup rate and lower emission from the process.

The MEA/H_2O system utilizes steam generated from its solution in the regenerator to assist the CO_2 stripping and facilitate the CO_2 removal from the column. The steam is produced by operating regenerator at near boiling point or over saturated temperature of the MEA/H_2O solution (Figure 51). While the steam is required for MEA/H_2O CO_2 stripping process, NAS system appeared to require insignificant amount of steam to facilitate the CO_2 removal from the rich solvent given that the solvent itself contained only 7wt% water. This is also evident by much lower temperature in the regenerator column and the operating condition was far from the boiling point of water while the system was capable of maintaining 90% capture efficiency.

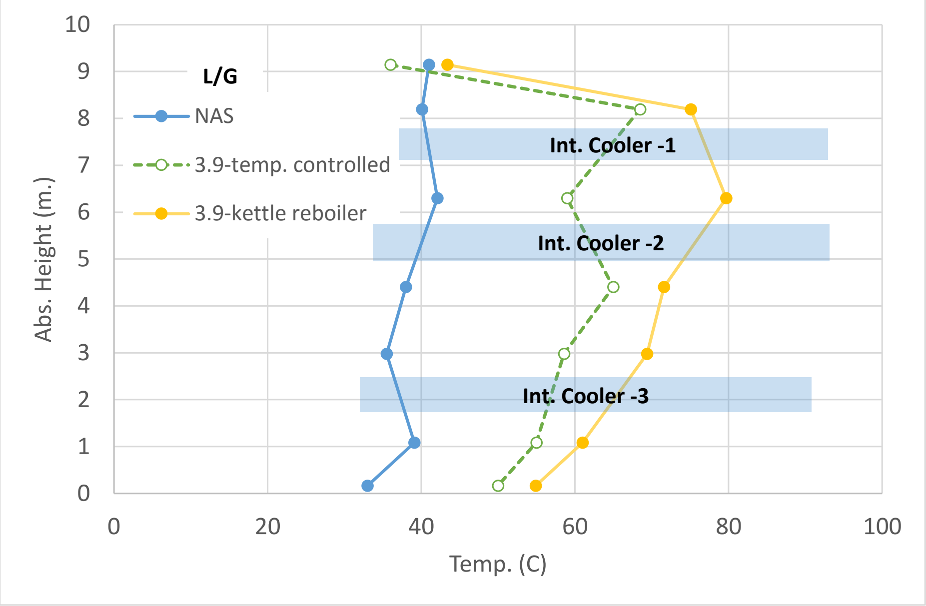


Figure 50. Comparison of the absorber temperature profiles of NAS run (run 12, solid blue line), separate MEA/H_2O solvent runs at L/G of 3.9 with interstage coolers (green dashed line) and regenerator operated in the kettle reboiler mode (solid yellow line).

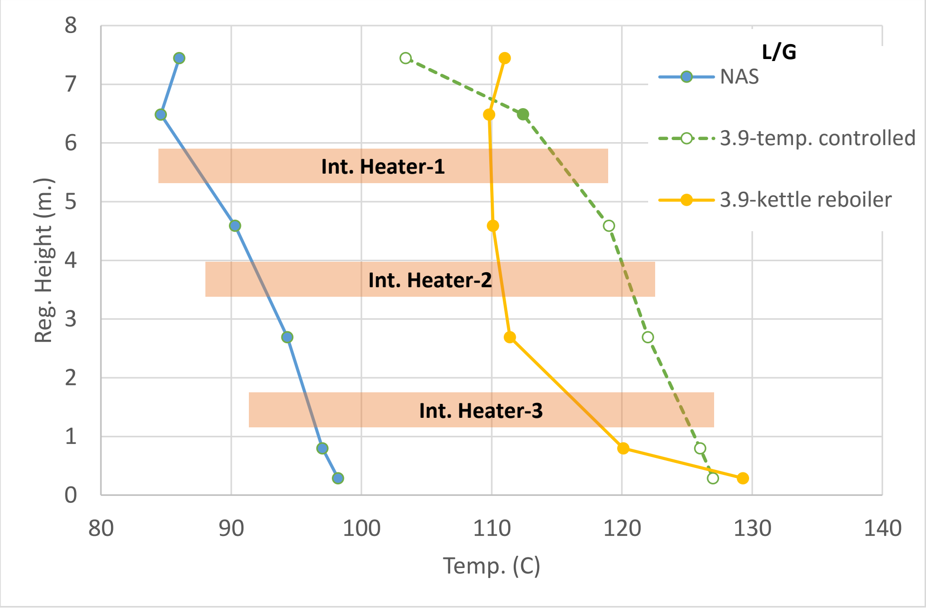


Figure 51. Comparison of the regenerator temperature profiles of NAS run (run 12, solid blue line), separate MEA/H_2O solvent runs at L/G of 3.9 with interstage coolers (green dashed line) and regenerator operated in the kettle reboiler mode (solid yellow line).

Absorber Concentration Profile

Figure 48 above shows the gas analysis of the system during Run 10. The MKS gas analyzer was used to investigate the concentrations of CO_2 and water throughout the absorber column. The gas at the top of each stage was sampled during the run as indicated by the different shades of the background in the figure. A summary of the concentration profiles and temperatures of each stage are shown in Table 11. The outlet of the absorber is from the top of Stage 5. There are interstage coolers in between Stages 1 and 2, 3 and 4, and 4 and 5. It was demonstrated earlier in this project that the NAS requires interstage cooling to control the temperature of the column due to the low specific heat of the solvent. As a result, cooling the solvent coming into the top of the absorber alone would require prohibitively cold temperatures to maintain the sump temperature near 40°C. Water is maintained near 7% throughout the absorber, and the majority of the CO_2 is captured near the top of the column in Stages 4 and 5.

Table 11. Summary table of temperature and concentration profile in the CO_2 absorber column during run 10

	CO_2	H_2O	Temperature
Feed	15.9	6.8	40.0
Stage 1	15.2	6.6	36.0
Stage 2	13.3	6.9	40.3
Stage 3	11.3	6.9	36.8
Stage 4	5.55	6.9	43.8
Outlet	1.60	7.0	43.4

Regenerator Pressure

A significant cost contribution in CO_2 capture process comes from the compression step after CO_2 is captured. Especially the first stage compression that rises the CO_2 pressure from near ambient to approximately 3.5 bar. Thus, it could benefit the economic aspect of the capture process if the CO_2 could be regenerated at higher pressure to reduce the compression cost in the downstream process. The NAS are much less sensitive to pressure than aqueous MEA solvents, and may be able to effectively regenerate CO_2 at higher pressures. The effect of regeneration pressure was examined by comparing Runs 4 and 5. The L/G ratio of these two runs are fixed at 10.5 while maintaining the same absorber temperature. The regenerator pressure was set at 2.5 and 3.75 bar for Runs 4 and 5, respectively. The regenerator temperature was adjusted to achieve 90% CO_2 capture. Raising the regenerator pressure caused the heat duty to increase from 2.2 to 2.7 MJ/kg-CO_2. Further tests are required to determine the optimum operating point at higher pressures, but it can be estimated that it will lead to approximately a 0.5 MJ/kg-CO_2 increase as opposed to operation at 2.5 bar. A preliminary assessment on economic impact on the CO_2 capture process with CO_2 regenerated at 3.75 bar will also need to be determined to weigh the compression costs saved against the increased regenerator heat duty.

Revalidation of BsTU with Aqueous MEA solution

It is known that the minimum energy requirement for CO_2 regeneration using the MEA solvent system is about 3.5 MJ/kg-CO_2 at L/G ranges between 4-4.5. The energy requirement increase significantly if the system operates outside of this L/G range. With its known energy requirement characteristic, 30% wt monoethanolamine (MEA) solution was used to revalidate the heat loss of BsTU to ensure the accuracy of the heat duty obtained for NAS. The heat loss determination using MEA/H_2O solution was performed in similar manner as that of NAS where the regenerator was maintained at a uniform temperature of 100, 120, 125, and 130 °C while the lean MEA solution was circulating throughout the system. The heat loss measurement was evaluated for NAS at 100, 112, and 120 °C. The condensate collection during the heat loss determination at different temperature from both NAS and MEA solutions are provided in Figure 52. In general, the condensate rate increases with higher temperature of the column and correlates well together. Though the liquid circulation rate and type of solvents were varied among these runs, it is worthwhile to note that the heat loss (i.e., condensate rate) appears to be independent from these two parameters. Examples are shown when maintaining the regenerator at 100 and 120 °C. Both NAS and MEA/H_2O shows a similar heat loss of 17 and 25 g/min for each temperature, respectively.

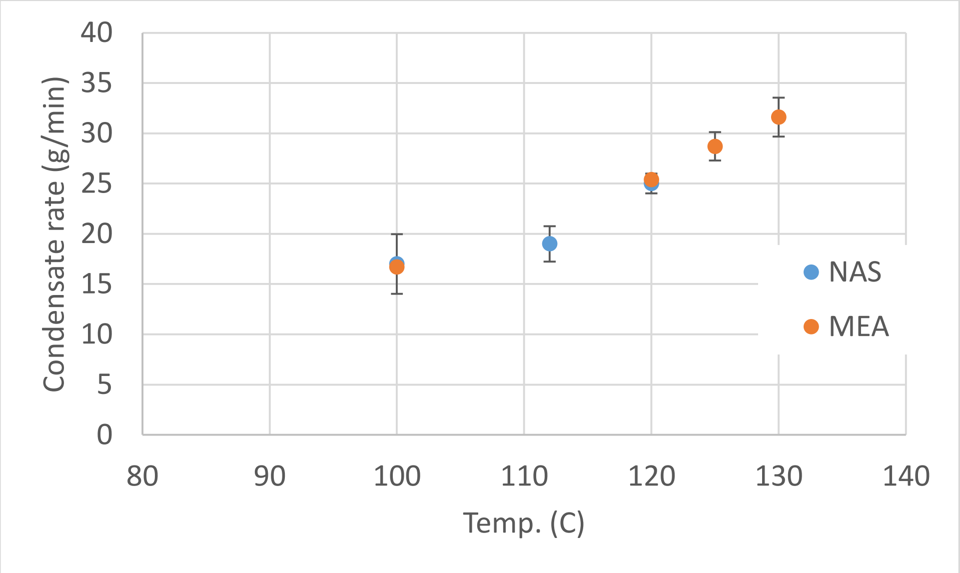


Figure 52. Condensate collection rate during the heat loss determination runs for BsTU at different temperatures.

Parametric Testing Conclusion

A set of CO_2 capture experimental runs using NAS were carried out in RTI's BsTU to evaluate the impacts of multiple operating parameters. Among other variables, the primary focus of these runs were to investigate the effect of the water introduced by the flue gas on the system overall performance and how to effectively balance water in the long-term operation. The results showed that the presence of water has a negative impact on the heat duty of the NAS with respect to increasing the heat capacity of the solution. However, it also decreases the solution's viscosity, yielding lower liquid circulation rate at the equivalent 90% CO_2 capture. The water balancing in the NAS system was demonstrated by manipulating the temperature of solvent return to the top of the absorber. By varying the solvent temperature at the top of absorber column, water-accumulating or water-stripping conditions can be created.

The implementation of inter-stage coolers at the absorber was to control and achieve a low temperature for absorption in the column. Low absorption temperature benefits NAS's working capacity and heat duty by increasing the rich loading and, subsequently, lowering the regeneration temperature, giving the overall lower energy requirement for CO_2 regeneration. Interstage-heaters were used to provide energy required to strip CO_2 from the rich solvent as it flows down the regenerator. These three-stage heaters allow higher granularity in control and improve the energy input to the system by supplying low pressure steam at the top of the column where the NAS does not require large energy to remove CO_2. Higher pressure steam at the middle and bottom stages provide more energy to remove the remaining CO_2 from NAS. The interstage coolers and heaters setup was evaluated during this testing campaign and has demonstrated to be a better process configuration which is more suitable for NAS than the kettle reboiler setup used for conventional MEA/H_2O. The regeneration pressure was also investigated to determine the impact on the heat duty. A substantial increase in the energy requirement was observed when increasing the pressure from 2.2 MJ/kg-CO_2 at 1.5 bar,g to 2.7 MJ/kg-CO_2 at 2.75 bar,g- a targeted pressure of the first stage CO_2 compression. For this particular solvent formulation, we were able to increase the amine concentration to a higher range of 36-38%wt without solid formation and achieved lower heat duty requirement to 1.9 MJ/kg-CO_2 at the optimal operating condition found during this testing campaign. The heat loss evaluation using MEA/H_2O was also performed to validate the accuracy of the heat loss obtained from the NAS runs. The heat loss results from MEA/H_2O and NAS runs agree well, confirming the accuracy of heat duty reported for NAS.

Task 6 – Solvent Degradation Testing

In Q7 SINTEF conducted extensive testing of a NAS in their facility in Trondheim, Norway. The testing was performed using a solvent degradation rig and occurred over the course of five weeks. The SDR is able to test for the impact of SO_2 and NO_x, and uses a high fidelity simulated flue gas to continuously test the solvent. A photo of the SDR is given in Figure 53. Task 6 consists of two parts. In the first part, Subtask 6.1, NAS is purged with a flue gas composition which represents coal-derived flue gas without pretreatment or polishing steps to reduce the concentrations of degradative components. This part was completed in Q7. The second part, Subtask 6.2, tests NAS with a flue gas composition which reflects the use of polishing steps on a coal-derived flue gas to reduce the concentration of SO_2 and NO_x,. Subtask 6.2 was performed in Q8. A summary of findings is given below, in general the solvents performed as expected with respect to SO_2 and NO_x, similar to MEA, and will need certain levels of SO_2 and NO_x removal to avoid degradation products.


Figure 53, SINTEF solvent degradation rig (SDR).

Prior to this work, thermal degradation experiments were conducted for four single component system and three mixtures. All single components and NAS formulation tested passed the thermal degradation experiment, both low amine loss and low concentration of metal. Metal concentration is used as indication on corrosion. Two NAS systems were tested under oxidative degradation conditions, for system 7 a loss of 90% was observed, while system 5 had comparable loss as with 30wt% MEA (around 10% amine loss).

Test of gas sampling was conducted in connection with the two SDR campaigns. The results show that an impinger system performs adequately with 0.1 N H_2SO_4 and the flow, temperature and volume conditions applied in the test experiments. The impinger system should have 3 bottles (1, 2 and 3) filled with liquid and preferable one extra empty bottle first (0) to collect condensate. For sampling of nitrosamines, an identical impinger system should be applied, except that the impinger liquid should be 0.1 M sulfamic acid.

Subtask 6.1 – Solvent Degradation Testing with Flue Gas Contaminants

The first SDR campaign was started on the 4th of May and was run for 5 weeks. The campaign was ended on 8th of June followed by two days with emission tests. The campaign used a NAS solvent and 5 wt% water. The campaign was run with a gas containing 7.4 vol% CO_2, 2.8 vol% O_2, 100ppmv NO_x, 10ppmv SO_2. The absorber temperature was held constant at 40°C and the reboiler temperature was maintained at 100°C and 2 bar. During the campaign aliquots were sampled on a weekly basis. Unused solvent (before being introduced to the rig) was also sampled as a baseline measurement. At the end of the campaign condensate from the condensate rig and samples from chilled gas washing bottles were analyzed to understand the composition of condensates and emissions from the NAS process. Emissions from the process were captured by cooling the treated gas in dry ice-cooled gas washing bottles which were filled with isopropanol or 0.1 N H_2SO_4 acid.

The analysis of solvent components and degradation products was conducted using LC-MS. In addition to the peaks of the primary solvent components, the analysis showed the presence of approximately nine other compounds which were present in minor amounts. Some of the compounds were stable of the course of the evaluation without significant increase while others increase in concentration, and are likely the degradation products.

The alkalinity of the solvent was monitored by titration over the course of the experiment and showed a relative decrease of approximately 10% after five weeks. The concentration of amine monitored by LC-MS indicates the loss is approximately 15% relative to the starting concentration. The discrepancy indicates the formation of another amine component which remains in solution and continues to contribute to the alkalinity. The concentration of Component 2 behaves similarly to the amine and decreases by about 15% relative to the initial concentration. The concentrations of hydrophobic diluents followed over time by LC-MS indicates that they suffered no significant losses during the campaign. The behavior of the M-H+ ion signals for the main components (amine, Component 2, and glycol diluents are shown in Figure 54 below. The decrease in the amine M-H+ ion signal (122.1) from week 0 to week 5 is qualitatively explained by the detection of the amine in the condensate which was collected and analyzed at the end of the five weeks of testing. The other solvent components are detected at much lower levels in the condensate.

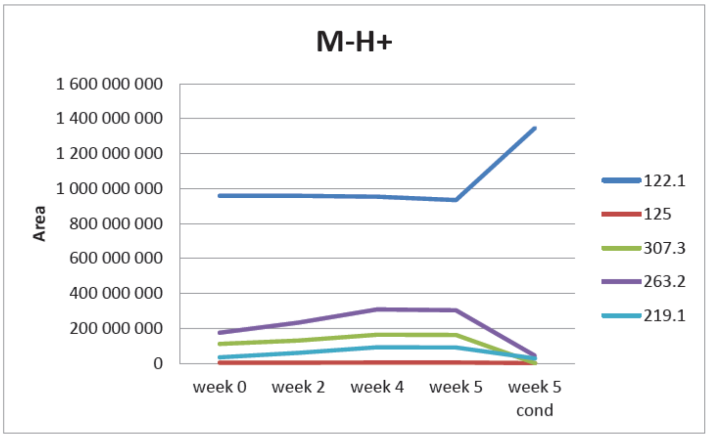


Figure 54. The behavior of the M-H+ ion signals for the main components.

Samples were also analyzed for metal ion (Fe, Ni, Cr, Cu) and sulphur content by ICP-MS. For Ni, Cu, and Cr all the results are quite low (<1mg/l) while for Fe there is an increase with time ending at a concentration of approximately 6 mg/l after five weeks. This amount is, however, relatively low and lower than what has been observed for 30% MEA after five weeks (10 mg/L), see Figure 55. The sulfur concentration increases linearly with time as expected and is observed at a concentration of approximately 14 mg/L at the end of the five weeks of testing when present at 10 ppm in the incoming flue gas (Figure 56).

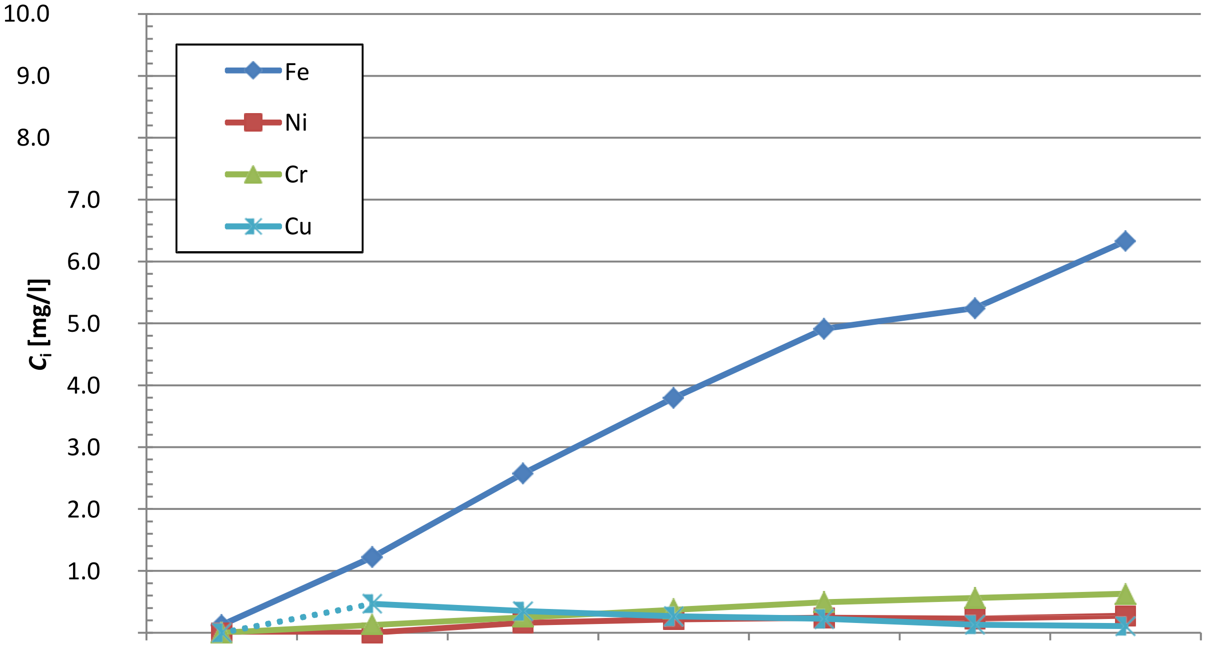
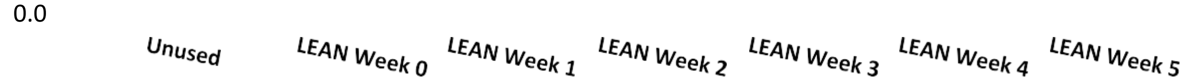


Figure 55. Determined concentrations of metal ions in lean solvent during SDR1 campaign. Aqueous 30% MEA typically has a value of approximately 10 mg/L over the equivalent time interval.



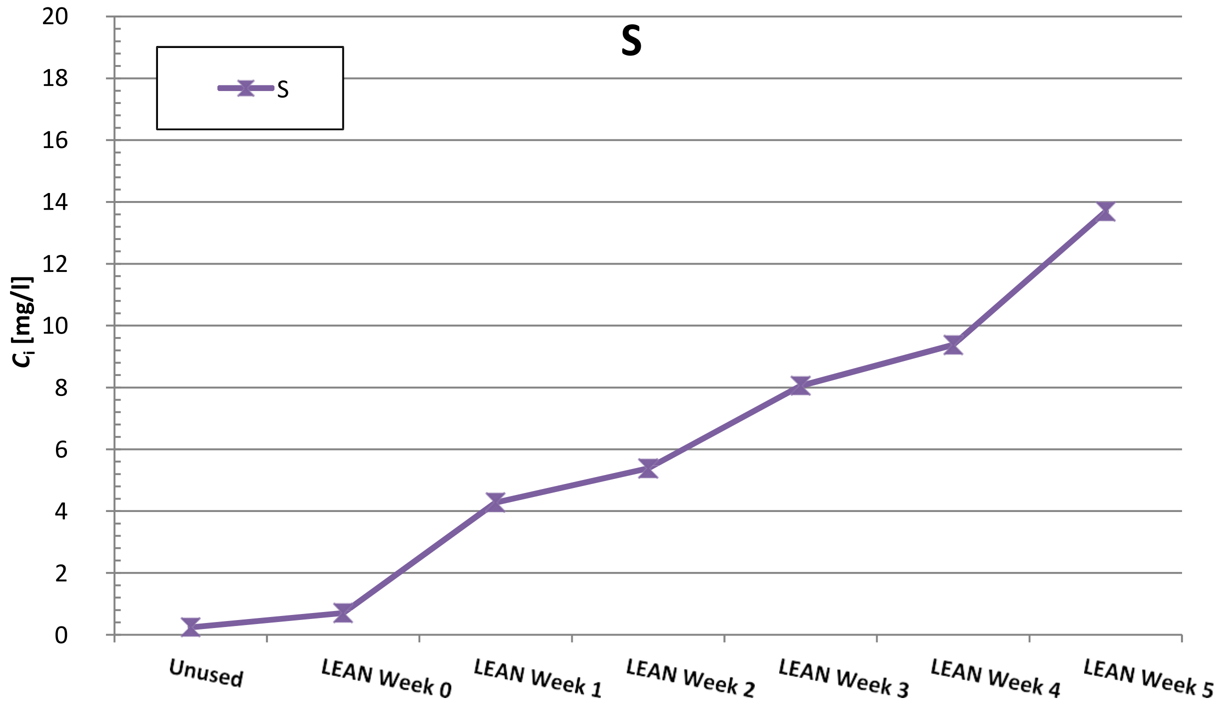


Figure 56. Determined concentration of sulfur in lean solvent during SDR1 campaign.

At the end of the five weeks of testing emissions testing was conducted by analyzing the contents of the chilled isopropanol and sulfuric acid gas washing bottles. The emissions testing reveals what volatile emissions might make it past a conventional condenser and require additional scrubbing before being released. The results indicate that that an aqueous solution of sulfuric acid is the best polishing method capturing about 0.225 mg/hr of amine over the course of the experiment. The relative distribution of compounds in the emissions including the amount captured in the condensate from the rig and the major compounds in the emissions is amine (~91%) and ammonia (~6.5%).

Subtask 6.2 – Extended Degradation Studies and Evaluation of Degradation Pathways

The second SDR campaign was started on the 4th of September and was run for 5 weeks. The campaign was ended on 10th of October followed by two days with emission tests. The campaign was started with a lower amount of NO_x/SO_2 in the gas and a higher stripper temperature than in the first campaign. After two weeks the NO_x/SO_2 was increased to the same level as in the first campaign, see Table 12.

Table 12. Conditions used in 2nd SDR campaign

Periode	$T_{Absorber}$ [°C]	$T_{Stripper}$ [°C]	O_2 [Vol%]	CO_2 [Vol%]	NO_x [ppmv]	SO_2 [ppmv]
Week 0-2	40	110	2.8	7.4	5	0.5
Week 3-5	40	110	2.8	7.4	100	10

For the second campaign a lower level of NO_x/SO_2 (10 times lower) was used for the two first weeks. The stripper temperature was around 100°C in the first campaign while it was increased to 110 °C for the second campaign. There were not observed any significant difference in solvent losses for the two campaigns, with observed amine loss 13-15 % during the 5 weeks (see Figure 58). The concentration of analyzed degradation products was also quite similar for the two campaigns, except for the nitrosamine. For the nitrosamine there were observed a significant increase when the NO_x level in the flue gas was increased in the second campaign. In addition there were also observed a decrease in formation rate with increased stripper temperature. For both campaigns lower levels of iron than in previous MEA campaign was observed in the solvent (< 7 mg/l), see Figure 57. At the end of both campaigns emission test were conducted, for both test ammonia and amine were the major emissions out of the rig (impinger train).

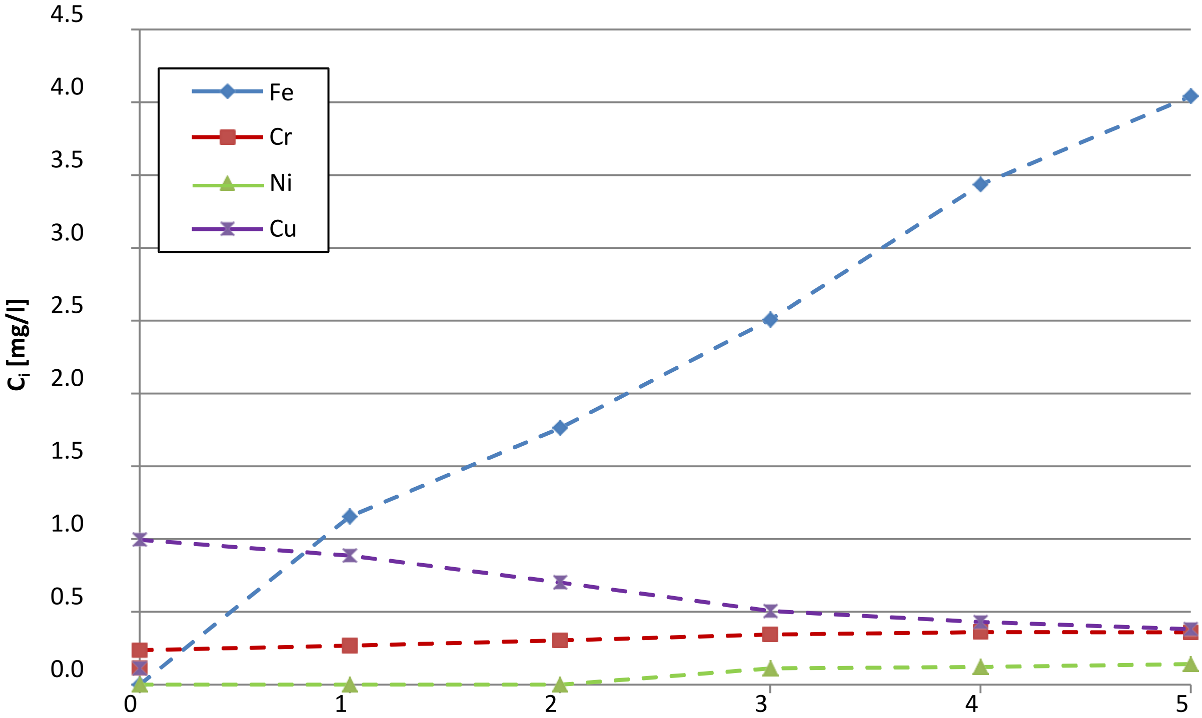


Figure 57. Concentration of metal ions in lean solvent during SDR2.

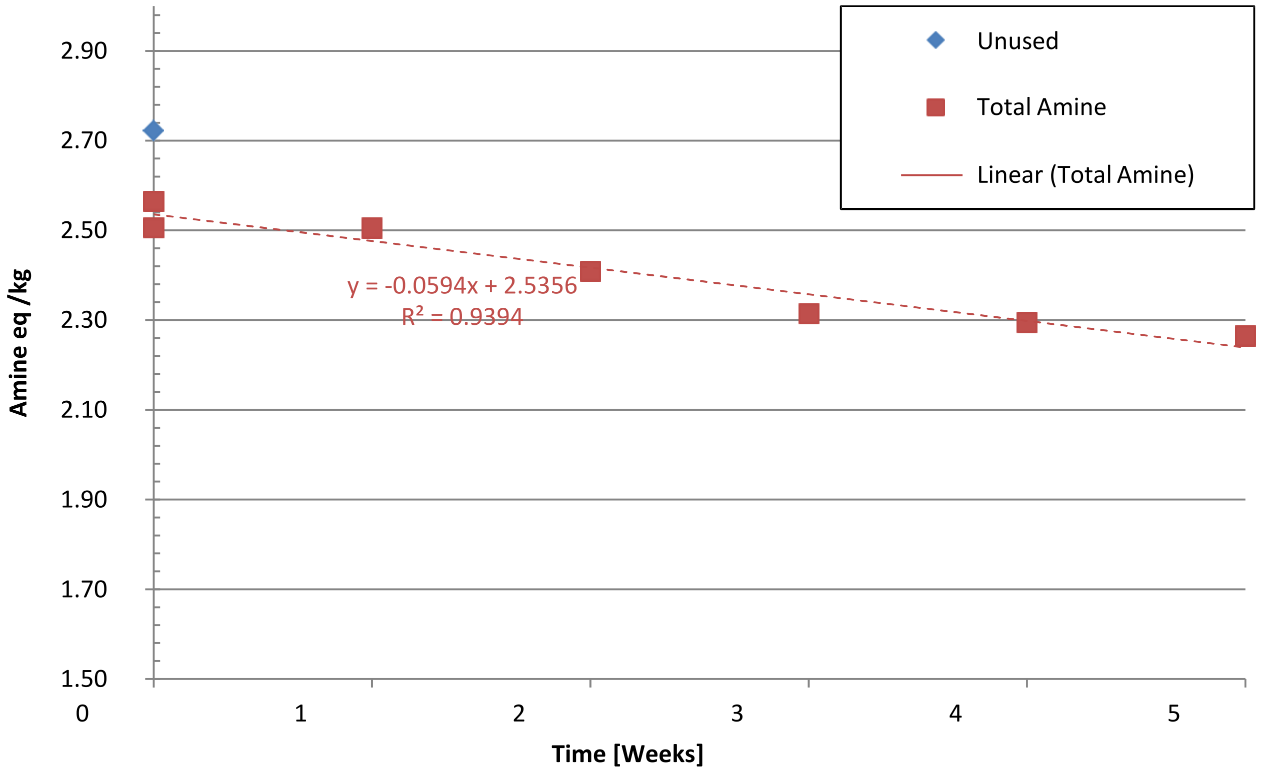


Figure 58. Total amine concentration in lean solvent during SDR2.

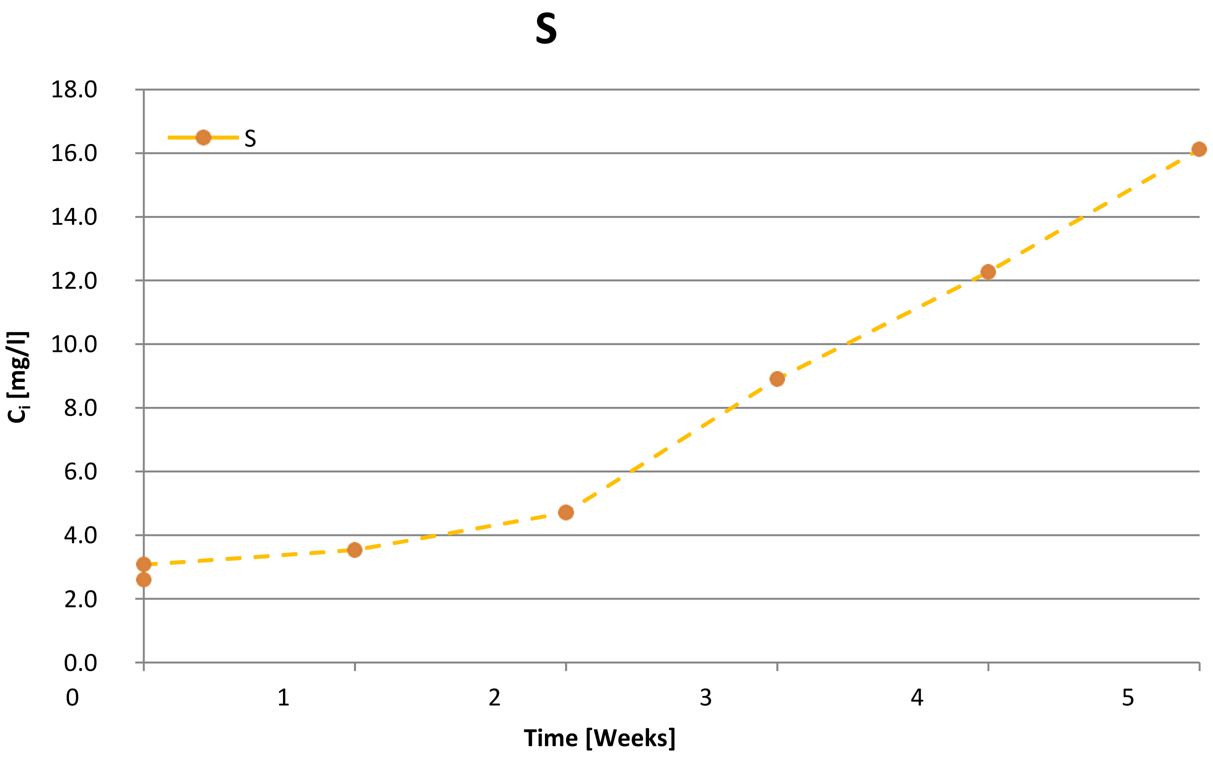


Figure 59. Sulphur concentration in lean solvent during SDR2.

In Figure 59 the sulphur concentration is plotted versus time. A small linear increase with time could be observed for the first and a higher increase after week 2 which is expected as the SO_2 in the flue gas was increased after week 2.

Further analytical work has mainly been performed with mass spectrometric instrumentation (gas chromatography – mass spectrometry (GC-MS), liquid chromatography – triple quadrupole mass spectrometry (LC-MS), inductively coupled plasma triple quadrupole mass spectrometry (ICP-MS), Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR-MS)). Quantitative methods were developed and applied in this project and include around 25 compounds in addition to qualitative analyses by several techniques like FT-ICR-MS. The evaluation of qualitative data for thermal, oxidative or SDR degradation experiments gave indications for degradation compounds. The compounds were urea or amide products as well as a small amount of nitrosamine. Nitrosamine speciation was confirmed with reference sample and quantitative analysis. The nitrosamine concentration correlated closely with the change in NO_x concentration during SDR2 , confirming that one way to mitigate formation is to keep the concentration of NO_x as low possible in the incoming flue gas.

Task 7 – Process Modeling

As reported in previous quarterly reports, the process model predicted lower reboiler duty (<2 MJ/kg$_{CO2}$) for higher amine concentrations. Therefore, experiments were also done in the BsTU with higher amine concentrations (38wt%) and found reboiler duty to be less than 2 MJ/kg$_{CO2}$. In addition, it was found that operating NAS saturated with water (7.6 wt.%) showed an even lower reboiler duty of 1.7 MJ/kg$_{CO2}$ at L/G of 7 with absorber operating at 38°C. Therefore, the process model which was built based on 33wt% amine formulation properties was re-regressed based on the 38wt% amine formulation with 7.6wt% water (NAS-Op). Vapor-Liquid equilibrium (Figure 60, Figure 61), heat of absorption (Figure 62, Figure 63) and reaction kinetics for NAS-Op (based on the solubility parameter which is a function of the dielectric constant of the solvent, Figure 64) are shown below in comparison to data for the formulation at lower amine concentration.[1] The increase in amine and water concentration increases the equilibrium CO_2 loading capacity in NAS and also raises the heat of absorption values as shown by comparing Figure 62 and Figure 63. Increasing the concentration of water in NAS increased the reaction rate of CO_2 with NAS as shown in Figure 65.

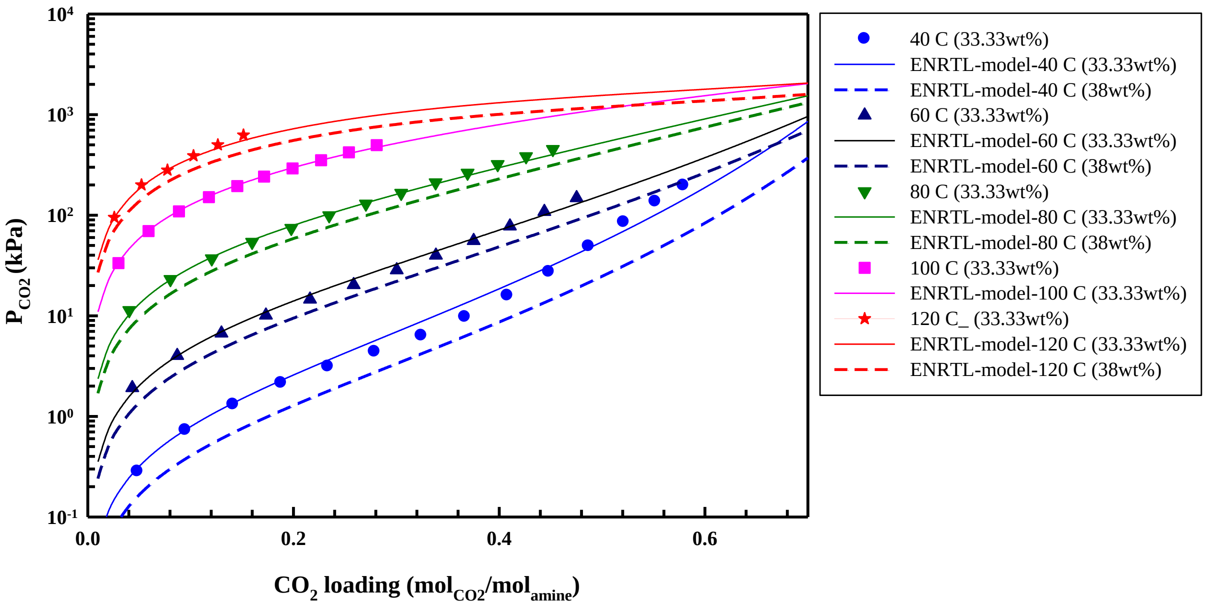


Figure 60. Experimental VLE of 33wt% amine (NAS-Old) and predicted effect of increase in amine concentration using ENRTL-SR model

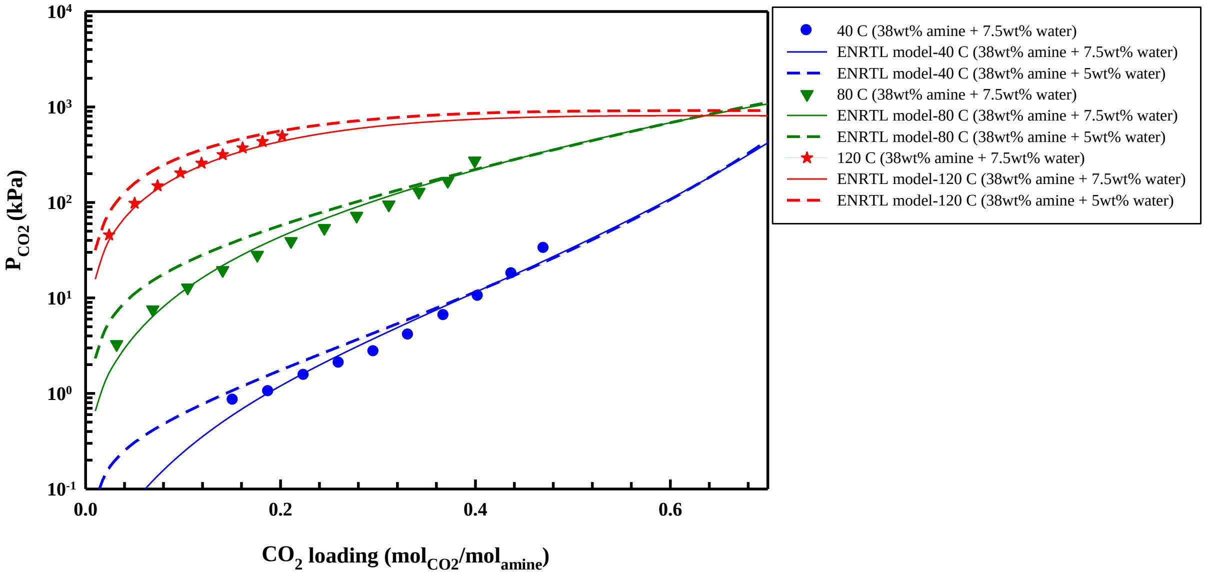


Figure 61. Experimental VLE of 38wt% amine with 7.5wt% water (NAS-Op) and predicted effect of decrease in water concentration using ENRTL-SR model

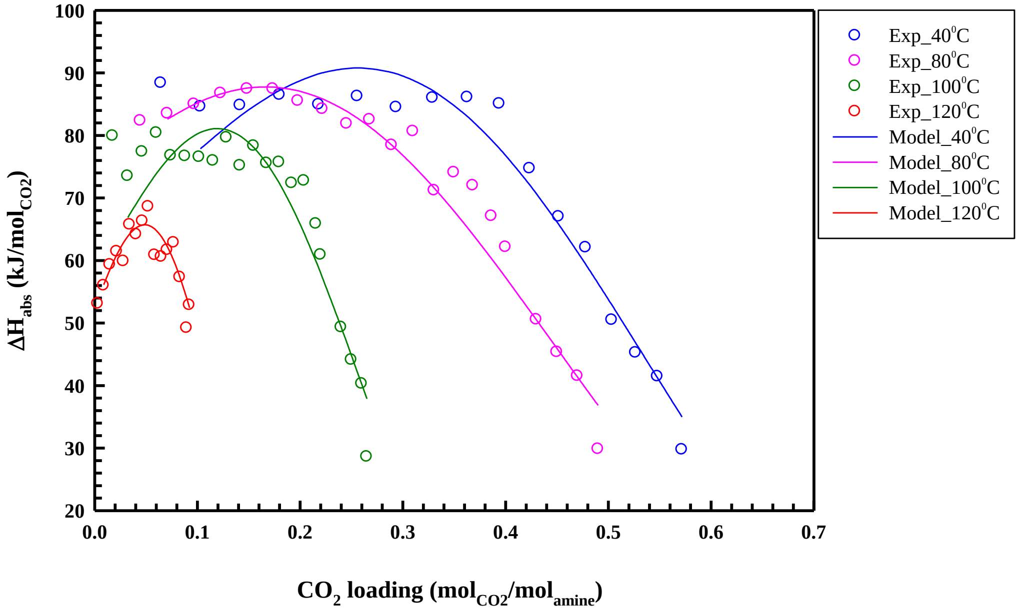


Figure 62. Experimental ΔH_{abs} of 33wt% amine (NAS-Old) and predicted using ENRTL-SR model

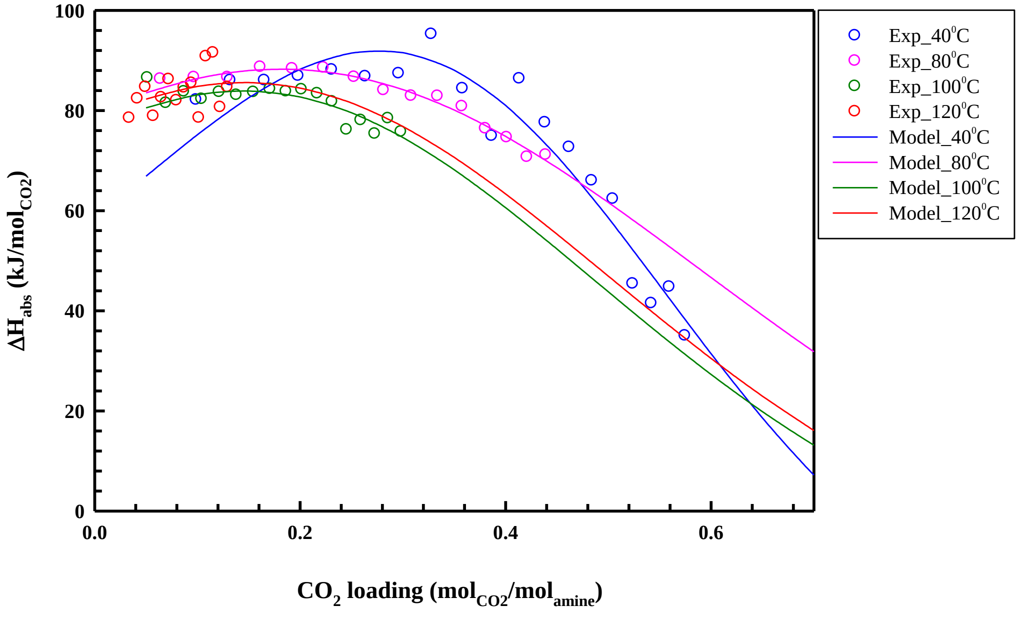


Figure 63. Experimental ΔH_{abs} of 38wt% amine with 7.5 wt% water (NAS-Old) and predicted using ENRTL-SR model

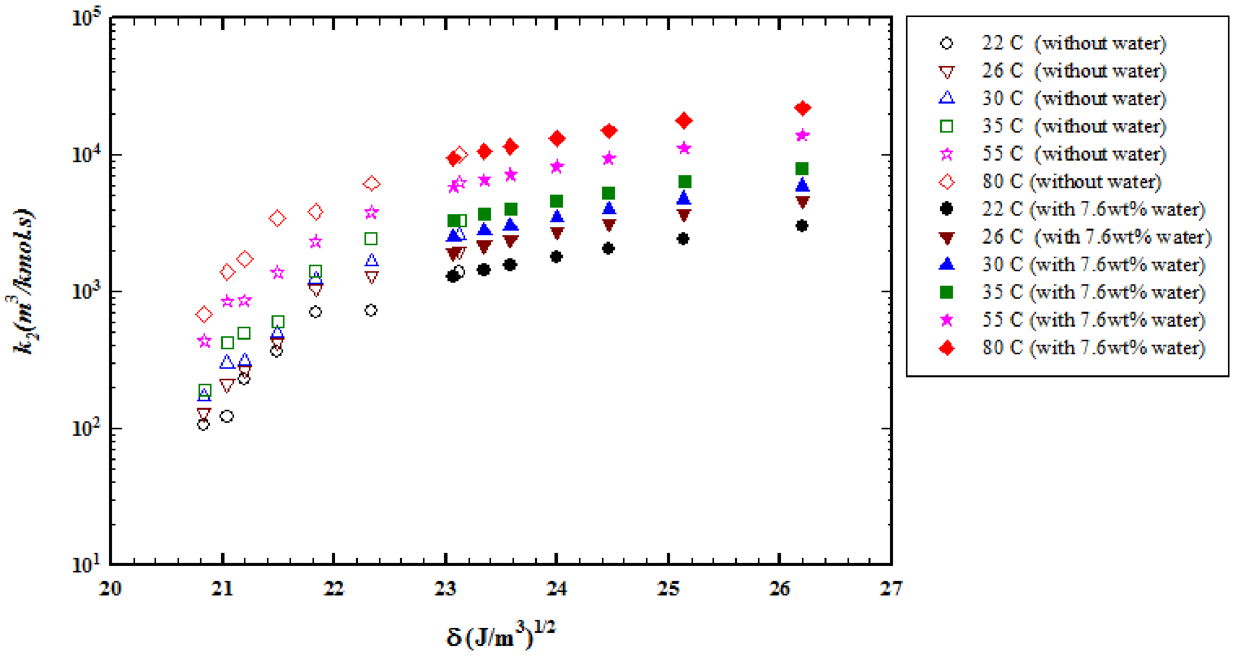


Figure 64. Predicted second order reaction kinetics of CO_2 with NAS-Op based on solubility parameter [2]

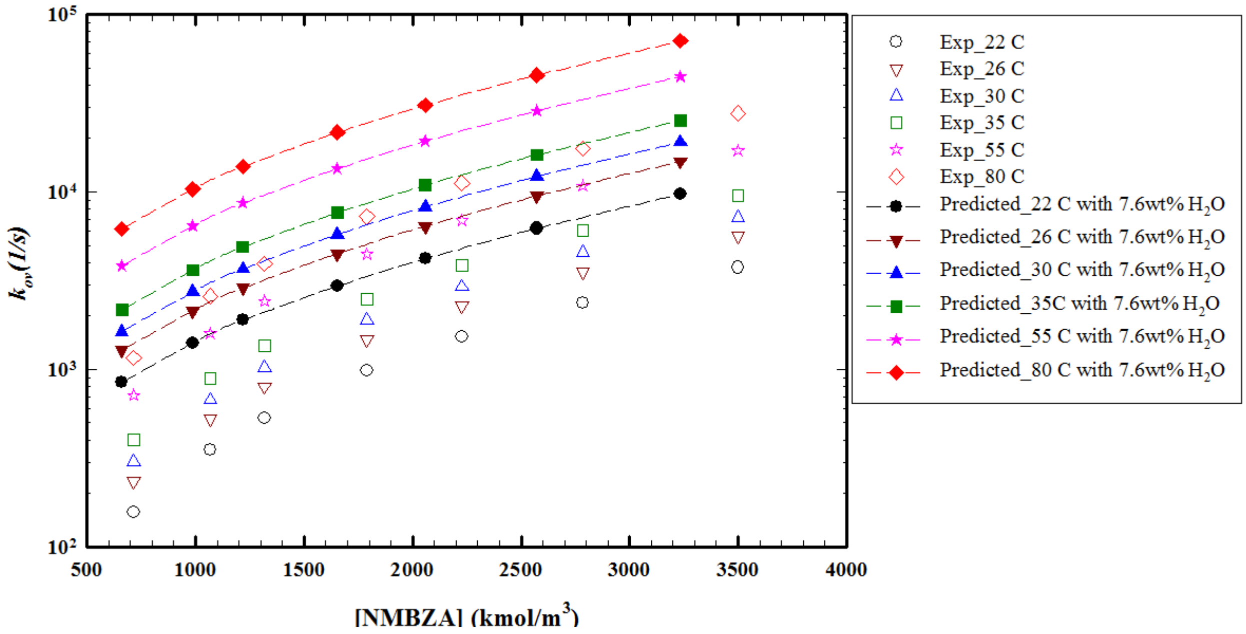


Figure 65. Predicted overall pseudo-reaction rates of CO_2 with NAS-Op

Based on the regressed parameters for the ENRTL-SR model, a process model was developed with and without intercoolers using the BsTU configurations for absorber and desorber. In the reaction chemistry, NAS with water was modeled with CO_2 to produce carbamates and bicarbonates. This was experimentally verified using ^{13}C-NMR experiments in our lab. Based on the available reaction pathways in Aspen-Plus, a bulk reaction is suggested for NAS-Op saturated with water as described in the equation below and their Arrhenius rate expressions were derived using the reaction kinetics data and used in the process model:

$$3\ amine + \ 2\ CO_2 + water \leftrightarrow carbamate + protonated\ amine + bicarbonate \quad \text{Equation 5}$$

Controlling the absorber temperature profiles using the intercoolers played an important role in reducing the reboiler duty for CO_2 capture using NAS system as explained in previous quarterly reports. As shown in Figure 66, reboiler duties for the process without intercoolers and without water in NAS showed values between 3.52 to 5.37 MJ/kg$_{CO2}$ for L/G of 7.57 to 14.45. The minimum reboiler duty of 3.52 MJ/kg$_{CO2}$ was obtained at L/G of 8.04. Reboiler duties for the process with NAS saturated with 7.6wt% of water showed values between 3.7 to 4.57 MJ/kg$_{CO2}$. The minimum reboiler duty of 3.65 MJ/kg$_{CO2}$ was obtained at L/G of 8.06. Process modeling with intercoolers operating at 25°C in absorbers showed reboiler duty values between 1.87 to 2.68 MJ/kg$_{CO2}$ for L/G of 6.84 to 15. The minimum value of 1.87 MJ/kg$_{CO2}$ occurred at L/G of 6.86.

The reboiler duties for CO_2 capture using NAS were measured using model-derived process conditions in the BsTU and shown in Figure 66. It can also be observed that increase in the concentration of amine and absorber bottom temperature reduces the reboiler duty and ratio of liquid to gas flowrate (L/G). The lowest reboiler duty was obtained from the BsTU at L/G of 7 with a value of 1.69 MJ/kg$_{CO2}$ with the absorber bottom temperature at 36°C, whereas process model predicted a values of 1.53 at 6.97 MJ/kg$_{CO2}$. Flue gas and lean solvent conditions used in the process model operating absorber bottom at 36°C along with the predicted values of CO_2 loading and reboiler duty are given in Table 13. Operating absorber at 32°C yielded low reboiler duties. At L/G =7 the reboiler was predicted to be 1.29 MJ/kg$_{CO2}$.

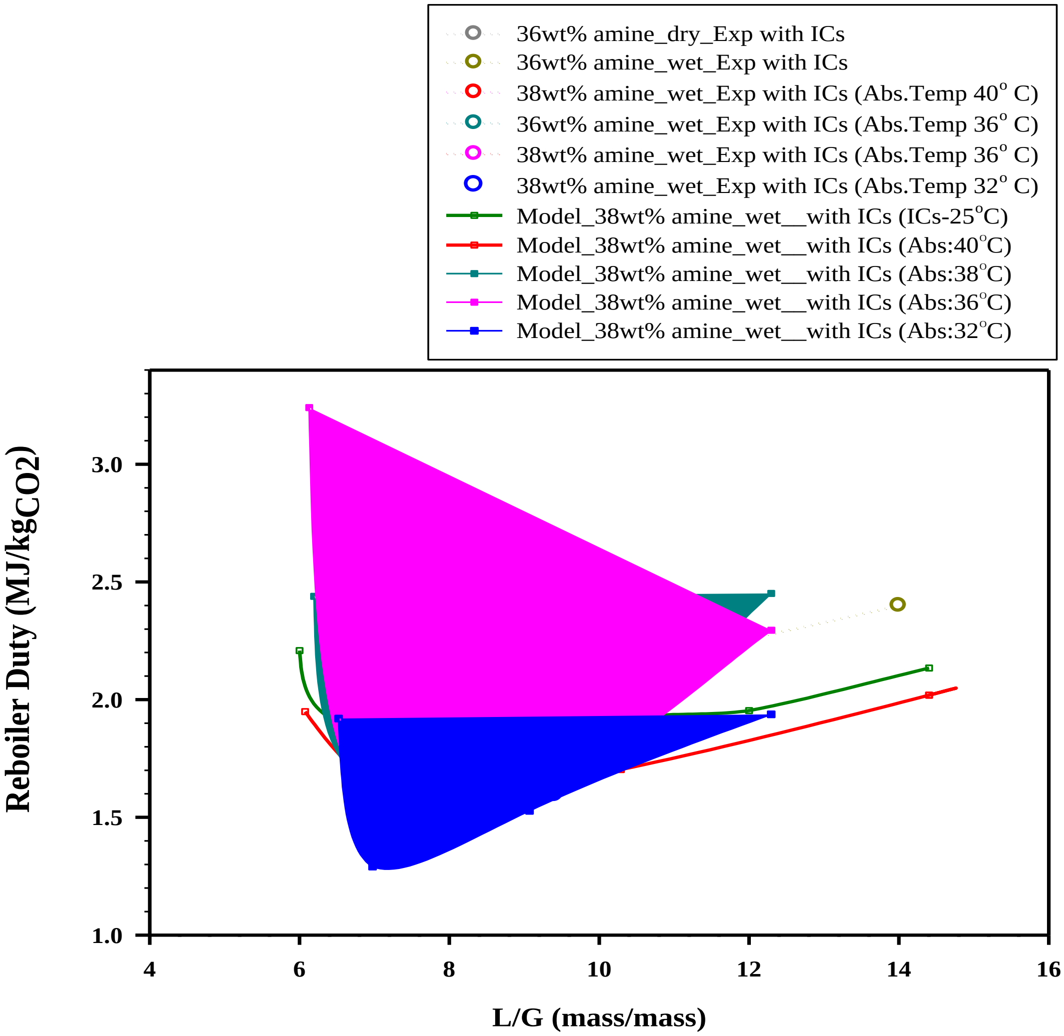


Figure 66. Reboiler of Duty of CO_2 capture using NAS from BsTU and Process model

Table 13. Process conditions used in process model for operating absorber at 36°C

FLUE GAS AND LEAN SOLVENT CONDITIONS								**REBOILER DUTY**
Flue Gas Temp °C	Lean Temp °C	Lean Loading mol_{CO2}/mol_{amine}	Rich Loading mol_{CO2}/mol_{amine}	CO_2 Capture %	L Kg/hr	G Kg/hr	FROM ASPEN L/G	Steam per CO_2 MJ/kg_{CO2}
40.00	38.64	0.275	0.444	94	41.203	6.722	6.13	3.24
40.00	37.13	0.277	0.401	90	46.877	6.722	6.97	1.53
40.00	37.10	0.268	0.372	90	55.879	6.722	8.31	1.73
40.00	38.10	0.263	0.356	90	60.963	6.722	9.07	1.78
40.00	38.60	0.258	0.336	90	69.155	6.722	10.29	1.80
40.00	25.22	0.389	0.311	90	82.660	6.722	12.30	2.29

The model validated above was used to do techno-economic analysis for scaled-up CO_2 capture process from flue gas using NAS system in 550 MW power plant. Reboiler duty less than 2 MJ/kg_{CO2} was achieved using NAS system at L/G of 7. Due to higher L/G required for the process compare to 30wt% MEA which is L/G of 3, the amount of solvent flow rate and size of absorber and desorber columns are high. Increasing the amine concentration further, may lead to lower L/G for process close to 3-4, thereby reducing the cost of process and lean solvent circulation rates.

Task 8: TEA and Technology EH&S Assessment of a Commercial NAS CO_2 Capture Process

Task 8 was completed and is submitted as a separate topical report to this final report.

4. Products

Publications, conference papers, and presentations

{Presentation} Lail, M., Soukri, M., Tanthana, J., Mobley, P. Coleman, L. Non-Aqueous Solvent (NAS) CO_2 Capture Process. 2014 CO_2 Capture Technology Meeting. Pittsburgh, PA. July 28-August 1, 2014.

{Conference Paper} Marty Lail, Jak Tanthana, and Luke Coleman. Non-Aqueous Solvent (NAS) CO_2 Capture Process. Conference Proceedings for the International Greenhouse Gas Technologies Conference (GHGT-12). Published in Energy Procedia 00 (2013) 000–000.

{Poster Presentation} Marty Lail, Jak Tanthana, and Luke Coleman. Non-Aqueous Solvent (NAS) CO_2 Capture Process. Conference Proceedings for the International Greenhouse Gas Technologies Conference (GHGT-12). October 5-9, 2014.

{Presentation} Marty Lail. Development and Scale-Up of Carbon Capture Technologies. Gordon Research Conference on Carbon Capture, Utilization, and Storage. Stonehill College, Easton, MA. May 31- June 05, 2015.

{Presentation} Jak Tanthana, Mustapha Soukri, Paul Mobley, Aravind Rabindran, Justin Farmer, Markus Lesemann, Marty Lail, Satish Tamhankar, Stevan Jovanovic, Krish Krishnamurthy, Andreas Grimstvedt, Solrun Johanne Vevelstad. Bench-Scale Development of a Non-Aqueous Solvents (NAS) CO_2 Capture Process for Coal-Fired Power Plants. 2015 NETL CO_2 Capture Technology Meeting. Pittsburgh, PA. June 23-26, 2015

{Presentation} Mobley, P. D., Tanthana, J., Soukri, M., Rabindran, A., Farmer, J. R., Lail, M. A., & Coleman, L. J. (Invited Speaker). (2015, June). *Non-Aqueous Solvent (NAS) CO2 Capture Process*. Presented at A&WMA ACE 2015, Raleigh, NC.

{Presentation} Lail, M. A., Lesemann, M., Mobley, P. D., Rabindran, A., Soukri, M., & Tanthana, J.(2015, September). *Non-Aqueous Solvent (NAS) CO2 Capture Process*. Poster presented at PCCC3: Post Combustion Carbon Capture Conference, Regina, Canada

{Presentation} Lail, M. A., Lesemann, M., Mobley, P. D., Rabindran, A., Soukri, M., & Tanthana, J.(2015, September). *Non-Aqueous Solvent (NAS) CO2 Capture Process*. Poster presented at PCCC3: Post Combustion Carbon Capture Conference, Regina, Canada

{Presentation} Jak Tanthana, Mustapaha Soukri, Paul Mobley, Aravind Rabindran, Thomas Gohndrone, Tom Nelson, Markus Lesemann, James Zhou, and Marty Lail, Bench-Scale Development of a Non-Aqueous Solvents (NAS) CO_2 Capture Process for Coal-Fired Power Plants. 2016 NETL CO_2 Capture Technology Meeting. Pittsburgh, PA. August 8-12, 2016

Websites

Nothing to report.

Technologies or Techniques

Nothing to report.

Inventions, Patent Applications, and Licenses

Nothing to report.

Other Products

Nothing to report.

Other Public Releases

Nothing to report.

5. Participants and Other Collaborating Organizations

Individuals

Individuals who have worked on the project heavily at RTI.

RTI International

Mobley, Paul

Name	Paul Mobley
Project Role	Technical Lead – bench-scale testing
Contribution to Project	Performed bench-scale Testing.
Funding Support	DOE award + Cost-share
Collaborated with individual in foreign country?	No
Country of foreign collaborator	n/a
Traveled to foreign country?	No
Duration of stay?	n/a

Farmer, Justin

Name	Justin Farmer
Project Role	Process Engineer
Contribution to Project	Support bench-scale testing efforts.
Funding Support	DOE award + Cost-share

Collaborated with individual in foreign country?	No
Country of foreign collaborator	n/a
Traveled to foreign country?	No
Duration of stay?	n/a

Lail, Marty

Name	Marty Lail
Project Role	Principal Investigator
Contribution to Project	Project management; client and subcontractor interaction;
Funding Support	DOE award + Cost-share
Collaborated with individual in foreign country?	Yes
Country of foreign collaborator	Norway
Traveled to foreign country?	No
Duration of stay?	n/a

Rabindran, Aravind

Name	Aravind Rabindran
Project Role	Process Engineer
Contribution to Project	Lead process modeling efforts.
Funding Support	DOE award + Cost-share
Collaborated with individual in foreign country?	No
Country of foreign collaborator	n/a
Traveled to foreign country?	No
Duration of stay?	n/a

Akunuri, Nandita

Name	Nandita Akunuri
Project Role	Task Lead – Techno-Economic Analysis
Contribution to Project	Perform techno-economic analysis.
Funding Support	DOE award + Cost-share
Collaborated with individual in foreign country?	No
Country of foreign collaborator	n/a
Traveled to foreign country?	No
Duration of stay?	n/a

Tanthana, Jak

Name	Jak Tanthana
Project Role	Technical Lead – Lab-scale Testing
Contribution to Project	Supported bench-scale testing efforts, upgrades of test systems, system controls, and long-term bench-scale test campaigns
Funding Support	DOE award + Cost-share
Collaborated with individual in foreign country?	No
Country of foreign collaborator	n/a

Traveled to foreign country?	No
Duration of stay?	n/a

Zhou, James

Name	James Zhou
Project Role	Program Director-Gas Separations
Contribution to Project	Advised bench-scale testing efforts, modeling, and techno-economic analysis.
Funding Support	DOE award + Cost-share
Collaborated with individual in foreign country?	Yes
Country of foreign collaborator	Norway
Traveled to foreign country?	No
Duration of stay?	n/a

Gohndrone, Thomas

Name	Thomas Gohndrone
Project Role	Postdoctoral Chemical Engineer
Contribution to Project	Supported bench-scale testing efforts, solvent formulation modification, and process modeling.
Funding Support	DOE award + Cost-share
Collaborated with individual in foreign country?	No
Country of foreign collaborator	No
Traveled to foreign country?	No
Duration of stay?	n/a

Organizations

Other organizations that have worked on the project include:

Linde LLC (Linde) located in Murray Hill, New Jersey. Linde staff activities in Q10 included over 250 hours of on-site support of the bench-scale testing. Engineer Devin Bostick and Engineering Technician, Felipe Quintanilla stayed for a total of four long-term visits (~twelve weeks total). In addition to bench-scale testing support, assisted with techno-economic assessment of the NAS technology. Linde contributes in-kind cost share to the project.

Stiftelsen SINTEF (SINTEF) located in Trondheim Norway. SINTEF staff activities included performing and analysis of the solvent degradation testing (Task 3 and Task 6). SINTEF work was complete at the end of Q9. SINTEF contributes in-kind cost share to this project.

Other Collaborators

None

Development of Human Resources

Nothing to report.

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Cost Status Report

The cost status report is provided below

Baseline Reporting Quarter	BP 1	Budget Period 2								
	Q6	Q1		Q2		Q3		Q4		Q5	
		(4/1/15 to 6/30/2015)		(7/31/15 to 9/30/2015)		(10/1/15 to 12/31/2015)		(1/1/16 to 3/31/2016)		(4/1/16 to 6/30/2016)	
	Cumulative Total	Q3 FY15	Cumulative Total	Q4 FY15	Cumulative Total	Q1 FY16	Cumulative Total	Q2 FY16	Cumulative Total	Q3 FY16	Cumulative Total
Baseline Cost Plan											
Federal Share	$1,210,153	$309,465	$1,519,618	$246,155	$1,765,773	$286,439	$2,052,212	$334,860	$2,387,072	$0	$2,387,072
Non-Federal Share	$329,267	$123,633	$452,900	$73,526	$526,426	$85,560	$611,986	$100,023	$712,009	$0	$712,009
Total Planned	$1,539,420	$433,098	$1,972,518	$319,681	$2,292,199	$371,999	$2,664,198	$434,883	$3,099,081	$0	$3,099,081
Actual Incurred Cost											
Federal Share	$942,989	$280,547	$1,223,536	$205,498	$1,429,034	$275,144	$1,704,178	$397,746	$2,101,924.03	$150,698	$2,252,622
Non-Federal Share	$280,412	$85,060	$365,472	$61,383	$426,854	$56,906	$483,760	$85,127	$568,887.01	$27,881	$596,768
Total Incurred Costs	$1,223,401	$365,607	$1,589,008	$266,881	$1,855,889	$332,049	$2,187,938	$482,873	$2,670,811.04	$178,579	$2,849,390
Variance											
Federal Share	$267,164	$28,918	$296,082	$40,657	$336,739	$11,295	$348,034	($62,886)	$285,148	($150,698)	$134,450
Non-Federal Share	$48,855	$38,573	$87,428	$12,143	$99,572	$28,654	$128,226	$14,896	$143,122	($27,881)	$115,241
Total Variance	$316,019	$67,491	$383,510	$52,800	$436,310	$39,950	$476,260	($47,990)	$428,270	($178,579)	$249,691

6. References

1. Park, S. W.; Choi, B. S.; Lee, J. W., *Korean Journal of Chemical Engineering* **2006,** *23*, 138.
2. Park, S.-W.; Choi, B.-S.; Lee, J.-W., Chemical absorption of carbon dioxide with triethanolamine in non-aqueous solutions. *Korean Journal of Chemical Engineering* **2006,** *23* (1), 138-143.

7. List of Acronyms

AC	alternating current
ARPA-E	Advanced Research Projects Agency-Energy
BP1	budget period one
BP2	budget period two
BsTU	bench-scale test unit
ΔH_r	enthalpy of reaction
DOE	Department of Energy
EH&S	environmental health and safety
E-NRTL	electrolyte non-random two liquid
ENRTL-SR	electrolyte non-random two liquid symmetric reference
ETDF	Energy Technology Development Facility
FG	flue gas
Gas Vel.	gas velocity
GC	gas chromatograph
HMI	human machine inteface
ICP-MS	inductively coupled plasma mass spectroscopy
L/G	liquid to gas
LC-MS	liquid chromatography mass spectroscopy
LP	low pressure
LsGAS	lab-scale gas absorption system
M	moles per liter
MEA	monoethanolamine
MKS	multiple gas analyzer
NAS	non-aqueous solvent
NDIR	non-dispersive infrared
NEPA	National Environmental Policy Act
NETL	National Energy Technology Lab
NMR	nuclear magnetic resonance
NRTL	non-random two liquid
PID	plumbing and instrumentation diagram
PMP	project management plan
Q*x*	quarter *x*
RTI	Research Triangle Institute

SDR	solvent degradation rig
Sim. FG	simulated flue gas
SLPM	standard liters per minute
SRK	Soave-Redlich-Kwong
TEA	techno-economic analysis
Temp.	temperature
TS&M	transportation storage and monitoring
VLE	vapor liquid equilibrium