FINAL SCIENTIFIC/TECHNICAL REPORT

BENCH-SCALE DEVELOPMENT OF AN ADVANCED SOLID SORBENT-BASED CO_2 CAPTURE PROCESS FOR COAL-FIRED POWER PLANTS

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Abstract

It is increasingly clear that CO_2 capture and sequestration (CCS) must play a critical role in curbing worldwide CO_2 emissions to the atmosphere. Development of these technologies to cost-effectively remove CO_2 from coal-fired power plants is very important to mitigating the impact these power plants have within the world's power generation portfolio. Currently, conventional CO_2 capture technologies, such as aqueous-monoethanolamine based solvent systems, are prohibitively expensive and if implemented could result in a 75 to 100% increase in the cost of electricity for consumers worldwide. Solid sorbent CO_2 capture processes – such as RTI's Advanced Solid Sorbent CO_2 Capture Process – are promising alternatives to conventional, liquid solvents. Supported amine sorbents – of the nature RTI has developed – are particularly attractive due to their high CO_2 loadings, low heat capacities, reduced corrosivity/volatility and the potential to reduce the regeneration energy needed to carry out CO_2 capture.

Previous work in this area has failed to adequately address various technology challenges such as sorbent stability and regenerability, sorbent scale-up, improved physical strength and attrition-resistance, proper heat management and temperature control, proper solids handling and circulation control, as well as the proper coupling of process engineering advancements that are tailored for a promising sorbent technology. The remaining challenges for these sorbent processes have provided the framework for the project team's research and development and target for advancing the technology beyond lab- and bench-scale testing.

Under a cooperative agreement with the US Department of Energy, and part of NETL's CO_2 Capture Program, RTI has led an effort to address and mitigate the challenges associated with solid sorbent CO_2 capture. The overall objective of this project was to mitigate the technical and economic risks associated with the scale-up of solid sorbent-based CO_2 capture processes, enabling subsequent larger pilot demonstrations and ultimately commercial deployment. An integrated development approach has been a key focus of this project in which process development, sorbent development, and economic analyses have informed each of the other development processes. Development efforts have focused on improving the performance stability of sorbent candidates, refining process engineering and design, and evaluating the viability of the technology through detailed economic analyses.

Sorbent advancements have led to a next generation, commercially-viable CO_2 capture sorbent exhibiting performance stability in various gas environments and a physically strong fluidizable form. The team has reduced sorbent production costs and optimized the production process and scale-up of PEI-impregnated, fluidizable sorbents. Refinement of the process engineering and design, as well as the construction and operation of a bench-scale research unit has demonstrated promising CO_2 capture performance under simulated coal-fired flue gas conditions. Parametric testing has shown how CO_2 capture performance is impacted by changing process variables, such as Adsorber temperature, Regenerator temperature, superficial flue gas velocity, solids circulation rate, CO_2 partial pressure in the Regenerator, and many others. Long-term testing has generated data for the project team to set the process conditions needed to operate a solids-based system for optimal performance, with continuous 90% CO_2 capture, and no operational interruptions. Data collected from all phases of testing has been used to develop a detailed techno-economic assessment of RTI's technology. These detailed analyses show that RTI's technology has significant economic advantages over current amine scrubbing and potential to achieve the DOE's Carbon Capture Program's goal of >90% CO_2 capture rate at a cost of < \$40/T-CO_2 captured by 2025.

Through this integrated technology development approach, the project team has advanced RTI's CO_2 capture technology to TRL-4 (nearly TRL-5, with the missing variable being testing on actual, coal-fired flue gas), according to the DOE/FE definitions for Technology Readiness Levels. At a broader level, this project has advanced the whole of the solid sorbent CO_2 capture field, with advancements in process engineering and design, technical risk mitigation, sorbent scale-up optimization, and an understanding of the commercial viability and applicability of solid sorbent CO_2 capture technologies for the U.S. existing fleet of coal-fired power plants.

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Executive Summary

The significant reduction of carbon dioxide (CO_2) emissions from existing and new coal-fired power plants presents an enormous opportunity for mitigating greenhouse gas emissions and ultimately global climate change. Development of technologies that cost-effectively reduce CO_2 emissions from coal-fired power plants is very important to retaining coal-fired power plants within the U.S.'s power generation portfolio if climate change regulations are enacted. Currently, conventional CO_2 capture technologies, such as aqueous-monoethanolamine (MEA) based solvent systems, are prohibitively expensive and if implemented could result in a 75 to 100% increase in the cost of electricity (ICOE) for consumers. Primary contributors to the high ICOE with the conventional capture technologies and the technical challenges associated with deploying them on a large scale are: a high parasitic energy load that reduces the power generation capacity of the coal-fired power plant by at least one-third, high capital costs associated with the scale and materials of construction of the process equipment, and insufficient demonstration of these technologies at commercial scale and with an appropriate duration of operational experience.

In this project, RTI and its major project partners, Pennsylvania State University (PSU) and Masdar, have developed and demonstrated a solid sorbent-based CO_2 capture process, utilizing novel polyethyleneimine (PEI) based sorbent materials that can substantially reduce the parasitic energy load and capital and operating costs for CO_2 capture from coal-fired power plants compared to conventional aqueous amine CO_2 scrubbing. The proposed technology has significant potential to meet DOE's performance target of >90% CO_2 capture with <\$40/T-CO_2 cost of CO_2 captured.

A key differentiator of RTI's technology is the synergistic integration of an advanced sorbent material and a proprietary moving, fluidized-bed process configuration along with a comprehensive techno-economic modelling effort which set the targets and guided the direction for the sorbent and process development efforts. RTI's process utilizes a polymeric amine-based CO_2 sorbent to capture CO_2 from coal-fired flue gas. The sorbent consists of a branched polyethylenimine (PEI) polymer supported on a high-surface area support, such as silica, that adsorbs CO_2 via carbamate and bicarbonate chemical reaction pathways. The process technology operates as a cyclic adsorption-regeneration thermal swing process where the solid sorbent is continuously circulated between two multi-stage, fluidized, moving-bed reactors (FMBR) – a CO_2 Adsorber and a sorbent Regenerator.

Under a cooperative agreement with the US DOE, and part of NETL's CO_2 Capture Program, RTI has led an effort to address and mitigate the challenges associated with solid sorbent CO_2 capture. The overall objective of this project was to mitigate the technical and economic risks associated with the scale-up of solid sorbent-based CO_2 capture processes, enabling subsequent larger pilot testing and ultimately commercial deployment. Through the integrated technology development approach, RTI's technology has advanced to TRL-4 (nearly TRL-5, with the one missing variable being testing on actual coal-fired flue gas), according to the DOE/FE definition. The sorbent used in RTI's process has been optimized and scaled-up to 100+ kg scale. The process and engineering and design has been refined through process modelling and lab-scale evaluations leading to the design and construction of a bench-scale prototype system used for confirmation of the technology's commercial viability. Critical process engineering data collected while operating the multi-stage fluidized bed bench-scale contactor evaluation unit (BsCEU) at RTI has proven the reliability, robustness, and superior performance of RTI's process designs. Parametric and long-term testing has provided a wealth of information, guiding the project team on the process conditions needed to operate a solids-based system for optimal performance, with continuous 90% CO_2 capture. Data collected and lessons learned throughout the project have enabled a detailed technology feasibility study. The following is a summary of the project's major accomplishments:

Lab-scale Sorbent Development and Screening:

- Transformed a high capacity, fixed-bed sorbent into a fluidizable form with good CO_2 capture capacity and desired hydrodynamic properties for fluidization.
- Substantially lowered the cost of the sorbent by substituting a low-cost, fluidizable, silica support for expensive, templated, mesoporous silica supports (like MCM-41).
- Achieved CO_2 capture capacities as high as 11.8 wt% CO_2 in a fluidizable form.

- Demonstrated significantly improved thermal stability of the fluidizable sorbent.
- Verified fluidizability of several sorbents over a range of PEI loadings and developed a clear understanding of the relationship with PEI loading, CO_2 capacity, and fluidizability.

Sorbent Scale-up:

- Optimized a conventional impregnation method which was successfully scaled-up to 135 kg by a commercial sorbent manufacturing partner.
- Sorbent from this 135 kg-batch retained all physical and performance attributes of the lab-scale produced sorbent; particularly CO_2 loading of 9 wt%.

Process Design Evaluations and Modeling:

- Identified commercially-feasible and scalable process designs for continuous CO_2 capture and sorbent regeneration.
- Proved need for heat management and use of fluidized-bed reactors and staged configuration for the most optimal performance of any solid sorbent-based CO_2 capture process.
- Developed a multi-physics based fluidized-bed reactor model to analyze the effectiveness of proposed CO_2 capture process configurations.

Bench-scale Technology Evaluations (TRL-4):

- Successfully designed and commissioned a bench-scale, multi-stage, fluidized bed CO_2 capture system with a flue gas processing capacity of 13 scfm, equivalent to ~7 kW_{th}.
- The multi-stage CO_2 Adsorber was able to achieve continuous 90% CO_2 capture from simulated flue gas under a variety of process conditions.
- Conducted several hundreds of hours of parametric and long-term performance testing and proved the robustness and efficiency of the process while identifying the conditions at which the process operated optimally.
- Experimental results clearly demonstrated the need for heat management and temperature control as well as a staged design for both the Adsorber and Regenerator.
- Full regeneration (i.e. very low sorbent lean loading) was not achieved in the single-stage Regenerator. While the single-stage design was effective, the sorbent is capable of much better sorbent regeneration in a two-stage Regenerator.

Techno-Economic Evaluations:

- Performed detailed techno-economic studies using DOE/NETL guidelines to validate the merit of RTI's technology.
- Initial technical feasibility study was updated following collection of performance data from extensive lab- and bench-scale testing
- Estimated cost of CO_2 capture with a conceptual commercial embodiment of our process is 43.3 \$/T-CO_2 cost of CO_2 capture. This estimate ultimately falls short of the DOE/NETL's cost target of \$40/T-CO_2, but there is a pathway to further cost reductions and potential to meet the target.
- Performed sensitivity analyses to identify critical R&D needs and performance targets for both the sorbent and process technologies.
- An EH&S analysis determined that RTI's technology has no major hurdles for commercial implementation.

Having proven the technical and economic viability of RTI's technology, and reducing technical risks (both for the sorbent and process technologies) through bench-scale testing, the next step in the development of this promising technology is to design and construct a pilot-scale system for testing at a coal-fired power plant. At a broader level, this project has advanced the whole of the solid sorbent CO_2 capture field, with advancements in process engineering and design, technical risk mitigation, sorbent scale-up optimization, and an understanding of the commercial viability and applicability of solid sorbent CO_2 capture technologies for the U.S. existing fleet of coal-fired power plants.

1. Introduction

1.1 Background

The most widely studied and applied post combustion CO_2 capture technologies are aqueous amine-based solvent scrubbing processes, such as Fluor's Econamine FG+, ABB Lummus's MEA scrubbing, Siemens' amino acid salt solution, Mitsubishi's KM-CDR, and Alstom's Chilled Ammonia process. Current cost and performance analyses of these technologies indicate that none have the potential to meet the US DOE's cost and performance targets. One promising alternative to conventional, liquid solvent-based CO_2 capture processes is solid, adsorbent-based processes. Solid adsorbent-based processes separate and recover CO_2 by a cyclic, thermal swing, adsorption-desorption process similar to the conventional solvent processes. Solid sorbents are considered promising because they:

- exhibit high CO_2 loadings (10 to 20 wt.% CO_2),
- have lower heat of regeneration as well as low heat capacities (1-1.5 kJ/kg˚K),
- are capable of generating a high partial pressure CO_2 stream without needing to vaporize a solvent,
- are typically less corrosive and therefore allow for the use of low cost materials of construction, and
- avoid the toxicity and volatility issues associated with liquid solvent systems.

Supported amines, which consist of impregnated- and grafted-amine materials, have attracted considerable attention as promising adsorbents for CO_2 separation from flue gas. As part of a DOE/NETL-funded project, Sjostrom and Krutka [2010] (Ref. 1) conducted a comprehensive experimental screening survey of physical and chemical sorbents, including carbon nanotubes, activated carbons, treated and unmodified zeolites, and supported amines, to evaluate their potential for reducing the regeneration energy. From this study, the only family of sorbents that were capable of achieving lower regeneration energies than the state-of-the-art technology, Econamine FG Plus process, was the supported amines. Although Sjostrom and Krutka (2010) identified a total of 10 sorbents, including several supported amines, one carbon nanotube, and a functionalized zeolite, the baseline regeneration energy of 4,530 kJ/kg CO_2 (1,934 Btu/lb. CO_2) used as the screening criteria is too high and a more recent value of 3,240 kJ/kg CO_2 (1,384 Btu/lb. CO_2) has been reported by Fluor [Reddy, 2010] (Ref. 2). As a result, the list of candidate sorbents can be reduced to a total of four supported amines. A similar conclusion that supported- or grafted-amines are currently the only viable solid sorbent option for post-combustion CO_2 capture has been made in a detailed technical review by Sayari et al. [2011] (Ref. 3).

These amine-based adsorbents were originally proposed as aqueous-amine analogues that could potentially achieve the high CO_2 loadings, high CO_2 selectivity, and rapid kinetics associated with aqueous-amines, without the high regeneration energy due to the high sensible heat load for heating water and high stripping steam requirement. The primary difference between the impregnated- and grafted-amine preparation approaches is the interaction between the amine and the surface of the support material with the impregnated-amines being characterized as primarily exhibiting weak amine-surface interactions. Grafted-amine adsorbents are prepared via anhydrous, condensation reactions between surface hydroxyl groups of a high surface area silica-containing support material and an aminosilane producing a surface tethered amine group. As a result, these adsorbents typically exhibit rapid kinetics due to large pores and relatively low loading capacities. Many of the commonly used mesoporous silicas, such as MCM-41, MCM-48, SBA-15, and KIT-6, and aminosilanes are commercially unavailable and their preparation costs are very high. Consequently, it is economically impractical to use grafted-amine adsorbents for large scale, cost-sensitive processes such as post-combustion CO_2 capture. In contrast, impregnated-amine adsorbents are typically prepared using a very simple wet impregnation technique in which a nitrogenous base is dissolved in a solvent, mixed with a support material, and heated, leaving a well-dispersed nitrogenous base in the pore structure of the support. Impregnated-amine adsorbents have much higher amine loadings, can effectively utilize polymeric amines, such as PEI, with high CO_2 loading potential, utilize low cost support materials, and utilize low cost nitrogenous bases instead of aminosilicates.

One of the most promising impregnated amine adsorbents was developed by Dr. Chunshan Song's group at Pennsylvania State University (PSU). Dr. Song's group developed this family of CO_2 adsorbents based on the CO_2-philic polymeric amine, polyethyleneimine (PEI), and had termed the materials "molecular basket sorbents" (MBSs). PSU's work was funded through various DOE/NETL projects. In that research, PSU had demonstrated that the MBS material is capable of achieving high CO_2 loadings (~14 wt.% CO_2), high CO_2/N_2 selectivity (> 1000), reasonable heat of adsorption (66 kJ/mol CO_2), and can be prepared from inexpensive high surface area materials while retaining performance. Typically the MBS adsorbent is prepared by loading sterically branched PEI, which consists of branched chains with numerous amine groups (primary, secondary and tertiary amines) onto a high-surface-area nano-pore material, such as MCM-41 and SBA-15, which have parallel-arranged pore channels. The chemical principles for CO_2 sorption using a functional polymer are based on the following equations:

Carbamate Pathways	Bicarbonate Pathways
Primary: $CO_2 + 2RNH_2 \rightleftarrows NH_4^+ + R_2NCOO^-$	Primary: $CO_2 + H_2O + RNH_2 \rightleftarrows RNH_3^+ + HCO_3^-$
Secondary: $CO_2 + 2R_2NH \rightleftarrows R_2NH_2^+ + R_2NCOO^-$	Secondary: $CO_2 + H_2O + R_2NH \rightleftarrows R_2NH_2^+ + HCO_3^-$
	Tertiary: $CO_2 + H_2O + R_3N \rightleftarrows R_3NH^+ + HCO_3^-$

PSU's MBS exhibited many of the desirable CO_2 capture performance characteristics noted above; however, at the time of award of this project it was simply a laboratory-scale adsorbent and had not been optimized for a specific process design. In addition, the MBS material had many development challenges remaining including the need to:

- improve thermal and chemical stability
- reduce production costs of the materials.

RTI and PSU partnered on this project to address these challenges.

Through several years of R&D RTI, PSU, and other project team members (e.g. Masdar and Masdar Institute) have developed the solid sorbent-based CO_2 capture process and demonstrated the ability to substantially reduce the parasitic energy load and capital and operating costs for CO_2 capture from coal-fired power plants. The key differentiator of this technology is a synergistic integration of 1) an advanced sorbent material, 2) a proprietary moving, fluidized-bed process configuration, and 3) a comprehensive techno-economic evaluation. RTI's process operates as a cyclic adsorption-regeneration thermal swing process where the solid sorbent is continuously circulated between two multi-stage, fluidized, moving-bed reactors (FMBR) – a CO_2 Adsorber and a sorbent regenerator. In addition to the sorbent-based benefits noted above, this type of process has additional advantages:

- Potential for reduced energy loads and lower capital and operating costs
- Superior reactor design for optimized and efficient CO_2 capture performance.

The remaining challenges for this technology are what have provided the framework for the project team's research and development the last four years. At the start of the project, these technology challenges included the need to:

- Achieve proper heat management and temperature control
- Manage solids handling and solids circulation control
- Impart physically strength and attrition-resistant within the sorbent
- Improve stability of sorbent performance.

Through the integrated technology development approach, the project team has advanced this novel sorbent-based CO_2 capture technology to TRL-4, according to the DOE/FE definitions for Technology Readiness Levels. The team has optimized the production and scale-up of its impregnated, fluidizable sorbents and has optimized the fluidized-bed process configuration. Critical process engineering data has been collected using RTI's multi-stage fluidized bed bench-scale contactor evaluation unit (BsCEU) which has allowed for the refinement of the process design as well as economic analyses.

Introduction to RTI's Solid Sorbent-based CO_2 Capture Process

A conceptual basic block flow diagram of RTI's solid sorbent-based CO_2 capture process, integrated into a pulverized coal (PC)-fired power plant, is exhibited in **Figure 1**.

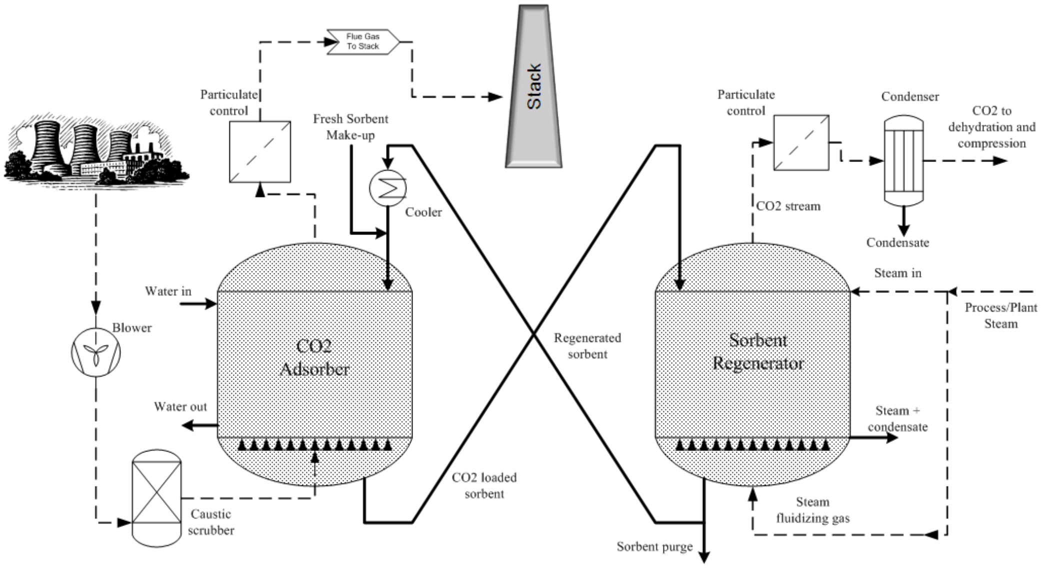


Figure 1. Block flow diagram of advanced solid sorbent CO_2 capture process.

The following is a description of the operating philosophy for a conceptual commercial version of RTI's technology: CO_2-rich flue gas from the PC power plant goes through a caustic scrubbing system, to remove strong acid gases, specifically SO_2 and NO_x, prior to entering the CO_2 Adsorber. Within the Adsorber, flue gas enters the bottom and flows upward, counter-current to the regenerated sorbent that is fed at the top of the Adsorber from the Sorbent Regenerator. The CO_2 Adsorber is designed as a staged FMBR containing heat transfer internals. Heat is generated as the sorbent adsorbs CO_2 and some water from the flue gas. This heat is removed using tempered water flowing through the heat transfer internals. Treated flue gas exits the top of the CO_2 Adsorber and enters into a bag house filter for removal of particulates, primarily attrited sorbent particles. Following particulate removal, the CO_2-depleted flue gas is then directed to the stack and vented.

CO_2-laden sorbent exits the Adsorber and is transported mechanically to the Sorbent Regenerator where a temperature-swing is used to regenerate the sorbent and recover CO_2. Low-pressure steam is used in the regenerator to maintain fluidization and as a stripping gas, at a temperature greater than its dew point. The Sorbent Regenerator design is similar to the CO_2 Adsorber, containing internal heat transfer tubes. Superheated steam is used inside those tubes to supply the heat load to regenerate the sorbent (i.e., reaction + sensible). CO_2 and H_2O released during regeneration, as well as fluidizing steam, exit the top of the reactor. Sorbent fines entrained with this gas stream are separated in a baghouse filter. Condensate water is separated from the gas stream in a cooler and the regeneration off-gas is then sent to a CO_2 dehydration and compression unit. At the bottom of the sorbent regenerator, regenerated sorbent exits and is mechanically transferred through a sorbent cooling unit and on to the top of the CO_2 Adsorber. Fresh sorbent is added to this stream to make-up for any attrited sorbent. A sorbent purge can also be taken here to control the concentration of adsorbed acid gases to maintain the required CO_2 removal activity.

1.2 Research Objectives

The overall objective of this R&D project was to thoroughly evaluate an advanced, solid sorbent-based CO_2 capture process utilizing a very promising PEI-based sorbent material, and demonstrate the potential for achieving the DOE's CO_2 capture process performance target of >90% CO_2 capture with <\$40/T-CO_2 cost of CO_2 captured through reducing the energy penalty related to the CO_2 capture and the associated capital and operating costs. The R&D efforts associated with attaining this objectives were divided into three Budget Periods (BPs).

Specific goals and objectives of the project scope of work, as divided into the project's three BPs, included the following:

Budget Period 1 Goals and Objectives:

- Improve the thermal stability and contaminant tolerance of the base PEI reactant to further improve critical CO_2 capture and regeneration performance characteristics
- Transition PSU's fixed-bed MBS materials into a fluidizable form while retaining the physical, chemical, and CO_2 capture performance characteristics
- Determine how critical process design elements such as reactor geometries, heat transfer tubes, gas velocities, and gas-solid flow influence reactor temperature profiles, heat and mass transfer rates, adsorption and regeneration kinetics, and solids flow hydrodynamics
- Establish design and cost performance baselines for a large-scale CO_2 capture process based on MBS materials, i.e., preliminary estimates of energy penalty, levelized cost of electricity and corresponding increase in the cost, capital costs, operating costs, and overall CO_2 capture cost.

Budget Period 2 Goals and Objectives:

- Produce an advanced, fluidized-bed sorbent exhibiting significant improvements in critical properties (thermal stability, CO_2 capture performance, scalability, physical properties)
- Experimentally demonstrate that the developed circulating fluidized-bed reactor process arrangement is capable of achieving >90% CO_2 capture and that heat management in the CO_2 Adsorber is critical for achieving optimal CO_2 capture efficiency. Utilize critical process data collected during testing to upgrade the regenerator portion of the bench-scale prototype
- Develop detailed design and engineering drawings of a bench-scale circulating fluidized-bed reactor process system
- Complete the construction of the bench-scale circulating fluidized-bed reactor process system
- Evaluate the performance of the bench-scale circulating fluidized-bed reactor process system and the CO_2 capture sorbent
- Demonstrate, on a bench-scale, the effective and continuous CO_2 capture using the bench-scale circulating fluidized-bed reactor process system
- Continue the advancement of the CO_2 capture sorbent and demonstrate improved CO_2 capture performance, fluidizability, and capability to scale-up to 100+ kg.

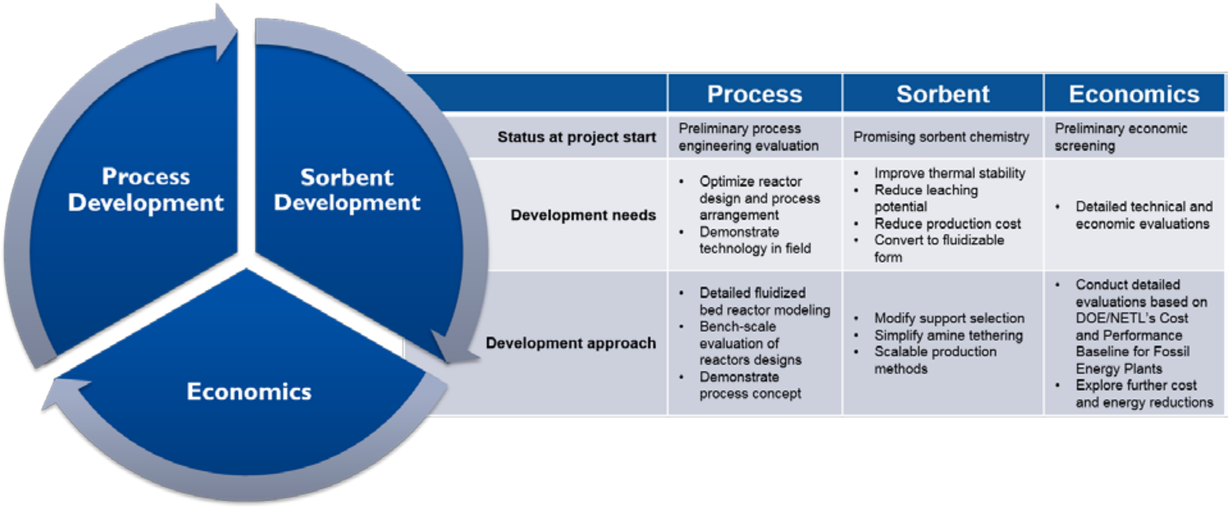
Budget Period 3 Goals and Objectives:

- Utilize pilot manufacturing equipment to scale-up production of the fluidized-bed PEI-based sorbent to 300 lbs to meet the inventory needs of RTI's bench-scale system, with the sorbent having comparable properties as the PEI-based sorbent prepared in the lab by the same preparation procedure
- Demonstrate, on a bench-scale, effective and continuous CO_2 capture from simulated coal-fired flue gas using the PEI-based sorbent within RTI's prototype system (i.e. conduct extensive parametric and long-term performance testing). Effective CO_2 capture implies that the CO_2 capture sorbent is chemically, thermally, and physically stable over multiple adsorption/regeneration cycles and shows significant potential to meet the DOE program targets for CO_2 capture

- Substantially prove the technical and economic competitiveness of the PEI-based CO_2 capture process through an updated technical feasibility study and environmental analysis of the process technology.

1.3 Research Approach

To achieve the project objectives noted in Section 1.2, the project team had divided R&D efforts into eight separate tasks spanning three budget periods. An integrated development approach has been a key focus of this project in which process development, sorbent development, and economic analyses have guided each of the other development processes. **Figure 2** shows the philosophy of RTI’s integrated technology development, status of development efforts at the beginning of the project, and the research approach taken to advance the technology through this project’s R&D efforts.



	Process	Sorbent	Economics
Status at project start	Preliminary process engineering evaluation	Promising sorbent chemistry	Preliminary economic screening
Development needs	• Optimize reactor design and process arrangement • Demonstrate technology in field	• Improve thermal stability • Reduce leaching potential • Reduce production cost • Convert to fluidizable form	• Detailed technical and economic evaluations
Development approach	• Detailed fluidized bed reactor modeling • Bench-scale evaluation of reactors designs • Demonstrate process concept	• Modify support selection • Simplify amine tethering • Scalable production methods	• Conduct detailed evaluations based on DOE/NETL’s Cost and Performance Baseline for Fossil Energy Plants • Explore further cost and energy reductions

Figure 2. RTI's philosophy of integrated technology development for the solid sorbent-based CO_2 capture technology

Early work in Budget Period 1 (BP1) included parallel efforts that focused on sorbent development, process development, and a technical feasibility evaluation. Sorbent development efforts focused on improving the base PEI CO_2 capture and regeneration performance and the chemical and thermal stability. In addition, the team focused on producing a promising first generation fluidized-bed sorbent by leveraging PSU’s previous work in developing a promising fixed-bed sorbent. Scale-up efforts were also conducted. In process development, fluidized-bed modeling was used to help guide the sorbent improvement efforts, to establish an understanding of how process elements influence CO_2 capture performance, and provided information for RTI’s technology feasibility study which proved the commercial viability and attractiveness of RTI’s PEI-based CO_2 capture technology.

Budget Period 2 (BP2) efforts were focused on process intensification and sorbent optimization. A bench-scale contactor evaluation unit (BsCEU), designed in BP1, was built and tested. This system used an inventory of sorbent manufactured by a commercial sorbent manufacturing partner. Experiments were conducted in the BsCEU evaluating key process variables to identify optimal process operating conditions and designs for the FMBR and heat transfer internals. In parallel, the project team focused on developing improved sorbents, needed for bench-scale testing in BP3, with improved CO_2 loading capacity, thermal and chemical stability, CO_2 capture rates, and other key properties. The knowledge gained through sorbent improvement and process evaluation was utilized in process design improvements made in BP3 on the bench-scale prototype.

Given successful attainment of BP2 milestones, the project team continued with bench-scale testing of the process system in BP3 collecting quality performance data to support a more detailed technology feasibility study. Enlisting a third-party fabrication company, the project team made several improvements to the BsCEU (including upgrades to the gas flow control, the tempered cooling water delivery, the particulate filtering mechanism, the heating capability of the current regenerator, and some process measurements) to optimize system performance. In addition, the attainment of a "high-fidelity" system was achieved through a more efficient, multiple-stage contactor design and subsequent execution of the construction and reconfiguration activities. RTI's sorbent manufacturing partner produced ~ 100 kg of the best-performing fluidized-bed sorbent material to replenish the sorbent inventory for bench-scale testing. Parametric and long-term performance testing of the bench-scale prototype were carried out at RTI's Energy Technology Development Facility (ETDF). Using operating data collected from parametric and long-term testing, a detailed update to the technology feasibility study (from BP1) was performed.

2. Summary of Project Accomplishments

2.1 Project Accomplishments

The project team has completed all project milestones, success criteria, and objectives. Completion of these objectives has resulted in a fully operational bench-scale CO_2 capture system, collection of important CO_2 capture and heat management performance data, significant improvement to the performance and stability of our PEI-based sorbent, and scale-up of this sorbent to a total of ~300 kg by a commercial manufacturer while retaining all of the performance and physical property metrics of our lab-scale sorbent. The specific accomplishments of BP1, BP2, and BP3 are summarized in **Table 1**.

Table 1. Summary of Project Team's accomplishments in BP1, BP2, and BP3

	Budget Period 1	Budget Period 2	Budget Period 3
Process	• Developed comprehensive techno-economic evaluation that shows RTI's solid sorbent CO_2 Capture Process exhibits significant cost and energy improvements over SOTA amine processes. • Developed a fluidized-bed reactor model. • Developed two reactor designs that have key features of effective heat management and counter-current flow of gas and solids. • Designed a bench-scale contactor evaluation unit to demonstrate key process concepts and validate fluidized-bed model.	• Constructed and installed a bench-scale contactor evaluation unit. • Demonstrated that the bench-scale fluidized moving-bed reactor (FMBR) unit was capable of continuous, stable CO_2 removal in the Adsorber and CO_2 desorption in the Regenerator. • Initial parametric testing, including heat management tests, reactor temperature tests, flue gas condition tests, were performed on the BsCEU. • Bench-scale tests showed that heat removal from the CO_2 Adsorber during CO_2 adsorption has a significant beneficial impact on the sorbent's CO_2 loading, particularly compared to tests that mimic the condition of no heat removal in the Adsorber. • Bench-scale tests determined that the BsCEU Regenerator is not optimally designed and a staged contactor approach to the Regenerator design will lead to more efficient and complete sorbent regeneration in the BsCEU.	• Completed a 100-hr long-term testing campaign on RTI's bench-scale contactor evaluation unit. • Staged BsCEU design showed robust operation without any downtime throughout the 100-hour testing campaign. • All BsCEU testing confirmed that 90% rate of CO_2 capture was easily controlled throughout tests by adjusting process control parameters. • Initial parametric testing, including heat management tests, reactor temperature tests, flue gas condition tests, were performed on the BsCEU. • Bench-scale tests showed that heat removal from the CO_2 Adsorber during CO_2 adsorption has a significant beneficial impact on the sorbent's CO_2 loading, particularly compared to tests that mimic the condition of no heat removal in the Adsorber. • Parametric tests correlated system performance to changes in the following parameters: Adsorber temperature, Regenerator temperature, Flue gas velocity, flue gas CO_2 concentration, Regenerator off gas (ROG) CO_2 concentration, solids-to-gas ratio.
Sorbent	• Significant progress made in improving PEI-based sorbent stability. • Replaced expensive mesoporous silicas with better-performing, low-cost silica materials. • Progress made in transitioning to a low-cost, fluidizable, attrition-resistant particle suitable for use in a fluidized-bed process.	• Manufactured 150 kg of 'best-candidate' PEI-based sorbent by a commercial manufacturer. Scaled-up sorbent retained all physical and performance metrics of the lab-scale produced sorbent. • Evaluated and identified suitable low-cost, commercial supports for sorbent manufacturing and optimized manufacturing approach. • Identified procedure for making next generation, extremely stable, high CO_2 loading (11 wt.%), water-stable sorbents.	• A systematic study of several sorbent preparation variables improved overall sorbent preparation procedure for scale-up. • A Design of Experiments statistical analysis indicated that sorbent exposure to oxygen at temperatures of >70 °C should be avoided. The impact of this finding was to modify the BsCEU system such that sorbent leaving the regenerator would be cooled below 70 °C prior to coming in contact with an air. • Initial concerns over sorbent degradation and stability were resolved and the sorbent maintained desired CO_2 capture

			performance stability after 5 months of parametric testing. • Use of organic templates in water-stable sorbent preparation procedure shows potential to improve bulk density and CO_2 sorption capacity.
Economics	• Developed comprehensive techno-economic evaluation that shows RTI's solid sorbent CO_2 Capture Process exhibits significant cost and energy improvements over SOTA amine processes. • Project team established a pathway to achieve DOE/NETL's programmatic economic goals.	• Collected process design and engineering data to be used in economic analysis performed in BP3.	• Updated technical and economic analyses showed the combined effect of changing process assumptions simultaneously was a 5.1 \$/T-CO_2 increase in the cost of CO_2 capture to a total of 45.0 \$/T-CO_2 captured. • Environmental, health, and safety analysis exhibited no major EHS-related hurdles to implementing RTI's technology at commercial-scale. • Various strategies were identified that have significant potential to further reduce the capital and operating costs and energy penalty of RTI's process technology.

2.2 Project Milestones

The project team has achieved all project milestones. The following table (**Table 2**) is a summary of the project milestones and descriptions of the team's achievements relative to each milestone.

Table 2. Overview of project milestones

Milestone	Description	Due Date	Completion	Status / Achievement
Budget Period 1				
A	Updated Project Management Plan	10/31/2011	6/21/13	***Milestone Achieved.*** Project Management Plan file delivered. PMP was also updated for BP2 and BP3 continuations.
B	Kick-off Meeting	12/14/2011	12/14/11	***Milestone Achieved.*** Kick-off meeting held in Pittsburgh, PA. Presentation file provided to DOE/NETL.
C	Successful scale-up of fluidized-bed MBS material	7/31/2013	6/27/14	***Milestone Achieved.*** Successful sorbent scale-up was completed in June 2014. It was recommended by RTI, and agreed upon by DOE/NETL, that scale-up of the sorbent be performed when the sorbent fully exhibited a desired combination of stability and CO_2 capture performance.
D	Favorable technology feasibility study	6/30/2012	7/9/2012	***Milestone Achieved.*** Techno-economic analysis was completed in July 2012. Delivered a "Preliminary Technology Feasibility Study" topical report in August 2012. Report clearly illustrates the potential of RTI's technology to meet DOE cost targets.
E	Working multi-physics, fluidized-bed model of FMBR design	12/31/2012	12/11/2012	***Milestone Achieved.*** Working fluidized-bed model was developed in BP1 by RTI and partner PSRI.
F	Fabrication-ready design and schedule for bench-scale FMBR unit	12/31/2012	12/12/2012	***Milestone Achieved.*** Design of bench-scale system was completed in December 2012 and Engineering Design Package delivered to DOE/NETL.
Budget Period 2				
G	Fully operational bench-scale FMBR unit capable of adsorption / desorption operation.	12/31/13	7/31/14	***Milestone Achieved.*** Construction and installation of a bench-scale contactor evaluation unit (BsCEU) was completed by June 2014. Calibration and validation of BsCEU system operation with an inert particle were completed in early July 2014. Roughly 75 kg of scaled-up CO_2 capture sorbent was loaded and the system was recalibrated for the new sorbent material. Experiments performed in late July 2014 demonstrated that the bench-scale fluidized moving-bed reactor (FMBR) unit

				was capable of continuous, stable CO_2 removal in the Adsorber and sorbent regeneration in the Regenerator. Initial parametric testing, including heat management tests, reactor temperature tests, and flue gas condition tests, were performed in BP2.
H	Fabrication-ready design and schedule for high-fidelity, bench-scale FMBR prototype.	6/30/14	9/30/14	***Milestone Achieved.*** This milestone refers to the final step required to make the BsCEU a true, high-fidelity system with the most optimal design for the CO_2 Adsorber and Sorbent Regenerator. This milestone refers to the design work required to replace the current Sorbent Regenerator with a staged contactor for regeneration. A design package for this new Regenerator was completed in BP2.
I	Successful scale-up of sorbent material with confirmation of maintained properties and performance.	6/30/14	6/30/14	***Milestone Achieved.*** 150 kg of our 'best-candidate' polyethyleneimine (PEI)-based sorbent was produced by a commercial manufacturer. Sorbent from the 150 kg-batch retained all physical and performance metrics of the lab-scale produced sorbent including: • *CO_2 loading:* 9 wt.% (2.05 mol CO_2/kg) • *Mean particle diameter:* 175 um • *Tap Density:* 0.6 g/cc • *Fluidizability:* Visually confirmed under realistic process conditions in RTI's vFBR system and BsCEU. The sorbent "passed" all fluidization tests.
Budget Period 3				
J	Operational FMBR prototype capable of 90% CO_2 capture.	6/30/15	7/22/15	***Milestone Achieved.*** Consistent operation and 90% CO_2 capture performance achieved with bench-scale system modifications and fresh scale-up batch of PEI-based sorbent. Operation of bench-scale system is very reliable. Reconfiguration of the BsCEU in BP3 also resulted in a prototype system capable of operating over 100 continuous hours without interruption.
K	Completion of 1,000 hours of parametric and long-term testing.	12/31/15	12/31/15	***Milestone Achieved.*** A total of ~300 hrs parametric testing hours and ~120 hrs long-term testing hours was completed. Although the total accumulated hours fell short of the 1,000 hrs described in the milestone, the project team has achieved the desired results expected from these tests having collected a wealth of CO_2 capture performance data at numerous process variables, identified how system performance varies due to changes in these process variables, and has proven the robust and reliable nature of the bench-scale system through continuous operation. Also, multiple shutdowns and start-ups have proven that the system can go from process standstill to steady-state operation (and back to standstill) without any difficulty.
L	Favorable technical, economic, and environmental study (potential to meet < 35% ICOE target; comparison to Task 2.0 shows improved environmental performance)	12/31/15	3/31/16	***Milestone Achieved.*** A wealth of data from BsCEU testing was collected by the project team and used to update the project team's original techno-economic analysis. These data were used to complete the final TEA and EHS studies. The combined effect of changing all the assumptions simultaneously was a 5.1 \$/T-CO_2 increase in the cost of CO_2 capture to a total of 45.0 \$/T-CO_2 captured. Potential to meet < 35% ICOE target relies on various process improvement and heat integration strategies that hold great promise for significant cost reduction, but require experimental verification.

2.3 Project Success Criteria

The project team has met all project success criteria. The following table (**Table 3**) is a summary of the project success criteria and descriptions of the team's achievements relative to each success criteria.

Table 3. Overview of project success criteria

Success Criteria Description	Status / Achievement
Budget Period 1	
Development of a favorable technology feasibility study showing potential to meet ICOE target of < 35%	***Success Criteria Achieved.*** Delivered the "Preliminary Technology Feasibility Study" topical report in August 2012. Report clearly illustrates the potential of RTI technology to meet DOE cost targets
Technology feasibility study should help define additional sorbent and process performance targets for an economically viable process	***Success Criteria Achieved.*** Sensitivity studies demonstrated economic impact of various variables, and provided guidance on future optimization to meet the cost targets.
Improve the thermal and chemical stability of PEI reactant while transitioning MBS material into a fluidizable form.	***Success Criteria Achieved.*** Significant sorbent stability improvement demonstrated at 120°C through process condition selection (H2O addition), metal-amine complexation, and cross-linking pathways. Sorbent also prepared through spray drying making a fluidizable particle.
Focus on low cost preparation of sorbents	***Success Criteria Achieved.*** A low cost silica support was identified as a superior base support material compared to 200 times more expensive mesoporous silica support proposed by PSU.
Favorable sorbent performance: >6.6 wt.% CO_2 loading capacity; Performance stability exhibited at a regeneration temperature of 100°C for >25 cycles	***Success Criteria Achieved.*** Exceeded these targets in BP1.
Budget Period 2	
FMBR unit is operational without significant interruptions and using scaled-up sorbent material is able to capture 90% of CO_2 in simulated flue gas	***Success Criteria Achieved.*** RTI's BsCEU system was fully commissioned on an inert commissioning material in early July 2014. CO_2 capture testing using the scaled-up sorbent started in July and operated through August 2014. Several tests show the BsCEU ability to achieve 90% capture in the simulated flue gas environment.
CO_2 capture performance of the scaled-up sorbent material improves when heat transfer internals (with cooling water) are inserted in the sorbent bed. CO_2 loading improves by > 20%.	***Success Criteria Achieved.*** Several extended heat management tests were performed in August 2014 using the BsCEU system. These tests showed that heat removal from the CO_2 Adsorber during CO_2 adsorption has a significant beneficial impact on the sorbent's CO_2 loading, particularly compared to tests that mimic the condition of no heat removal in the Adsorber (i.e. heat management in our solid sorbent CO_2 capture process was shown to be of critical importance). At certain points in the extended heat management tests, heat removal from the CO_2 Adsorber resulted in an improvement of 55 percentage points in terms of CO_2 capture rate.
Full regeneration of the fluidized-bed sorbent material is possible at 100°C in simulated conditions.	***Success Criteria Achieved.*** Several tests have shown that sufficient regeneration of the fluidized-bed sorbent is achievable at 100°C, though work in BP2 has proven the following: 1) the optimal regeneration temperature for the sorbent is between 110 - 130°C, 2) full regeneration (i.e. leaving 0 wt.% CO_2 on the regenerated sorbent), though possible, is not practical for economical operation of the CO_2 capture process, and 3) the BsCEU Regenerator is not optimally designed and a staged contactor approach to the Regenerator design will lead to more efficient and complete sorbent regeneration in the BsCEU (this is already proposed as an activity in BP3).
Sorbent scale-up to 30 lbs of the fluidized-bed sorbent material retains lab-scale performance properties within +/- 10% of targets.	***Success Criteria Achieved.*** This success criteria target actually increased to 150 kg – as this was the amount needed to supply the BsCEU inventory. 150 kg of our 'best-candidate' polyethyleneimine (PEI)-based sorbent was produced by a commercial manufacturer (Hadsell Chemical). The sorbent from the 150 kg-batch retained all physical and performance metrics within 10% of the lab-scale produced sorbent.
Commercial manufacturer has demonstrated the scalability of the MBS material and is confident and has preparation procedures in place to produce a 1,000 lb. batch.	***Success Criteria Achieved.*** 150 kg of our 'best-candidate' polyethyleneimine (PEI)-based sorbent was produced by a commercial manufacturer (Hadsell Chemical). Hadsell Chemical has capabilities to confidently scale production to 1,000 lb. scale. Silica support was sourced through SiliCycle, Inc – a commercial manufacturer of silica materials. SiliCycle, Inc currently produces the desired silica support in ton-scale quantities.
Budget Period 3	

1,000 hours of bench-scale field testing logged. 90% CO_2 capture and full sorbent regeneration achieved under reasonable, commercially-feasible process conditions	***Success Criteria Achieved.*** A total of ~300 hrs parametric testing hours and ~120 hrs long-term testing hours has been completed. Although the total accumulated hours has fallen short of the 1,000 hrs milestone, the project team has achieved the desired results expected from these tests having collected a wealth of CO_2 capture performance data at numerous process variable, identified how system performance varies due to changes in these process variables, and has proven the robust and reliable nature of the bench-scale system through continuous operation. Also, multiple shutdowns and start-ups have proven that the system can go from process standstill to steady-state operation (and back to standstill) without any difficulty.
Scale-up to 1,000 lbs MBS material retains same sorbent properties and performance	***Success Criteria Achieved.*** 150 kg of our 'best-candidate' polyethyleneimine (PEI)-based sorbent was produced by a commercial manufacturer. Sorbent from the 150 kg-batch retained all physical and performance metrics of the lab-scale produced sorbent
Higher level of confidence that technology can meet ICOE target of < 35%	***Not Achieved.*** Test data collected during bench-scale evaluations has led the team to modify the assumptions that went into the techno-economic evaluation. The combined effect of changing these assumptions simultaneously is an increase of 5.1 \$/T-CO_2 which increases the total cost of CO_2 capture to 45.0 \$/T-CO_2 for RTI's solid sorbent-based CO_2 capture process.
More efficient, and cost-effective, process and heat integration strategies identified	***Success Criteria Achieved.*** Several process and heat integration strategies were identified, including the effective recovery of heat from the CO_2 Adsorber and compression train and novel heat integration approaches such as the use of an Organic Rankine Cycle to recover heat from the CO_2 Adsorber.
Acceptable Environmental, Health and Safety assessment	***Success Criteria Achieved.*** A detailed EHS assessment identified no major EHS-related hurdles to implementing RTI's technology on a commercial-scale.

3. Experimental Methods

3.1 Materials

3.1.1 Preparation of PEI-Impregnated CO_2 Capture Sorbent ("Generation 1" Sorbent)

The main sorbent which has been used throughout this project is the "Generation 1" sorbent material prepared by impregnating PEI on a silica support. In carrying out the impregnation approach, the pores of a chosen silica support are first dried in a laboratory oven under nitrogen. In parallel, within a reactor vessel, polyethyleneimine (PEI) is slowly dissolved in a chosen alcohol (e.g. ethanol, methanol, etc.) under vigorous stirring. After a set time of mixing, the dried silica support material is added slowly to the reactor vessel while the whole mixture is vigorously stirred for an extended period of time. After complete addition of silica, the mixture is then heated to ~65˚C under atmospheric pressure, to help remove the alcohol solvent. After complete drying, sorbent samples are taken for characterization analysis and performance screening tests.

The procedure above was also followed using functionalized silica supports which are used to promote PEI tethering within the silica support pores. After heat treatment, these sorbents are washed with a copious amount of water (~2.5 L of water/g of sorbent). This water washing step represents a rigorous way to prove whether PEI leaching may be prevented by the PEI tethering to the silica support. It is theorized that water washing ensures that any untethered PEI is rinsed away in the effluent water and any tethered PEI remains on the support and thus will be available to capture CO_2 during screening tests. During the water washing step, the pH of the eluent is regularly measured, and the rinse is continued until the pH becomes neutral. In the preparation (and subsequent washing) of some sorbents, low pH measurements (in the basic range) were observed and are assumed to be indicative of untethered (or weakly-bound) PEI being washed away from the support. Additionally, water washing may be a viable approach to remove PEI from the outer support surfaces (not just from inside the pores) which allows for better fluidizability of the sorbent particles since the "sticky" amine will no longer be present on the outer surfaces of the sorbent. The water washing step was also performed for many sorbents prepared using the standard PEI impregnation approached (i.e. using non-functionalized silica supports). The water washing used for evaluating PEI leaching is a much more rigorous treatment than the surface stripping.

Portions of the sorbents prepared using this impregnation approach were saved prior to water washing so that "baseline" sorbents were available to contrast the impact washing has on a sorbent's CO_2 capacity.

3.1.2 Preparation of Water-Stable CO_2 Capture Sorbent ("Generation 2" Sorbent)

Though the "Generation 1" sorbents met all of the project team's testing criteria for CO_2 loading capacity, density, particle size, and fluidizability, there remained a concern that the PEI was not immobilized well enough within the support to prevent PEI leaching (as exhibited by a significant drop in CO_2 loading capacity when the sorbent candidates were water-washed). To overcome this concern, the project team pursued a sorbent procedure that results in stronger PEI-silica tethering. The project team achieved success in utilizing $Si(OR)_4$ type reagents (where $R = C_2H_5$) in the preparation procedures to produce the next generation material, water-stable "Generation 2" sorbents.

Two preparation approaches were used when investigating $Si(OR)_4$ type reagents. The first involved reacting tetraethylorthosilicate (TEOS) with PEI in the absence of any additional silica support. Since TEOS is used to prepare several mesoporous silica materials, it was theorized that mesoporous solids would form in the presence of PEI and potentially trap or react with PEI leading to a strong PEI-silica bond which would prevent leaching. When TEOS is added to methanol acidified with .1M HCl (under vigorous stirring) a homogeneous solution is observed. A separate homogeneous solution of PEI (1 mol equivalent to TEOS) and alcohol (e.g. methanol, ethanol) is prepared and upon addition to the TEOS solution, results in the formation of white solid precipitates. The mixture is then filtered, water-washed, and dried, with the resulting solid observed to be a dry particulate solid and free of adhesion between particles.

The second water-stable sorbent preparation approach involves similar steps as noted in the "Generation 1" sorbent approach (Section 3.1.1) by treating PEI-impregnated silica sorbent with TEOS (or other $Si(OR)_4$ type reagents) through wet impregnation, drying, and water washing.

3.1.3 Other Sorbent Preparation Methods

In addition to the "Generation 1" and "Generation 2" CO_2 capture sorbents investigated in this project, the project team also explored tethering strategies to prevent PEI leaching. The experimental approach in this area was narrowed down two types of syntheses to achieve tethering of PEI to the silica support surface. These approaches were:

1. Deposition of metals on the silica support surface for metal-amine complexation
2. Treatment of the silica support surface with reagents that can react with PEI and help promote PEI tethering

In carrying out these approaches, first, the silica supports were modified with the surface bonding strategy listed above. In some instances, the silica support is treated first followed by PEI introduction to the modified surface. In other instances, the silica support is first impregnated with PEI then treated with a tethering agent. After the surface bonding method is complete, the solid sorbents are either delivered for CO_2 capture performance testing or are first water washed prior to testing.

Regarding the second tethering approach noted above, the project team evaluated PEI tethering through the use of specialty reagents. These reagents can react with amines as well as with the silica support surface. It was theorized that this reactivity can be used to create a chemical bond between PEI and the surface of a silica support. The project team also explored the chemistry solely between the specialty reagents and PEI in the absence of a solid support. The use of these new tethering reagents included two general preparation procedures. In the first procedure a solution of the reagent was added to a slurry of a silica support under vigorous mixing, both with and without additional heating. PEI was then added to the mixture while stirring of the mixture continued. The mixture was then dried and delivered for CO_2 capture test screening. The other approach used in preparing the sorbents by this new method, involved a complete modification of the steps involved in which the reagent and PEI were added to the mixture, how the sorbent was dried, and when water washing was performed.

3.2 Analytical, Characterization, and Screening

Within this project, sorbent analysis, characterization, and screening tests were conducted to provide insights into the physical and chemical properties of sorbents, to evaluate the impact of different variables on CO_2 capture performance, and to identify the worst performing sorbents and eliminate them from consideration for additional testing and evaluation. In terms of general characterization, the project team was able to use existing equipment to measure the following properties of prepared sorbents: BET surface area, pore volume, pore size, density, particle size, and attrition-resistance/physical strength. Related to sorbent performance testing and screening, the project team built two critical pieces of equipment – an automated packed-bed reactor (PBR) system and "visual" fluidized-bed (vFBR) system – for screening sorbents based on CO_2 capture performance and fluidization properties respectively. Additionally, thermogravimetric analysis (TGA) systems and IR spectroscopy equipment were also used for sorbent analysis and screening.

3.2.1 Automated, Packed Bed Sorbent Screening Apparatus

A simplified process flow diagram of the PBR system is provided in **Figure 3** and photograph of the unit is exhibited in **Figure 4**. This system consists of four main sections:

1. Flue Gas Generation
2. Packed-Bed Reactor
3. Gas Switching Valves, and
4. Gas analysis.

The Flue Gas Generation system consists of a bank of electronic gas mass flow controllers and a temperature controlled water saturator. This arrangement allows for the generation of a wide range of flue gas compositions including "neat" (CO_2-H_2O-N_2) to "realistic" (CO_2-H_2O-SO_2-O_2-N_2) flue gas mixtures. All lines downstream of the Flue Gas Saturator are heated to avoid H_2O condensation in the feed lines. The Packed-bed Reactor is constructed from a ½ in. OD by 8 in. long stainless steel tube and the reactor temperature is controlled by two well-tuned, external, electric heaters. A thermowell consisting of four very small K-type thermocouples, spaced 1" apart, runs down the centerline of the reactor. This thermowell allows for measurement of the thermal profile through the sorbent bed during CO_2 capture and regeneration. The addition of six solenoid switching valves allows our system to switch between five states (Feed Composition Analysis, Adsorption, Purge, Regeneration, and Cooling) necessary for completing a CO_2 capture-regeneration cycle. These valves switch automatically based on process measurements allowing for continuous, unmanned, cycling experiments. The CO_2 concentration of the gas is measured by an on-line, continuous CO_2 analyzer. The reactor effluent gas passes through a condenser to knockout H_2O prior to being sent to the gas analysis system. An SO_2 analyzer was also installed giving the team a capability to measure the effect of SO_2 on sorbent performance. Process measurements and control are achieved by an in-house developed data acquisition and process control system.

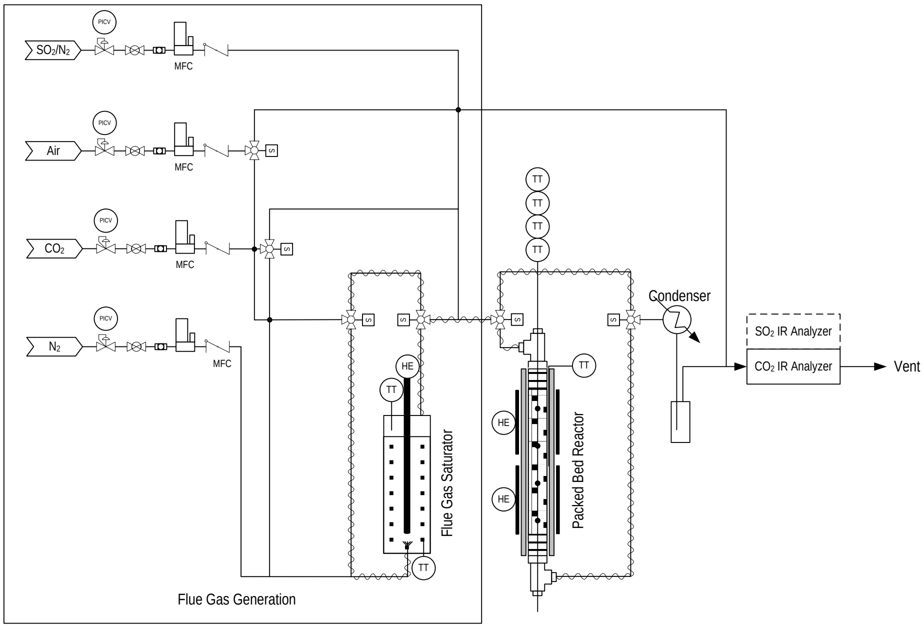


Figure 3. Simplified Process Flow Diagram of RTI's Packed-bed Reactor system for multi-cycle testing

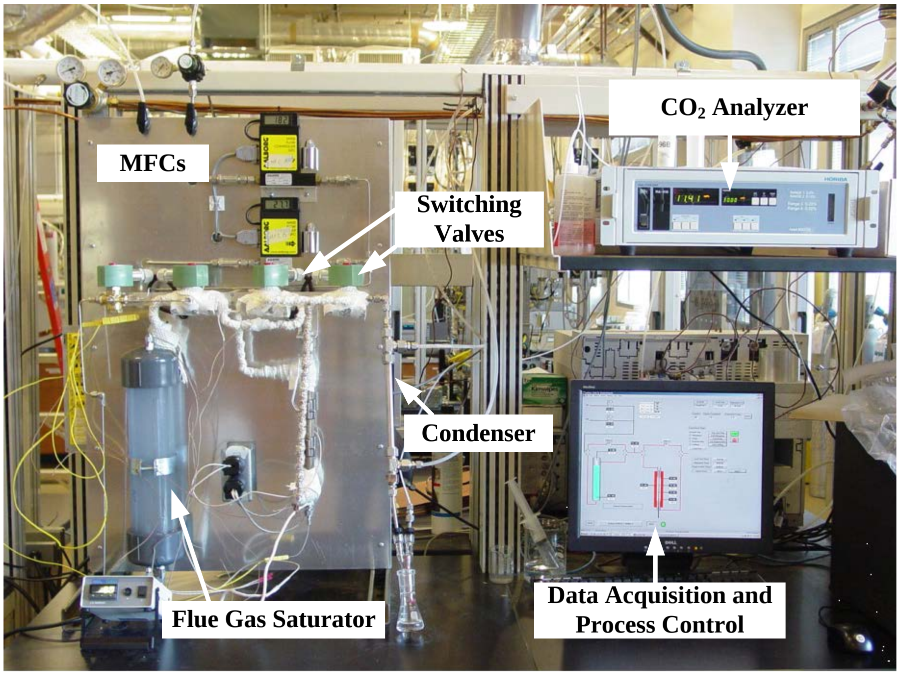


Figure 4. RTI's Packed-bed Reactor system for multi-cycle testing

3.2.2 "Visual" Fluidized-Bed Reactor (vFBR) System

The ability to measure and observe the "fluidizability" of prepared sorbents was a critical aspect of the sorbent development and improvement efforts and necessitated the development and construction of a "visual" fluidized-bed reactor (vFBR) system. The vFBR was developed to systematically evaluate the fluidizability of prepared sorbents under relevant process conditions. **Figure 5** shows the vFBR as constructed in RTI's laboratory. Being constructed of glass, the vFBR allows for visual observation of fluidizing particles under specific process conditions. An opaque steel apparatus would make it difficult to evaluate fluidization behavior and observe PEI leaching. This system is also useful for determining a variety of process-related sorbent characteristics such as minimum fluidization velocity, fluidizibility, attrition loss, and CO_2 loading. The vFBR is operated at a relatively wide range of temperatures (between 25°C to 150°C) allowing the sorbent to perform CO_2 adsorption at near room temperature and regenerate at an elevated temperature.

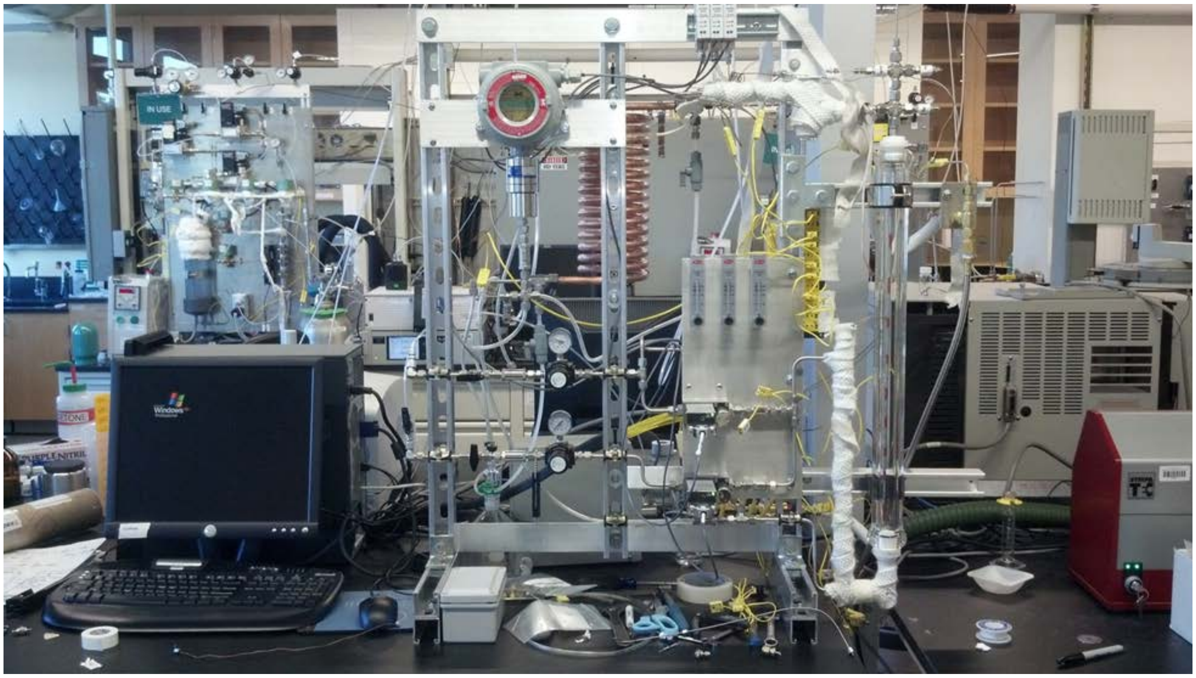


Figure 5. RTI's visual fluidized-bed reactor (vFBR) system used for screening fluidizable sorbents

Testing of new sorbent candidates in the vFBR was carried out as such: samples of new sorbent formulations (~200g) are loaded into the vFBR for testing under realistic process conditions. The vFBR testing cycle occurs under four sets of process conditions (varying the temperature and humidity within the vFBR) – each one corresponding to envisioned conditions within a commercial solid sorbent CO_2 capture process. The four sets of process conditions, which every sorbent candidate was cycled through, were established to mimic the following:

1. the top of the CO_2 Adsorber (low CO_2 %, lower adsorption temperature)
2. the bottom of the CO_2 Adsorber (high CO_2 %, higher adsorption temperature)
3. the top of the Sorbent Regenerator (higher CO_2 and H_2O content, higher regeneration temperature)
4. the bottom of a Sorbent Regenerator (lower CO_2 and H_2O content, higher regeneration temperature).

Following vFBR testing, the sorbent candidates were given simply a “pass” or “fail” grade. A passing grade indicates that the sorbent particles fluidize smoothly with little to no agglomeration, maintain CO_2 capture performance, and exhibit little to no PEI leaching. A failing grade indicates that these three sorbent metrics were not met for any of the four sets of process conditions.

3.2.3 Other Analytical, Characterization, and Screening Equipment

Thermogravimetric Analysis (TGA). Thermal properties and sorption-desorption performance of PEI-based sorbent samples were evaluated using thermogravimetric analysis by both RTI and PSU using in-house TGA equipment. Typical TGA procedures carried out in the project included first loading the TGA with ~10 mg of the sample and increasing the temperature at a rate of 10 ºC/min from 30 ºC to 100 ºC. The sorbent sample is then kept at 100 ºC for ~40 mins under N_2 flow of 100 ml/min to remove any trapped moisture, solvent, or other adsorbates potentially on the sample. The TGA temperature is then reduced to the desired temperature (e.g., 70 ºC), the gas is switched from N_2 to pure CO_2 (or a gas mixture) at a flowrate of 200 ml/min, and held at the desired temperature for ~50 mins for the CO_2 sorption. After CO_2 sorption is complete, the TGA temperature is increased to ~120 ºC, and the gas flow is switched back to N_2 for desorption. The mass-based CO_2 sorption capacity (mg-CO_2/g-sorb) was calculated according to the weight change of the sample recorded by the TGA analyzer.

Diffuse reflectance infrared Fourier-transform spectroscopy (DRIFTS). Another method of sorbent screening employed was diffuse reflectance infrared fourier-transform spectroscopy. RTI in particular used DRIFTS to be able to test sorbent candidates in a controlled environment and to provide insights in CO_2-amine interaction, adsorption-desorption mechanisms, and specific degradation pathways. **Figure 4** exhibits a simple schematic of RTI's in-situ DRIFTS unit.

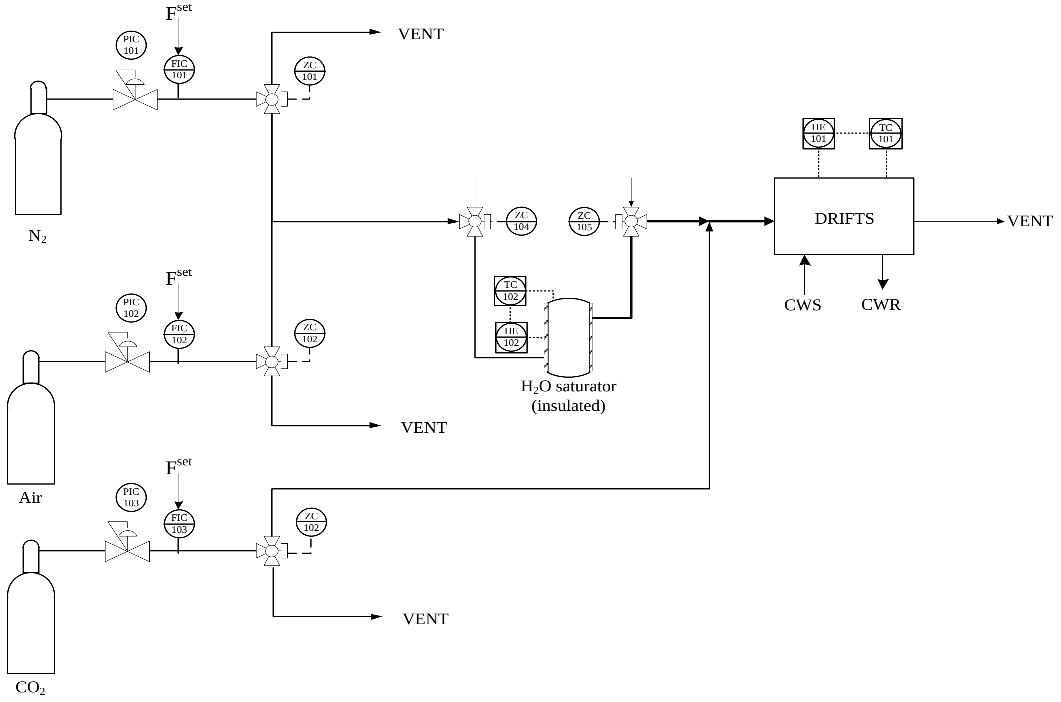


Figure 6. Schematic of RTI's in-situ DRIFTS-IR unit.

In-situ DRIFTS allowed the team to study supported-PEI sorbent degradation, performing multi-cycle CO_2 capture and regeneration and eliminating the potential for experimental error and uncertainty caused by preparing a sample in a separate reactor system, storing it, and analyzing in a different reaction environment. CO_2 adsorption kinetics were also studied where the formation of adsorption peaks during CO_2 capture provided critical information relating reaction kinetics and the formation of intermediate species.

3.3 Equipment and Facilities

3.3.1 RTI's Energy Technology Development Facility

The bench-scale system which was constructed for this project was housed in RTI's Energy Technology Development Facility (ETDF). RTI's ETDF is a large, fully-equipped high-bay research facility which supports various energy-related process systems in bench- or pilot-scale phases of testing and demonstration. This facility was constructed in the last few years to give RTI strategic positioning and greater flexibility in executing large-scale research projects. One of these large-scale process units housed in the ETDF is shown in **Figure 7**. The ETDF provides RTI with the space, utilities, flexibility, and proximity to RTI staff offices needed to successfully execute large bench- and pilot-scale projects. This facility supports technology development in RTI's various energy-related programs: Carbon Capture, Advanced Gasification, Biomass & Biofuels, and Fuels & Chemicals.

RTI's ETDF consists of a main building that is 50' x 50' x 45' at peak height and two control room structures. The building is equipped with the following utilities:

- *Air:* air compressor delivers compressed, filtered and dried air
- *Nitrogen:* process N_2 is supplied by a large N_2 dewar
- *Cooling Water:* chiller unit supplies chilled cooling water
- *Electricity:* electrical supply to meet load demands of many large process units
- *Flue gas:* either generated from on-site gas containers and/or future capabilities will be added to generate FG from hydrocarbon combustion

Given the space and height required to test RTI's bench-scale CO_2 capture test unit, it was decided that this unit would be fully housed and operated within RTI's ETDF. The flue gas used during the project's testing periods was simulated from on-site gas cylinders, as well as the air and N_2 supply. Electricity, water, and steam needs were met on-site also. The process was monitored and controlled from the on-site control room.

Figure 7. RTI's Energy Technology Development Facility

3.3.2 Bench-Scale Solid Sorbent CO_2 Capture System

In this project, a bench-scale solid sorbent CO_2 capture system – the BsCEU – was designed, constructed, modified, and tested. **Figure 7** is a picture of the BsCEU as initially constructed within RTI's ETDF. The BsCEU was constructed with the intent to provide a testing platform to advance our technical understanding of a fluidized-bed sorbent-based CO_2 capture process, building on the work already done on fixed-bed sorbent testing and reactor modeling. Section 4.3 of this report covers in exhaustive detail information related to the design, engineering, construction, operation, and test parameters studied for this unit. The overall design and layout of the BsCEU is not too different from what would be expected in a commercial process flow diagram. The BsCEU consists of five sections including:

- Flue gas generation
- CO_2 Adsorber
- Sorbent Regenerator
- Process gases, instrumentation and control, and
- Analytical equipment.

The BsCEU was used to gain understanding of how specific sorbent properties and operating parameters, such as attrition rate, sorbent density, S/G ratio, will affect the operation, performance, and economics of the process. The scale of the BsCEU was selected based on the minimum column diameter at which stable solids circulation can be ensured (as recommended by our engineering partner, PSRI). A column diameter of 6" was selected for the staged, FMBR design to avoid issues related to bed slugging that would lead to poor CO_2 capture performance and could possibly damage the columns. Based on the column diameter and the range of gas velocities that can be accommodated within the BsCEU, the following are some important specifications for the bench-scale test unit:

- *Flue gas processing capacity*: 300 to 900 SLPM of flue gas,
- *Solids circulation range*: 75 to 450 kg/h,
- *Sorbent fill capacity*: ~75 kg, and
- *CO_2 processing capacity*: ~150 kg-CO_2/day (~10 kW equivalent)

Additional details related to RTI's BsCEU are covered in Section 4.3.

3.4 Software

3.4.1 *Aspen Process Engineering*

RTI has licensed copies of AspenPlus and AspenIcarus process engineering software, which were used primarily for the techno-economic evaluations conducted in this project. AspenPlus is a widely used process modeling tool for design, optimization, and performance monitoring for the chemical industry. AspenPlus includes a large database of pure component and phase equilibrium data. RTI used AspenPlus to simulate the novel solid sorbent-based CO_2 capture process for application in a reference coal-fired power plant. The equipment cost associated with RTI's CO_2 capture process, as modeled in AspenPlus, was estimated using AspenIcarus. AspenIcarus is a powerful project scoping tool, in the early phases of our process development, to evaluate the economic impact of proposed design modifications.

4. Results and Discussion

4.1 Project Management (Task 1)

The overall goal of Task 1 was to ensure the successful execution of the project with on-time and on-budget deliverables and milestones. The project team recognized the critical importance of project management and used resources and tools available to ensure successful execution of the project, including: a project financial analyst, invoicing system, spend plan software, project meetings, and report and publication preparation services.

4.1.1 *Outreach to Scientific Community (Presentations, Papers, Posters)*

The project team authored many presentations, papers, and/or posters during the timeframe of this project. **Table 4** lists the presentations, papers, and posters authored by the project team:

Table 4. Overview of project team's scientific outreach

Type of Outreach	Project Team Member	Role	Outlet	Location	Timing
Budget Period 1					
Presentation	RTI International	Author	11th Annual Carbon Capture, Utilization, and Sequestration Conference	Pittsburgh, PA	April/May 2012
Presentation	RTI International	Author	DOE/NETL CO_2 Capture Technology Meeting	Pittsburgh, PA	July 2012
Poster	Pennsylvania State University	Author	DOE/NETL CO_2 Capture Technology Meeting	Pittsburgh, PA	July 2012
Presentation	RTI International / Masdar	Co-Author	World Future Energy Summit	Abu Dhabi, UAE	January 2012

Presentation	RTI International / Masdar	Co-Author	CO_2 Capture Workshop at Society of Petroleum Engineers Conference	Abu Dhabi, UAE	November 2012
Poster	RTI International / Masdar	Co-Author	Greenhouse Gas Control Technologies (GHGT) Conference	Kyoto, Japan	November 2012
Budget Period 2					
Presentation	RTI International	Author	DOE/NETL CO_2 Capture Technology Meeting	Pittsburgh, PA	July 2013
Presentation	RTI International	Author	DOE/NETL CO_2 Capture Technology Meeting	Pittsburgh, PA	July 2014
Poster	RTI International / Masdar	Co-Author	Greenhouse Gas Control Technologies (GHGT) Conference	Austin, Texas	October 2014
Budget Period 3					
Presentation	RTI International	Author	DOE/NETL CO_2 Capture Technology Meeting	Pittsburgh, PA	June 2015
Presentation	RTI International	Author	A&WMA Annual Conference and Exhibition	Raleigh, NC	June 2015
Poster	RTI International	Author	3rd Post Combustion Capture Conference	Regina, Canada	September 2015
Poster	RTI International	Author	2015 Carbon Management Technology Conference	Houston, TX	November 2015

4.1.2 Reports

During the project, the project team prepared and submitted to DOE/NETL the following reports:

- Seventeen (17) quarterly technical progress
- Seventeen (17) quarterly financial status reports
- Two (2) topical reports related to techno-economic analyses performed for RTI's technology
- One (1) final scientific/technical report.

4.1.3 Publications

The project team authored several publications during the timeframe of this project (see **Table 5** for a list of publications):

Table 5. Overview of project team's publications produced during project timeframe

Type of Outreach	Project Team Member	Role	Outlet	Location	Timing
Budget Period 1					
Journal Paper	RTI International / Masdar	Co-Author	Published by Elsevier as part of the GHGT conference	N/A	November 2012
Budget Period 2					
Journal Paper	RTI International / Masdar	Co-Author	Published by Elsevier as part of the GHGT conference	N/A	October 2014
Budget Period 3					
Journal Paper	RTI International / Masdar	Co-Author	International Journal of Greenhouse Gas Control	N/A	September 2015
Journal Paper	RTI International / Masdar	Co-Author	*Pending*: Power Technology	N/A	2016

4.1.4 Intellectual Property

R&D work during the project led to the following invention and provisional patent application:

- *Solid Sorbent Materials for Acid-gas Separation*, which describes our invention in producing water-stable, coprecipitated solids from polyethyleneimine and tetrealkoxysilicates for adsorption applications (specifically CO_2 capture application).

The provisional patent application was shared with DOE/NETL in September 2014.

4.1.5 Training

The project team has advanced the professional knowledge and skills of various engineers, chemists, and other scientists at RTI, PSU, and Masdar through this project. Professional knowledge and skills were developed in thse specific areas of expertise: process engineering and design, bench-scale test unit fabrication and construction, process operations, materials chemistry, materials screening, materials scale-up, and techno-economic evaluations. Of particular interest is that several RTI staff members received training related to the continuous operation of a bench-scale CO_2 capture system. These staff developed critical professional knowledge by understanding the philosophy and strategy behind the design and operation of solid sorbent CO_2 capture systems.

4.1.6 Collaborators

Other organizations that have worked on the project include:

- Pennsylvania State University's (PSU) Earth and Mineral Science Energy Institute located in University Park, Pennsylvania. PSU staff were actively focused on sorbent improvement, optimization, characterization, and screening activities throughout the project. PSU staff participated in regular project update meetings with RTI staff.
- Masdar and Masdar Institute of Abu Dhabi, United Arab Emirates provided technical guidance on some project activities related to process engineering and techno-economic evaluations. Masdar and Masdar Institute staff participated in project update meetings with RTI staff throughout the project.
- Third-party Vendors. RTI worked with various third-party vendors in both process and sorbent development areas. A preferred Engineering/Fabrication company was involved extensively in the fabrication, construction, and reconfiguration of RTI's bench-scale CO_2 capture system. RTI worked with a preferred sorbent manufacturing partner in scaling up the sorbent preparation to the quantities needed for bench-scale testing. Various other vendors participated in the supply of various equipment, instrumentation, materials, chemicals, etc. needed to execute the project activities.

4.2 Sorbent Development (Tasks 3, 6, and 7)

Having started with the promising PEI-based CO_2 capture sorbents first developed by PSU, the main goal of further sorbent development was to improve the overall stability of a PEI-based sorbent while transitioning to a fluidizable form. Prior to the start of this project, researchers at RTI had demonstrated that the PEI-based sorbents were capable of achieving very good CO_2 capture performance, but suffered from thermal degradation at relatively high adsorption temperatures [5]. In order to produce a commercially-viable sorbent, the PEI-based sorbent required improved thermal stability at higher regeneration temperatures and an optimized form and improved physical strength for fluidized-bed application. Following 4 years of research and development on the CO_2 capture sorbent, RTI and the project team have achieved the following:

- Transformed a high capacity, fixed-bed sorbent into a fluidizable form with good CO_2 capture capacity and desired hydrodynamic properties for fluidization.
- Substantially lowered the cost of the sorbent by substituting a low-cost, fluidizable, silica support for expensive, templated, mesoporous silica supports (like MCM-41).
- Optimized a simple impregnation method which was successfully scaled-up to 200+ kg scale by a commercial sorbent manufacturing partner. Scaled-up sorbent retained all physical and performance attributes of the lab-scale produced sorbent; particularly CO_2 loading of 9 wt.%.
- Achieved CO_2 capture capacities as high as 11.8 wt.% CO_2 in a fluidizable form.
- Demonstrated significantly improved thermal stability of the fluidizable sorbent.
- Verified fluidizability of several sorbents over a range of PEI loadings and developed a clear understanding of the relationship with PEI loading, CO_2 capacity, and fluidizability.
- Proved effective sorbent performance in hundreds of hours of parametric and long-term testing.

The following sections of this report detail, in chronological order, additional sorbent development accomplishments and learnings from this project.

4.2.1 PEI Improvement & Fluidized-bed Sorbent Development (Task 3)

Subtask 3.1: Polyethyleneimine (PEI) Base Sorbent Improvement

The objective of Subtask 3.1 was to improve the thermal, chemical, and long-term stability of PEI while retaining the PEI's desirable CO_2 capture performance and reducing the sorbent cost. The project team used the following approach to achieve the Subtask 3.1 objective:

- Modification of process conditions
- Modification of preparation variables
- Selection of different PEIs (e.g., different molecular weights, various degrees of polymer branching, etc.)
- Strengthening of PEI and support material chemical bond (e.g., through surface functionalization and transition metal-amine complexation)
- Performance stabilization through cross-linking/copolymerization of PEI

As noted in Section 3.2, RTI's and PSU's extensive array of lab-scale reactor systems were used to evaluate these approaches on the overall stability and performance of the PEI base material. Measurements were made on the CO_2 capture performance, sorbent regeneration performance, multi-cycle performance, and chemical stability, and a comparison was made to a baseline CO_2 capture sorbent to evaluate the efficacy of the improvements.

Modification of process conditions

Based upon our review of the open literature on CO_2 capture performance testing of SOTA amine-based sorbents, we noted that most of the testing was conducted with no water present in either the simulated flue gas used for CO_2 adsorption or stripping gas used for regeneration. The absence of steam during this testing is not representative of commercial operation as any real-life application of a CO_2 capture system will include the presence of moisture under both adsorption and regeneration. In this study, we used moisture both in the simulated flue gas as well as in the regeneration sweep gas streams to mimic a commercial operation.

Initially, water was added only to the simulated flue gas to understand the effect of moisture on the adsorption performance. **Figure 8** shows the results of testing on the baseline sorbent (PEI 600MW on MCM-41) with "humidified" flue gas as well as dry flue gas over a range of adsorption temperatures. Our PBR testing conditions were as follows: 13.3% CO_2, 2.35% O_2, 5.02% H_2O, and balance N_2 with regeneration at 110ºC under pure N_2. For the dry flue gas tests the CO_2 adsorption capacity of the baseline sorbent steadily increases with increasing sorption temperature. In the "humidified" gas tests, the CO_2 adsorption capacity remains essentially stable over the range of adsorption temperatures, 65°C to 95°C, and is stable at the highest loading capacity achieved in the dry flue gas testing, ~10 wt.% CO_2 capacity. The adsorption capacity of the sorbent is greatly improved at lower adsorption temperatures when moisture is present in the flue gas. This increase in CO_2 loading capacity is believed to be related to the formation of amine bicarbonates and possibly improved utilization of PEI's primary and secondary amine sites due to the presence of water. Comparing these results, we believe it shows that CO_2 reacts with PEI in more than one reaction pathway.

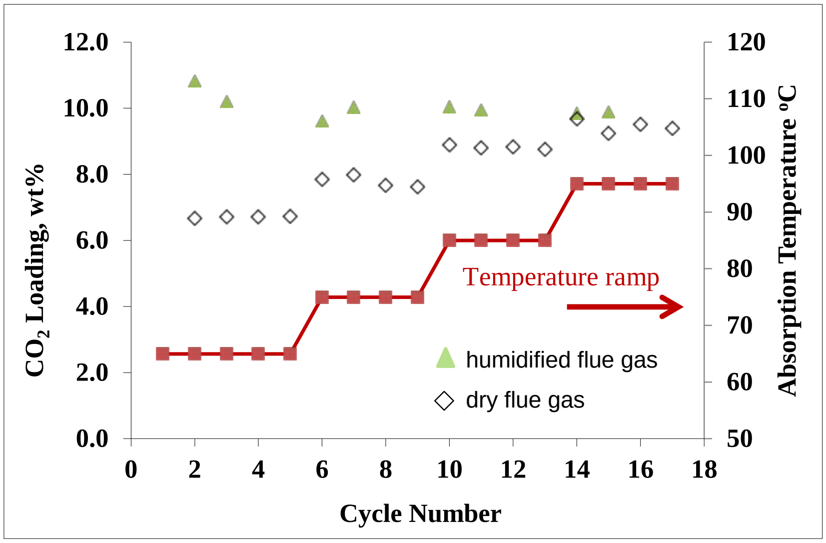


Figure 8. PBR tests showing the effect of moisture in flue gas on PEI-based Sorbent CO_2 sorption performance

We also studied the effect of moisture in the regeneration gas on the baseline sorbent stability and performance. For process design consideration, it may not be desirable to have water in the regeneration sweep gas to lower the energy consumption during the regeneration and subsequent dehydration required prior to CO_2 compression. Nonetheless, the presence of water in the regeneration sweep gas may be unavoidable in a typical commercial operation, as sorbent regeneration may produce some water along with CO_2. Therefore, it is prudent to include water to study the regeneration performance.

We performed PBR tests where the adsorption temperature was held constant and moisture was added to the regeneration sweep gas. Standard performance testing conditions as well as "long-term aging" conditions were used in separate experiments. Standard testing conditions for PEI(600) loaded on MCM-41 were as follows: 13.3% CO_2, 2.35% O_2, 5.02% H_2O, and the balance N_2 with regeneration at 110°C with 3% H_2O in N_2. In the "dry ROG" case, the same baseline sorbent was tested using the same adsorption conditions, but with regeneration in pure N_2. Multi-cycle testing (75 cycles) was performed, which allowed us to understand the impact of moisture over a longer test period. Under "long-term aging" conditions (i.e. conditions which were selected to see higher rates of performance degradation) testing conditions for PEI(600) loaded on fumed silica were as follows: 3 cycles of adsorption and regeneration are carried out, then the sorbent is switched to "aging" conditions for 10 hours and then back to the 3-cycle adsorption-regeneration conditions, and repeating this pattern for a desired length of time. The definition of "aging" conditions was: adsorption at 14.77% CO_2, 2.61% O_2, 5.65% H_2O, balance N_2 with regeneration at 120°C with 100% CO_2 (dry tests) or 10% H_2O in CO_2 (moisture tests).

Figure 9 and **Figure 10** clearly show that the performance stability of PEI-based sorbents is greatly improved when moisture is present in the regeneration sweep gas. The dry gas (pure N_2) testing shows a steady decline in CO_2 loading capacity over time in the standard testing conditions and a rapid decline under "aging" conditions. When moisture is present during regeneration, the CO_2 loading capacity after 75 cycles of standard testing is nearly the same as the initial adsorption/regeneration cycle (**Figure 9**). The decline in capacity over 6 days of aging is only about 17%, compared to 87% in the absence of water in the regeneration gas (**Figure 10**). The observed stability enhancement in the presence of moisture may be related to the reduced formation of thermally-stable urea during regeneration. This was confirmed through attenuated total reflectance (ATR) IR spectroscopy analysis which showed an increase in the adsorption intensity at wavenumber 1660 cm^{-1} (i.e. carbonyl peak) suggesting more urea was present on the samples tested with dry regeneration gas compared to a fresh sample and samples tested under "humidified" conditions. It is clearly evident that the stability of PEI-based sorbents can be improved by modifying reaction conditions. This result may have a significant effect on the required operating conditions of a commercial process. The cost associated with having moisture in the regeneration gas has been included in our preliminary feasibility analysis and the beneficial impact on the sorbent performance outweighs the cost of the additional steam consumed.

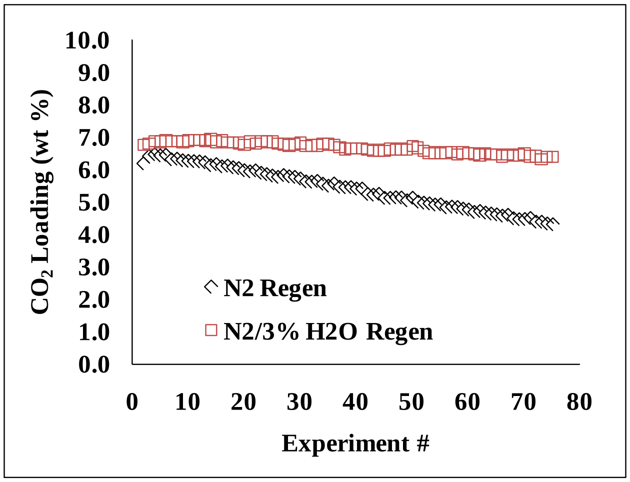


Figure 9. "Standard" PBR tests of PEI-based sorbent showing stability effect of moisture in regeneration gas

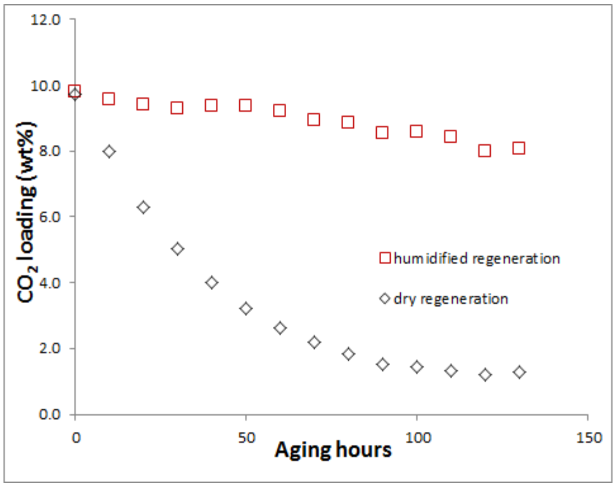


Figure 10. "Aging" PBR tests of PEI-based sorbent showing stability effect of moisture in regeneration gas

Modification of sorbent preparation variables

In addition to evaluating performance and stability impacts of moisture in simulated flue gas and regeneration sweep gas, we also evaluated the effect of sorbent preparation conditions. The following key variables were investigated:

- PEI loading (15 to 70 wt.%)
- Sorbent drying temperature (40 to 100°C)
- Quantity ratio of solvent to PEI (4:1 to 10:1)
- Oven vacuum conditions
- Sorbent drying time (hours to a day)
- Quantity ratio of solvent to PEI (4:1 to 10:1)
- Oven starting conditions (cold start or warm start)

Of the above conditions studied, the PEI loading amount and the drying temperature of the prepared sorbent had an impact on CO_2 capture performance. The other variables were found to have minimal impact on the sorbent performance.

Standard CO_2 capture sorbents (PEI(600) on MCM-41) with four different PEI loadings (ranging from low to high) were prepared and CO_2 capture performance tested in our PBR system. Experiments were carried out under the following conditions: adsorption gas of 15% CO_2; 4.5% O_2 and N_2 balance at 75°C; regeneration at 75°C under pure N_2. Low PEI loadings hold the potential benefit of reduced sorbent cost (i.e. less reagent material) while higher PEI loadings may lead to improved CO_2 capture performance due to increased quantity of CO_2 adsorption sites. The effect of PEI loading is shown in **Figure 11**.

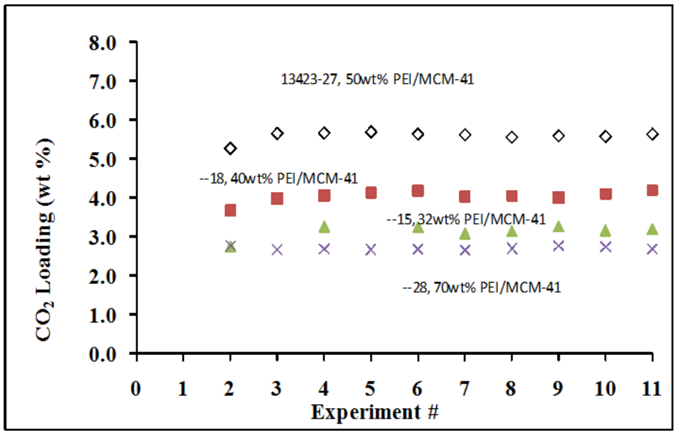


Figure 11. Effect of PEI loading on CO_2 capture performance for RTI's CO_2 capture sorbents

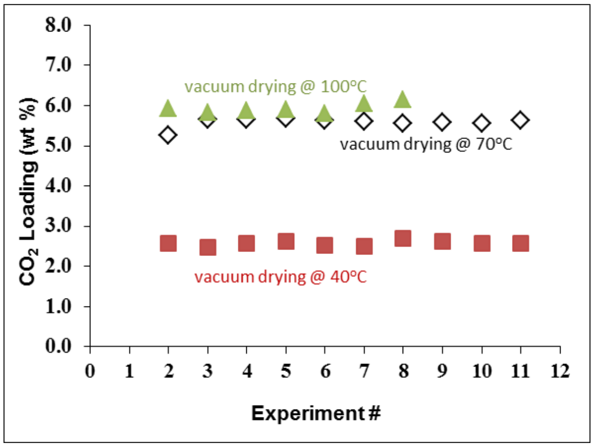


Figure 12. Effects of sorbent drying temperature on RTI CO_2 capture sorbent performance

It is clear from the results provided in **Figure 11** that at 50wt% PEI loading, the PEI-based sorbent has the highest CO_2 adsorption capacity. Based on the pore volume of the baseline MCM-41support (0.78cc/g), the maximum loading of PEI inside the pore structure was expected to be about 43wt%. As MCM-41 is loaded with PEI above 43wt%, the additional PEI will likely reside outside the pores and on the support surface, potentially resulting in a "sticky" sample that may be difficult to handle. The 50 wt.% PEI-loaded sorbent exhibits the best CO_2 capture performance, which likely indicates that PEI inside the pore structure is accessed by the flue gas and PEI on the external surface also participates in CO_2 capture. Overall, it appears that a range of 30 to 60wt.% PEI loading is a reasonable target for sorbent preparation and this served as a basis for all our sorbent synthesis throughout the project. A more detailed evaluation of PEI loading impact (and optimization of this loading) was studied in BP2 as the silica support material was transitioned to a material available from commercial manufacturers (Section 4.2).

The effect of drying temperature during sorbent preparation was also studied. Drying of samples prior to testing is required to ensure that the alcohol solvent used in preparation is evaporated completely and possibly to remove any adsorbed water. **Figure 12** shows the effect that drying temperature has on the sorbent performance. **Figure 12** clearly shows that increasing the drying temperature up to 70°C has a significant positive impact on CO_2 capture performance. At temperatures above 70°C, however, CO_2 adsorption capacity does not improve by much. It is theorized that we need a minimum drying temperature of 70°C to complete the alcohol evaporation, remove adsorbed water, and possibly improve the mobility of the PEI reagent for better dispersion inside the support structure.

Selection of different types of PEI

Polyethyleneimine comes in many forms, most of which were not tested (by the project team) prior to this project. Selection of the proper PEI-type was a variable studied extensively in BP1. More specifically, PEIs of varying molecular weights were procured and studied along with linear and branched PEI structures having varying molecular weights also.

PEI Molecular Weight (MW): It was theorized that the use of PEI with higher MWs may result in better thermal stability for CO_2 adsorption-regeneration at higher temperatures due to strong inter- and intra-molecular interactions between polymer molecules. Various PEI-based sorbent samples were prepared with PEI of varying MWs. CO_2 sorption/regeneration testing was performed in RTI's PBR system. The support material was kept consistent as MCM-41 to clearly understand the effect of PEI type. Standard PBR testing was carried out: adsorption with 15% CO_2, 4.5% O_2, and N_2 balance at a temperature of 75°C and regeneration at 75°C under pure N_2. **Figure 13** shows the CO_2 capture performance of various sorbents including low MWs – PEI (600) and tetraethylenepentamine (TEPA) – and larger MW PEIs – MWs of 1,800 and 10,000. These results clearly show that CO_2 capture performance improves as the PEI MW is reduced, with TEPA exhibiting the best CO_2 loading capacity. The decrease in CO_2 uptake with increased PEI MW may be attributed to a decrease in primary amine content and increase in tertiary amine content within the PEI. It is widely accepted that the propensity of CO_2 adsorption follows the pattern: primary amine > secondary amine > tertiary amine, and the tertiary amine does not react with CO_2 under dry conditions. In addition, smaller PEI molecules may have better access to the internal surface of the support, resulting in increased dispersion of PEI in the pores, and thus better CO_2 capture performance.

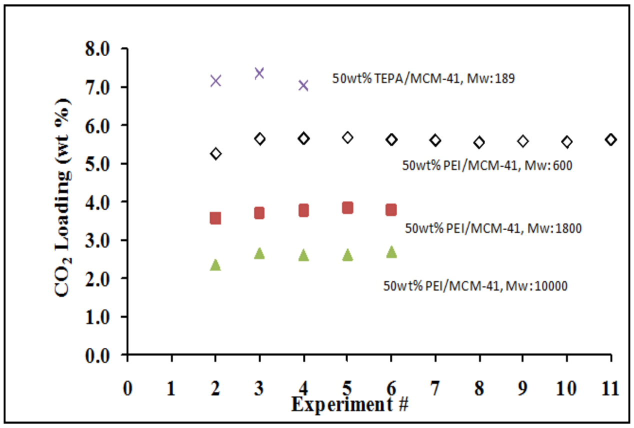


Figure 13. Effect of different MW PEIs on a sorbent's CO_2 capture performance

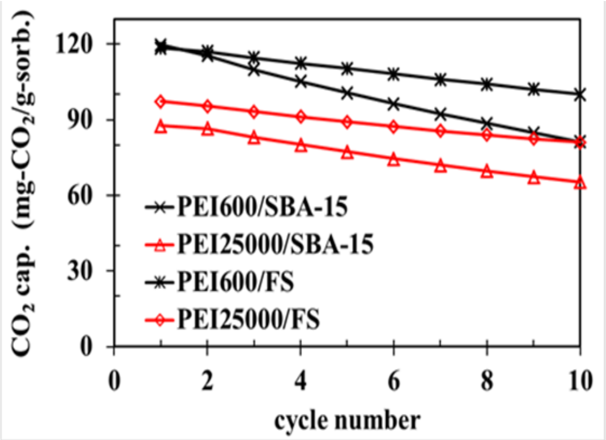


Figure 14. Comparison of additional sorbent samples with low and high MW PEI supported on SBA-15 and FS

Additional analysis on PEI MW was carried out with a much higher MW PEI, 25,000, selected for testing and comparison to 600 MW PEI. In addition, the support material was varied to evaluate the impact of using expensive mesoporous silicas versus cheaper fumed silicas. **Figure 14** also shows a comparison of CO_2 adsorption capacity of PEI(600) and PEI(25,000) supported on two supports – SBA-15 and fumed silica. The adsorption temperature was 90 °C under pure CO_2 flow and regeneration was carried out at 120°C under 100% N_2 flow. The adsorption capacity results indicate that 1) lower MW PEIs result in higher CO_2 adsorption capacity even when the support structure is changed; and 2) compared to SBA-15, which is expensive and not commercially available, fumed silica (FS) based sorbents exhibit better CO_2 capacity. With the increasing number of adsorption-regeneration cycles, all four sorbent samples exhibit a decrease in CO_2 adsorption capacity, but sorbents made with fumed silica exhibit a slightly lower rate of CO_2 capacity decrease. The ability to apply fumed silica as a support material choice for RTI's CO_2 capture sorbent is a very important finding. This support material not only manifests into higher CO_2 adsorption capacity, but also leads to improved stability and regenerability, regardless of PEI type used.

PEI molecular structure: The performance of sorbents prepared with linear PEI (LPEI), and different MW LPEIs was examined and compared with branched PEI. **Figure 15** compares the regenerability of branched PEI(25,000) on FS and linear PEI(25,000) on FS sorbents for CO_2 adsorption for 10 cycles under the same CO_2 sorption-regeneration procedure. The percentage reduction in CO_2 uptake over time is listed in **Table 6**. After 10 cycles, the adsorption capacity of BPEI(25,000) on FS sorbent decreased by 17%, while this decrease was only 2% for LPEI(25,000) on FS. These results clearly demonstrate that sorbents prepared using linear PEI have improved performance stability over time.

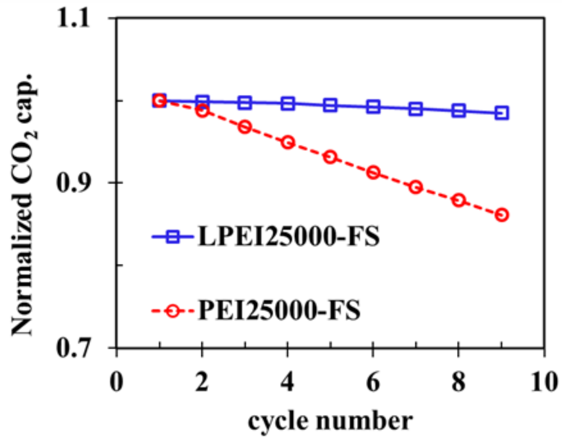


Figure 15. Comparison of performance stability of PEI-based sorbents prepared by branched and linear PEI

Table 6. Comparison of performance stability of PEI-based sorbents prepared by branched and linear PEI

Sample	**Reduction in CO_2 uptake 10 cycles, (%)**
BPEI(600 MW)/ FS	16
BPEI(25,000 MW)/ FS	17
LPEI(25,000 MW)/ FS	2

LPEI of lower MW (e.g. 2,500) was also tested to explore whether it exhibited similar stability retention as seen in higher MW LPEIs. We carried out 30 cycles of sorption-regeneration for the LPEI(2,500) on FS. As shown in **Figure 16**, the total CO_2 capacity loss after 30 cycles was only 3.9% from the initial loading. Linear PEIs of lower MW are attractive due to significantly improved stability and relatively high CO_2 capacity; however, their cost remains significantly higher than low MW BPEIs (e.g. 200x more expensive) and thus may have limited value in the development of this technology. The high cost of LPEI materials are a hindrance to the economics of RTI's process technology and thus the project team moved away from pursuing further study of LPEIs in this project. It is important to note, however, that if LPEI costs are able to be reduced substantially, further exploration would be desired.

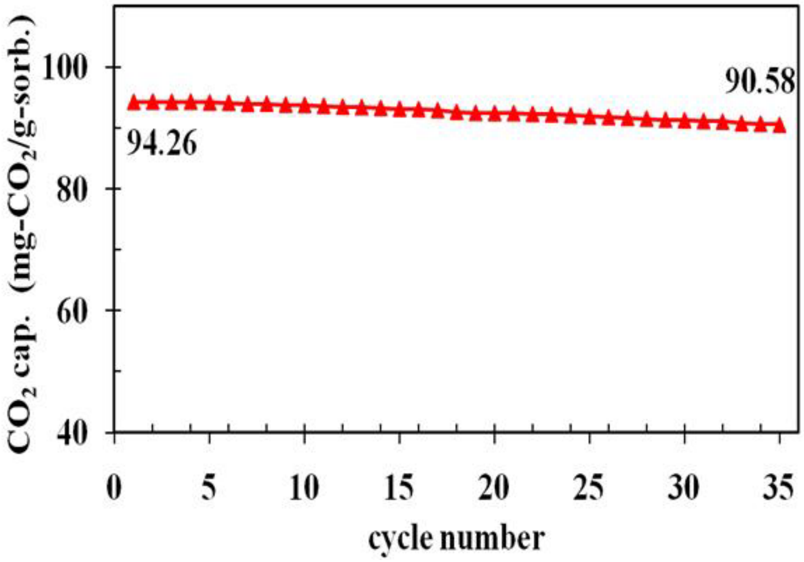


Figure 16. CO_2 adsorption capacity stability of LPEI(2,500) on FS over 30 test cycles.

Strengthening of PEI and support material chemical bond (Me-amine complexation)

Early in the project, the project team encountered the challenge of preventing PEI from leaching out of the sorbent. We developed strategies by which PEI could be affixed (i.e. tethered or otherwise) within the sorbent support structure. One pathway we investigated was the interaction of PEI with transition metals (particularly Zn and Cu) – transition metal-complexation. **Figure 17** exhibits a possible complexation pathway associated with coupling PEI nitrogen groups to a transition metal core. Complexation of PEI to a solvated metal center is likely to occur in a multi-dentate fashion involving the coordination of two, three, or four nitrogen atoms. The complexed PEI is anticipated to create molecular geometries inside the pores which would hinder the PEI polymer from being expelled. Complexation may result in inter- and intra- molecular interactions between the metal and PEI oligomers, likely resulting in CO_2 capture sorbents having improved stability.

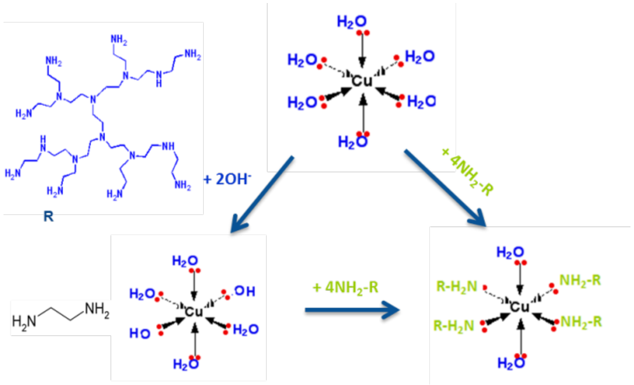


Figure 17. Transition metal-amine complexation pathway

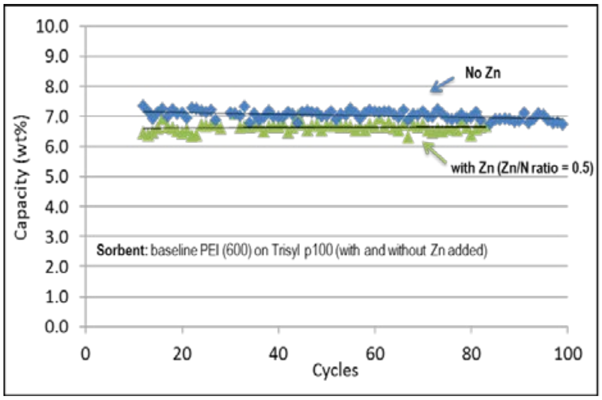


Figure 18. CO_2 sorption comparison of baseline PEI(600) on low cost silica and a Zn-complexed sorbent

In this project, metal-amine complexed sorbent samples were prepared and evaluated for CO_2 capture performance in our PBR test systems. A series of Cu- and Zn-amine complex sorbents were screened before longer-term stability was evaluated through our "aging" testing method (described previously in this section) to determine the relative stability of the sorbent prepared by this method with our baseline sorbents.

Figure 18 shows results of sorbent screening, where the testing conditions were as follows: adsorption at 65°C, 14.77% CO_2, 5.65% H_2O, 2.62% O_2 with balance of N_2 and regeneration at 110°C, 5.65% H_2O with balance of N_2. **Figure 18** provides CO_2 adsorption results and a comparison of a sorbent sample prepared through Zn-amine complexation and a new baseline sorbent (PEI(600) on Trisyl P100). This figure shows that both sorbent samples are relatively stable during multi-cycle tests and have similar CO_2 loading capacity; however the baseline composition (without Zn) shows a slightly greater rate of decay over 100 cycles. The Zn-amine sorbent shows stable performance over the equivalent number of cycles, likely due to formation of a Zn-amine complex.

Similarly, Zn-PEI supported on fumed silica sorbents were prepared and tested for multiple cycles – results are shown in **Figure 19**. The sorbent with 50wt.% Zn-(600) loading had reasonably high CO_2 capacity (9.63 wt.%) and over 80 cycles, it remained reasonably stable at 9.40wt.%. Tests of PEI(10,000) on fumed silica showed a CO_2 capacity of around 7.3wt%, again exhibiting the result that lower MW PEIs may be more beneficial in developing a commercial support compared to their higher MW counterparts, even if they are synthesized through Me-amine complexation route. Comparison of the PEI (600) and PEI (10,000 Me-complexed samples) shows no clear stability difference between the two sorbents after 80 cycles of testing. **Figure 20** shows the results of "aging" Zn-amine complexed sorbents as compared to baseline PEI(600) on fumed silica. The "aging" experiments on metal-amine sorbents yielded mixed results.

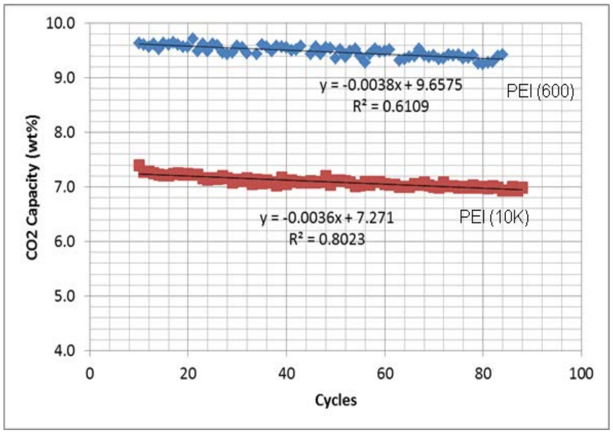


Figure 19. Comparison of CO_2 capture performance between 50wt% Zn-PEI(600) and PEI(10,000) with a Zn/N ratio of 0.5

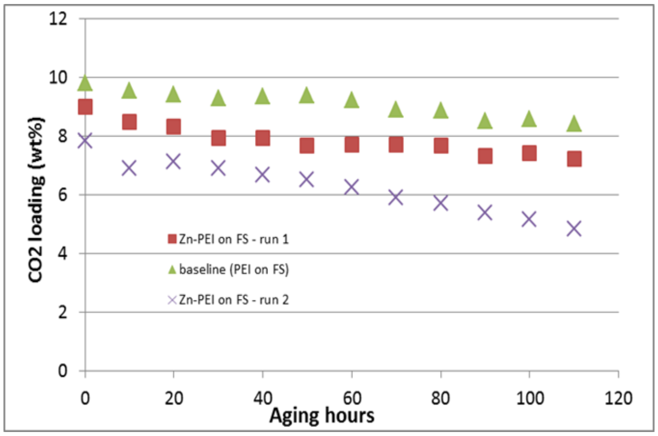


Figure 20. Long-term aging experiments conducted on a baseline sorbent and Zn-complexed sorbents

Figure 20 shows that the same Zn-PEI on fumed silica sorbent was tested in two separate "aging" runs. The first run shows promise as the sorbent maintains significant stability over 115 hours of aging. This data, however, exhibits similar stability to the baseline PEI on FS sorbent. Both sorbents achieve CO_2 capture performance (stability and CO_2 loading) that meet project goals for Budget Period 1. A repeat experiment of the Zn-PEI sorbent (run 2) showed a greater decline in CO_2 capture performance over time compared to the baseline sorbent. Although uncertainty remains as to the true benefit of metal-amine complexation, one observation that indicates an improvement due to reduced PEI leaching is the color of the collected condensate downstream of the PBR. **Figure 21** is an image comparing the color of the collected condensates for both the baseline and Zn-PEI sorbents. The color of the condensate from the baseline sorbent is much darker than the Zn-PEI sample indicating that more PEI leached from the baseline sorbent and indicates that Zn-amine complexation may reduce PEI leaching from the support. Given the mixed results exhibited by this metal-amine complexation pathway, the project team decided to evaluate stronger metal-amine complexes in an effort to reduce PEI leaching and improve sorbent stability.

Figure 21. Condensed liquids collected from RTI's PBR condenser both for baseline and Zn-amine sorbents

Performance stabilization through cross-linking/copolymerization of PEI

In another effort to improve the thermal stability of PEI-based sorbents, the project team explored a PEI cross-linking strategy through use of a cross-linking agent. Evaluations by the research team in this area proved that hexamethylene diisocyanate (HDI) would make an excellent crosslinking agent for the modification of PEI. The amount of HDI added to PEI was 2.5%, 5% and 10% on molar basis. **Table 7** lists the CO_2 adsorption capacity achieved with sorbents prepared with HDI cross-linked PEI. As can be seen, the CO_2 adsorption capacity of these sorbents decreased with the increase in HDI amount. A possible reason for the decrease may be that the diisocyanate functional groups in HDI reacts with amine groups of PEI to form urethane, thus reducing the amine sites for CO_2 adsorption.

Table 7. CO_2 adsorption performance of RTI sorbent prepared by HDI-modified BPEI

Sample	**CO_2capacity (mg-CO_2/g-sorb)**
BPEI(50)-600/FS	130
2.5% HDI- BPEI(50)-600/FS	110
5% HDI- BPEI(50)-600/FS	96
10% HDI- BPEI(50)-600/FS	65

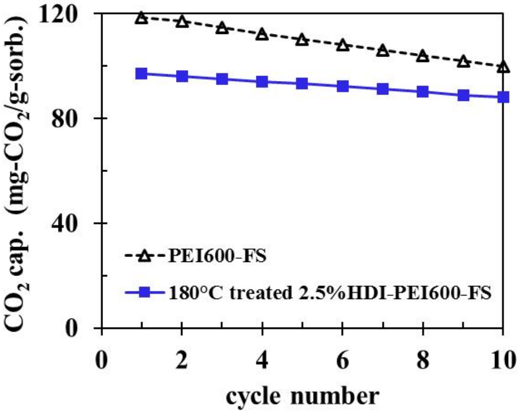


Figure 22. CO_2 adsorption capacity comparison of BPEI(600)/FS and HDI-crosslinked BPEI(600)/FS (initially treated at 180 °C)

When testing the stability of 2.5% HDI-BPEI(600)/FS through thermal loss-on-ignition (LOI) TGA tests, three peaks were observed at 180, 340 and 380°C, respectively. Compared to non-crosslinked BPEI(600)/FS, a shift in peak position was observed after HDI addition, which may indicate the formation of cross-linking between PEI and HDI molecules. A weight loss peak at 180°C was attributed to the decomposition of HDI, meaning some HDI remained unreacted which is undesirable. To mitigate this problem, HDI-based samples were further treated at 180°C for approximately 30 minutes to remove unreacted HDI. TGA studies confirmed that HDI was successfully removed from the sorbent. The project team conducted 10 cycles of regenerability testing on the 2.5% HDI-BPEI(600)/FS sample and compared to the baseline sorbent. The results are shown in **Figure 22**. The rate of CO_2 adsorption capacity reduction is slightly lower for 2.5% HDI-BPEI(50)-600/FS than for the baseline sample. Better thermal stability was obtained using HDI to cross-link PEI(1800 MW) after a 200°C treatment of the sorbent sample. As shown in **Figure 23**, the reduction in adsorption capacity was found to be 1.5% --much lower than the 9% loss shown in **Figure 22**. There appears to be some optimization required, as the HDI crosslinked sample using 600 MW PEI and 180 °C treatment retains a higher CO_2 adsorption capacity of about 9.5 wt.% compared to 6 wt.% for the HDI crosslinked sample using 1800 MW PEI and 200 °C treatment. Both samples have better stability performance than non-crosslinked PEIs. These results confirm the positive effect of PEI crosslinking with HDI. Therefore, based on all of the work conducted in Subtask 3.1, it is concluded that it is possible to improve the regenerability of PEI-based sorbents through crosslinking with other diisocyanate compounds, improve CO_2 capacity by PEI MW selection, and improve performance and stability through selection of optimized process conditions and preparation variables.

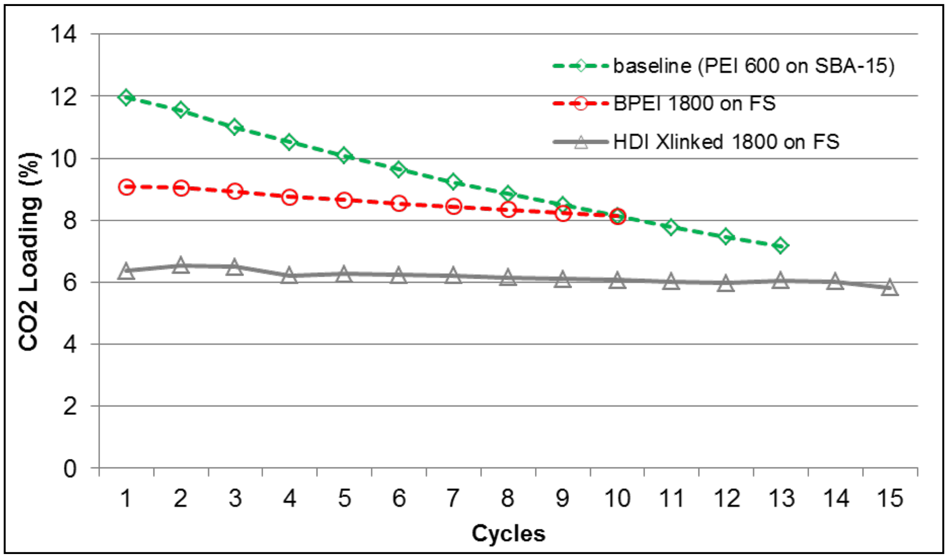


Figure 23. CO_2 adsorption comparison of 2.5 wt% HDI-BPEI(1800)/FS (treated at 200 °C), BPEI(1800)/FS, and baseline PEI(600)/FS

Subtask 3.2: Fluidized-bed Sorbent Formulation

In addition to optimizing the CO_2 loading capacity and thermal stability of PEI-based sorbents, the project team directed research efforts at the challenge of converting a PEI-impregnated sorbent from powder form to a low-cost, attrition-resistant particle suitable for fluidized-bed operations. Fluidized-bed sorbent research, in the early phase of this project (Subtask 3.2), was focused on:

- identifying a suitable low-cost, commercially-available support material
- improving the fluidizability and attrition resistance of the best support materials, and
- evaluating methods for scaling production

Identifying a suitable low-cost, commercially-available support material

One of the key challenges in the development of a low-cost, attrition-resistant sorbent particle is the cost of raw materials used – including the support and active agent materials. RTI's preliminary techno-economic indicate that a commercially-produced sorbent must cost ≤$10/kg to make the technology viable commercially. The cost of mesoporous silicas commonly reported in literature, e.g. MCM-41 and SBA-15 which were previously used by PSU, cost on the order of $100 to $1,000/kg leading to a sorbent cost in excess of $50 to $500/kg (assuming the support makes up ~ 50 wt.% of the total sorbent weight). Therefore, one of the main goals of this project was to identify inexpensive, commercially-available support materials to replace expensive mesoporous silicas and explore whether these supports can be used to produce a sorbent that maintains desired CO_2 capture performance characteristics. To this end, RTI began screening commercially-available support materials and selected candidates based on an ideal combination of attributes. The target attributes for this screening process included:

- Cost: <$5/kg
- BET surface area: >200 m^2/g
- Pore volume: >0.8 cc/g
- Pore size distribution: ~2 to ~15 nm
- Particle size: < 150 µm
- Potential for producing an attrition-resistant particle

An extensive survey of commercially-available support/carrier materials revealed that there are very few silica support materials meeting these requirements. In fact, only two materials were identified meeting all requirements, namely Grace Davison's Trisyl P100 and conventional fumed silica. A comparison of the physical properties and the cost of these materials as compared to MCM-41 is provided in **Table 8**. Both Trisyl P100 and conventional fumed silica meet all of the desired properties, including the cost target.

Table 8. Physical properties and cost of commercially-available SiO_2 candidates

Material	Source	BET SA [m^2/g]	Pore volume [cc/g]	Pore size [nm]	Particle size D$_{50}$ [□m	Tap density [g/cc]	Cost [$/kg]
MCM-41	MSU	1000	0.78	2.5	60.87	0.17	>1000X*
Trisyl P100	Grace Davison	730	1.2~1.4	5~6	18.80	0.24	4~6.52**
Fumed Silica	Cabot Corp	200	N/A	N/A	31.98	0.05	2.3~3.5***

* currently not produced at commercial scale
** based on 25lb/bag; cost will be lower for larger quantities
*** based on 500 kg level; cost will be lower for larger quantities

The suitability of these materials to be effective supports for PEI was evaluated by impregnating the support materials with 50wt% PEI (MW423) using our standard preparation method. A comparison of the CO_2 loading as a function of temperature at representative flue gas feed conditions is provided in **Figure 24**. The CO_2 loading measurements indicate that the low-cost silica materials may in fact be superior supports compared to high-cost, mesoporous supports (MCM-41). Based on these results, both Trisyl P100P100 and fumed silica were selected as suitable low-cost, commercially-available support materials.

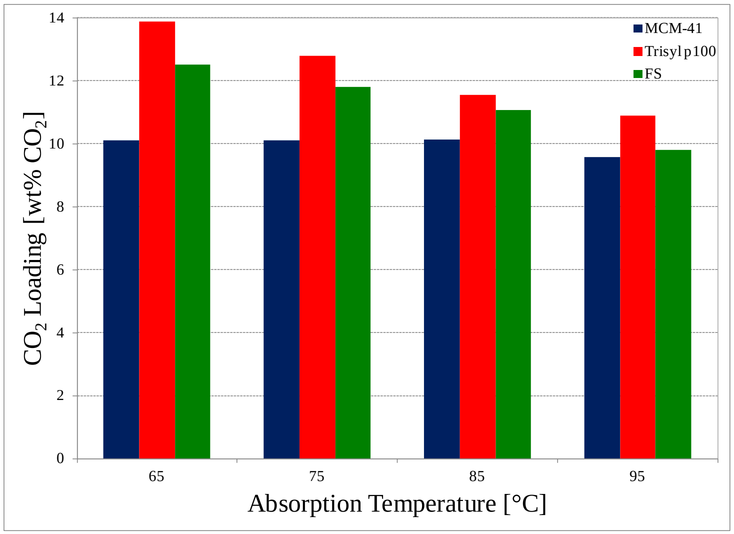


Figure 24. Comparison of PEI-based sorbents prepared with different silica support materials.

Improving the fluidizability and attrition resistance of the best-performing support materials

The next challenge faced in developing a suitable sorbent for RTI's fluidized-bed CO_2 capture process was to convert the low-cost silica supports into fluidizable, attrition-resistant support materials using commercially-relevant production methods. To this end, we prepared numerous silica-based powders via conventional spray drying using our in-house, lab-scale Niro spray dryer. This was a necessary step in achieving fluidizable, attrition-resistant support materials because, as-received, the Trisyl P100 and fumed silica were not suitable for fluidization due to small mean particle diameters, low particle densities, and multi-modal particle size distributions (PSDs). To increase the particle size and density of the low-cost silicas, they were blended with binding agents including boehmite (an alumina precursor), sodium silicate, and a zinc-aluminum hydroxide (a $ZnO/ZnAl_2O_4$ precursor) using a high shear mixer to ensure homogeneity of the preparation. The prepared slurries were then spray dried resulting in fine particulates with narrow PSDs. It should be noted that the mean particle size is limited to <70 μm due to the size of RTI's lab-scale spray dryer – larger particles can be prepared using larger spray dryers (as found in commercial manufacturing facilities). The physical properties of the resulting spray-dried powders are provided in **Table 9**.

Table 9. Physical properties of low-cost silicas spray dried with a variety of binding agents

	Trisyl P100			Fumed Silica
	Na Silicate	Boehmite	Zn-Al hydroxide	Zn-Al hydroxide
Particle Diameter D_{50} [μm]	41.4	35.4	43.9	69.0
Tap density [g/cc]	0.46	0.27	0.33	0.36
BET SA [m^2/g]	679.8	680.4	504.5	147.1
Davison Attrition Index [%]	12.6	20.3	---	---

The mean particle size and density increased for each of the spray dried materials into ranges that are reasonable for fluidization. The density remained low, but it was expected upon impregnation with PEI, the density would increase to ~0.7 g/cc, making the sorbent consistent with many Geldart Group A particles. The resulting spray dried powders were non-cohesive, free-flowing particles that easily fluidize forming stable bubbling beds. The fluidizability of these materials was verified by visual observation of the particles being fluidized in RTI's vFBR using dry and humidified room temperature (r.t.) N_2. A picture of the spray dried fumed silica material being fluidized is shown in **Figure 25**. The spray-dried support materials fluidized easily and a smooth circulation pattern in the bed was observed indicating the material forms a stable fluidized bed.


a
b

Figure 25. Visual confirmation that the spray-dried, low-cost silica supports are fluidizable with a) r.t. dry N_2 and b) r.t. humidified N_2

The attrition index, a measure of a fluidizable material's resistance to physical wear, was measured using RTI's Davison attrition index test rig. Two of the spray-dried materials had measureable attrition indices below our BP1 target of 24%. The Davison attrition index for the remaining spray-dried support materials was not measureable since a significant portion of the sample was ejected from the jet cup due to low particle size and density.

Using the spray dried silica powders, PEI-impregnated sorbents containing 50wt.% PEI (MW423) were prepared using the standard preparation method. As expected, the tap density of the PEI-impregnated particles increased from 0.36 to 0.71 g/cc for the spray-dried materials. These powders were found to be non-cohesive, free-flowing particles that easily fluidize forming stable bubbling. The fluidizability of a PEI-impregnated sorbent was again evaluated by visual observation using dry and humidified r.t. N_2 (**Figure 26)**. However, when a moisture-containing gas having a relative humidity <100% was used, the bed rapidly agglomerated forming a stationary, agglomerated bed with permanent 'rat holes' formed in the bed to allow the feed gas to pass through (**Figure 26b** and **c**). Switching the feed gas to r.t. dry N_2 returned the bed to a stable fluidized bed after approximately 30 minutes. From these results it is clear that the combination of moisture in the feed gas and water-adsorbing PEI on the surface of the particle leads to particle agglomeration, but that the agglomeration is reversible. To address this issue, two approaches were evaluated: 1) operating the fluidized bed at a temperature at which PEI does not adsorb water, and 2) to remove the PEI from the external surface of the particle by washing/rinsing the particles.

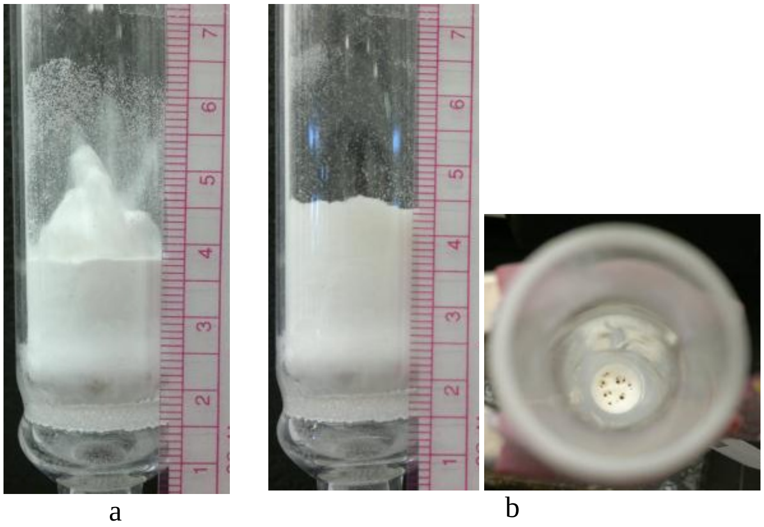
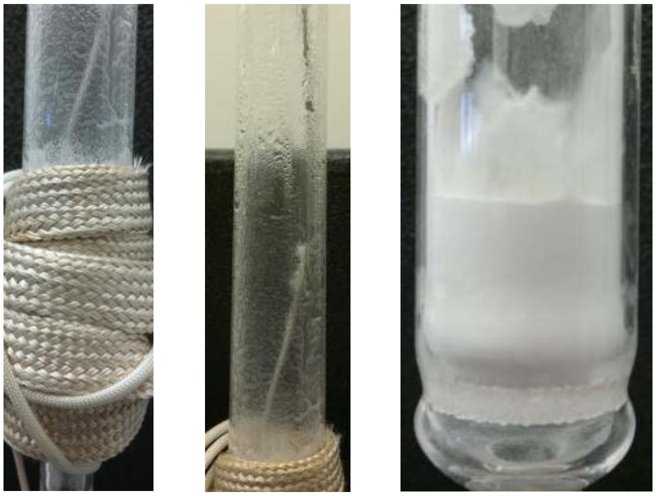


Figure 26. PEI-impregnated spray-dried materials being fluidized in a) r.t. dry N_2 and b) r.t. humidified N_2.

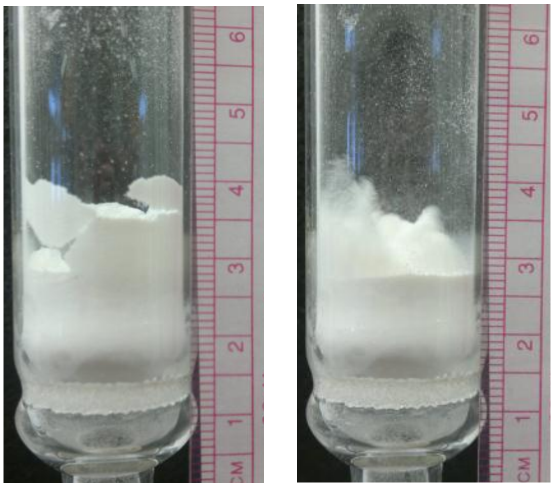
Upon heating the stationary, agglomerated bed (**Figure 26b**) to 70°C (consistent with the operating temperature of the CO_2 Adsorber) and feeding r.t. humidified N_2 gas, condensate was observed in the top section of the glass tube indicating that previously adsorbed water was released by the sorbent (**Figure 27b**). Over a period of ~30 minutes, the bed transformed from a stationary, agglomerated bed to a stable fluidized-bed exhibiting a good solids circulation pattern (**Figure 27c**). This finding indicates that water adsorption by PEI on the external surface of the particle is an equilibrium-driven process meaning that it can be mitigated by controlling the partial pressure of water in the feed gas and the temperature of the fluidized-bed. This issue is not unique to supported-PEI sorbents but must be overcome by all CO_2 capture sorbents since many CO_2 adsorbing species also have a propensity for adsorbing water and the fact that deep desulfurized flue gas is typically saturated with water.

Subsequently, the project team explored rinsing the prepared sorbents with alcohol to remove PEI from the external surface of the particles. The fluidizability of the resulting rinsed powder was evaluated using humidified r.t. N_2 and it was found to agglomerate after about 1 hour on stream (**Figure 28a**). The sorbent was then rinsed a second time. The fluidizability of the resulting rinsed powder was evaluated a second time using humidified r.t. N_2 and it was found to fluidize very well exhibiting a good solids circulation pattern (**Figure 28b**). The CO_2 loading capacity of the twice rinsed sorbent was evaluated and compared with the unwashed sample. Rinsing resulted in a significant reduction in CO_2 loading (**Figure 29**); however, the amine utilization ratio increased from 0.14 mmol-CO_2/mmol-N of PEI (fresh) to 0.55 mmol-CO_2/mmol-N of PEI for the rinsed sorbent, indicating that optimization of amine loading is required to achieve good performance and fluidizability. Based on these results, it is concluded that both the identification of operating conditions (i.e., temperature and H_2O partial pressure) that reduce/eliminate water adsorption and ensuring that the external surface of the particle is free of PEI are necessary for the development of a fluidizable PEI-based sorbents.



a b c

Figure 27. Visual observation that PEI-impregnated spray-dried powder is fluidizable in humid gas, heated to 70°C. a) heating the bed b) condensate resulting from water release, and c) stable fluidized bed at 70°C and r.t. humidified N_2



a b

Figure 28. Fluidization tests of PEI-impregnated spray-dried sorbent using r.t. humidified N_2. a) first rinse and b) second rinse.

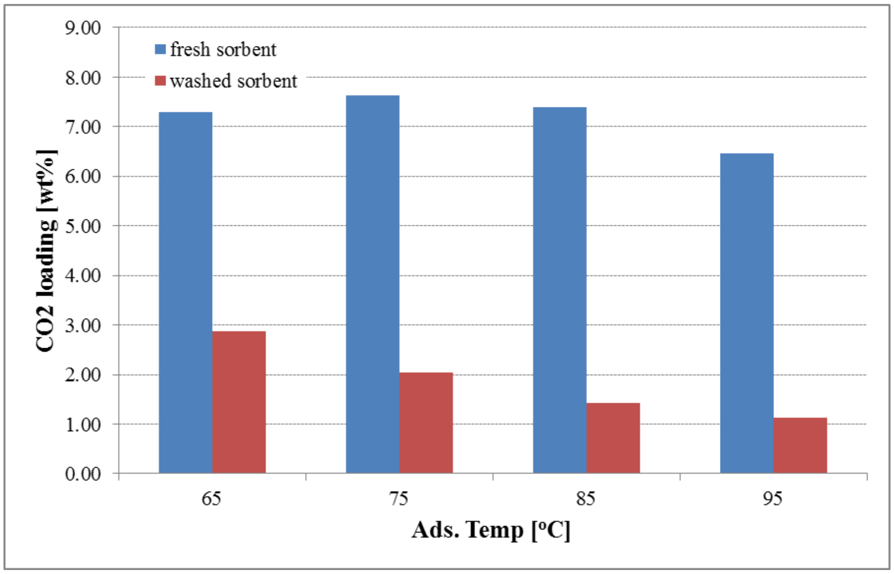


Figure 29. CO_2 loading comparison between fresh and alcohol washed sorbent at various adsorption temperatures

4.2.2 Fluidized-bed Sorbent Optimization (Task 6)

The goal of continued sorbent development efforts in BP2 of this project was to optimize and scale-up the fluidizable, attrition-resistant supported-PEI CO_2 capture sorbent to support bench-scale testing efforts. Our optimization approach built upon advancements made in BP1 and was divided into two major subtasks: 1) identifying low-cost methods for improving sorbent stability and 2) enhancing the fluidized-bed sorbent preparation method for scale-up. Sorbents prepared in Task 6 were evaluated and screened by similar methods used in BP1:

1. measuring CO_2 loading capacity and stability using simulated flue gas mixtures in our PBR systems.
2. evaluating fluidizability through visual verification in RTI's vFBR

Subtask 6.1: PEI-based Sorbent Improvement

The goal of Subtask 6.1 was to develop a low-cost, easily implementable method for improving the stability of a supported-PEI sorbent by eliminating the leaching of PEI from the sorbent which could negatively impact the sorbent's CO_2 working capacity and fluidizability. The project team continued their work in attempting to tether PEI to silica-based supports and cross-link/copolymerize PEI. The primary goal of this task was to identify a method that stabilizes sorbent CO_2 capture performance in a cost-effective manner.

Sorbent Improvement Approaches

The project team continued the BP1 efforts to improve the performance and stability of PEI-based sorbents. It was hypothesized that highly viscous PEI liquid, simply impregnated in the pores of a solid support, could migrate out of the pore on to the surface of the support or away from the particle altogether. PEI is miscible with water, and so there also was an elevated concern for a humid process if there is condensation or adsorption of water on the sorbent. The overall impact would be a decrease in CO_2 capacity due to loss of PEI from the support and/or agglomeration of particles in a fluidized process due to adhesion through PEI surface coatings. The team investigated many strategies to improve PEI-based sorbent stability (and prevent PEI leaching) with varied success. Strategies attempted include:

1. impregnation of commercially-available silicas
2. impregnation of in-house developed silica-based supports
3. deposition of metals on a silica surface for metal-amine complexation
4. bromination of surface silanol groups on the support directly, followed by reaction with PEI, and
5. treatment of silica-support surfaces with SiX_4 or SiR_4 reagents which can react with PEI to make a silica-PEI bond.

Approach #1 became the basis for our "Generation 1" sorbent used in subsequent bench-scale testing. Approach #5 represents what is believed to be a very promising path forward to the next generation PEI-based sorbent ("Generation 2") which has much better stability and higher CO_2 loading performance.

In evaluating the effectiveness of the approaches listed above, a rigorous evaluation/verification step was taken during the preparation and screening of these sorbent candidates and is described here: Materials are modified with a surface bonding approach. In some instances, this involved treating the silica support first, then introducing PEI to the modified surface or it involved impregnating a silica support with PEI followed by treatment with a tethering agent. The resulting solid sorbents were then washed with copious volumes of water. This water washing step was instituted by the team as a strategy for determining whether PEI was sufficiently bound to the silica support. It was hypothesized that strongly-bound PEI (particularly within the support material's pores) would remain on the support after washing and any PEI not bound (or at least having high potential for leaching) would be washed away in the water eluent. During the water washing step, the pH of the eluent was measured, and the rinse continued until the pH became neutral. In this sorbent preparation step, some sorbents exhibited low pH measurements (in the basic range), which was assumed to be indicative of untethered (or weakly-bound) PEI being washed away. It should also be noted that the project team had also employed water washing as a preparation step for stripping surface PEI from the support material in order to improve the fluidizability of the particle. The water washing used for evaluating PEI tethering is a much more rigorous treatment than the surface stripping method.

PEI-Impregnated CO_2 Capture Sorbent ("Generation 1" Sorbent)

PEI-impregnated CO_2 capture sorbents exhibit many promising attributes which make them a suitable candidate for RTI's CO_2 capture technology (e.g. CO_2 loading capacity, stability, fluidizability, cost, etc). However, when followed by the water washing step, we observed that these prepared sorbents exhibited low CO_2 capacities which do not meet the team's minimum performance criteria identified in the project's R&D milestones (> 6 wt.% CO_2 loading). In fact, even when the PEI impregnation approach was coupled with tethering and/or amine-complexation steps, the washing of these sorbents still reduced significantly their capacity for CO_2 adsorption. This result bolstered our concerns about sorbent performance in humid process conditions, such as humid flue gas and steam within the Regenerator. These results showed that the tethering approaches selected were largely unsuccessful, as they did not translate to a robust sorbent with reasonable capacity. Impregnated sorbents that do not go through the water washing step had much higher CO_2 capacities than washed sorbents (upwards of 10 – 12 wt.%). Numerous PEI-impregnated sorbents have been identified which are well above out taregt CO_2 capacities – but exhibit these capacities in the absence of water washing. **Figure 30** shows CO_2 capacities achieved for various unwashed sorbent candidates.

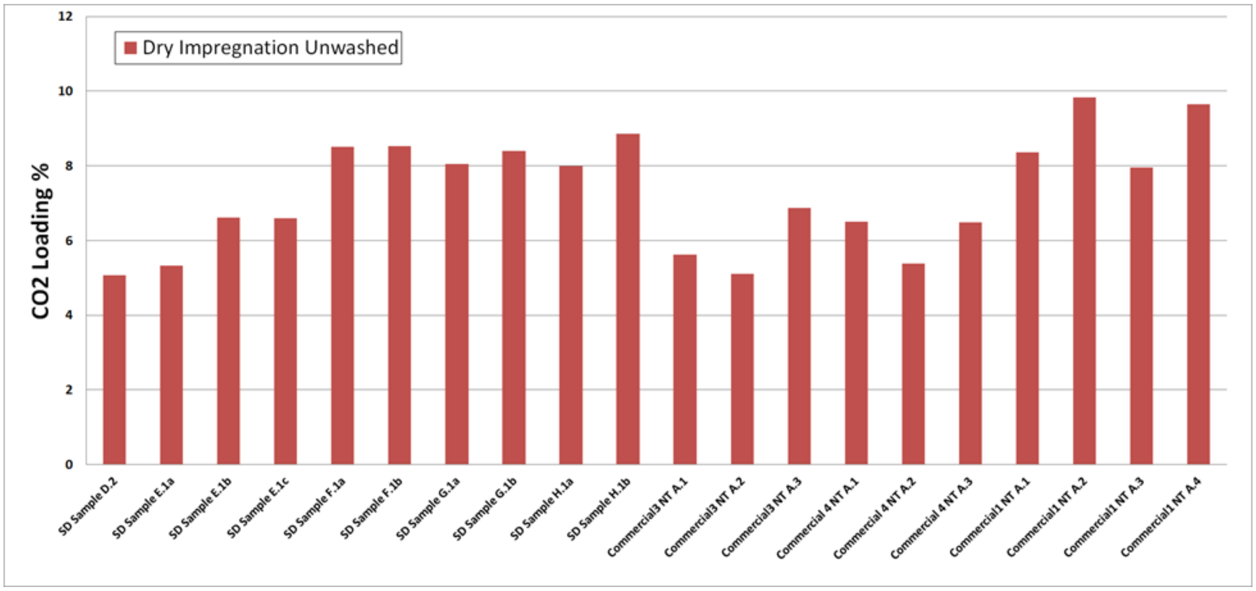


Figure 30. CO_2 capacities of unwashed PEI-impregnated silica supports.

The candidate sorbents exhibited in **Figure 30** include several commercial silica supports which have densities and average particle sizes that make them favorable for a fluidized-bed process. These commercial silica supports passed all of our fluidization tests – even without the water washing step (additional details provided in the section related to Subtask 6.2). These supports proved to be ideal candidates for carriers of the PEI reagent and represent the basis for the "Generation 1" sorbent which was selected for scale-up and primary testing in our bench-scale prototype system.

Water-stable CO_2 Capture Sorbent ("Generation 2" Sorbent)

Although our PEI-impregnated sorbents ("Generation 1") met all of our target criteria for CO_2 loading capacity, density, particle size, and fluidizability, there was still concern that the PEI may not be immobilized well enough to prevent leaching when operated in a commercial process. It was believed that a more commercially-viable sorbent may be one that exhibits stronger PEI-silica tethering, however, as noted previously, the project team experienced little to no success in tethering approaches (particularly utilizing SiX_4 reagents) as all samples failed screening after a rigorous water wash. Our investigation of $Si(OR)_4$ type reagents, where $R = C_2H_5$, was more successful.

Two preparation approaches were used when investigating $Si(OR)_4$ type reagents. The first effort involved reacting tetraethylorthosilicate (TEOS) with PEI in the absence of any additional silica support. Since TEOS is used to prepare several mesoporous silica materials, we considered it could form mesoporous solids in the presence of PEI and potentially trap or react with PEI and prevent leaching. The second approach involved treating the sorbent with TEOS only after the silica support was first impregnated with PEI. This approach was carried out by wet impregnation or as a slurry in an organic solvent.

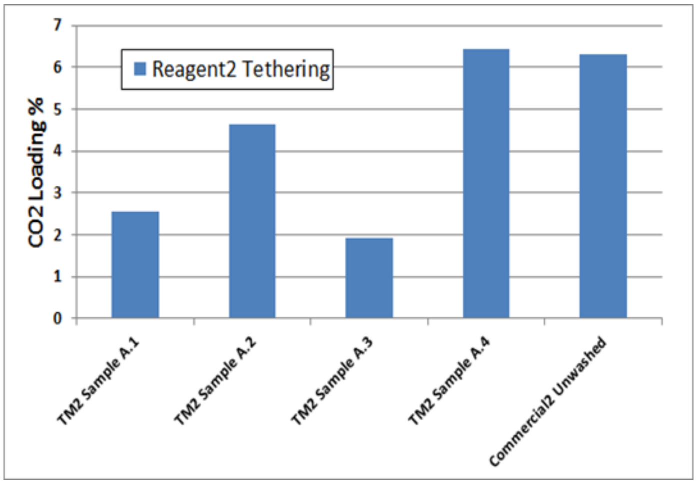


Figure 31. CO_2 capacity of water-washed sorbents derived from a TEOS/PEI reaction method (compared to unwashed sorbent)

Approach #1 – TEOS utilization prior to PEI impregnation: Approach #1 for the water-stable sorbent preparation involved adding TEOS to methanol that is acidified with .1M HCl and stirring vigorously. In parallel, a separate homogeneous solution of PEI (1 mol equivalent to TEOS) and methanol is made and added to the TEOS solution, resulting in the formation of a white solid precipitate. The precipitate is then filtered and washed and was observed to be a dry particulate solid free of adhesion between particles. When sorbents made by this pathway were tested for CO_2 capacity they showed a reproducible 4.6 wt.% CO_2 loading, the highest of any washed sorbent developed previously. Additional work in this area focused on optimizing the preparation conditions and modifying the sequence of reaction steps. After thorough water washing of these optimized sorbents, they exhibited even higher nitrogen content and CO_2 capacity (6.43 wt.%). CO_2 capacity measurements for sorbents made by this TEOS/PEI reaction method are exhibited in **Figure 31** side-by-side with an unwashed sorbent prepared using a commercial silica support. The preparation procedure described here was the first method robust enough to meet target CO_2 capacities even after rigorous water washing. The method employed to produce these sorbents is novel and has been protected by RTI through a provisional patent application.

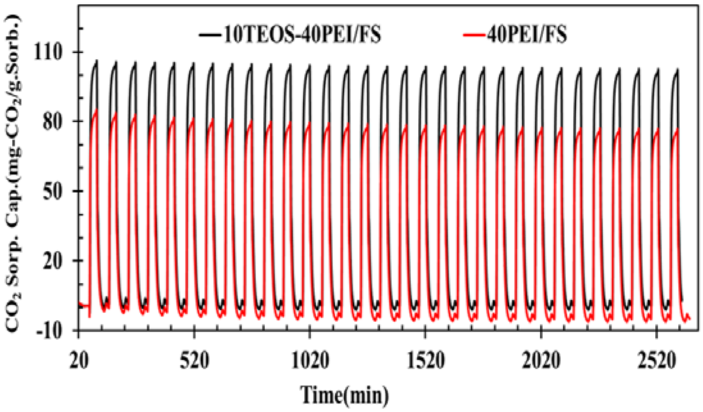


Figure 32. Cyclic CO_2 capacity of TEOS-treated sorbent (black) compared to PEI impregnated on silica support (red).

Approach #2 – TEOS treatment following PEI impregnation: Approach #2 for the water-stable sorbent preparation investigated the impact of treating already-impregnated PEI-silica sorbents with TEOS. It was theorized that this method would result in the formation of additional silica layers to the surface of the sorbent, effectively trapping the PEI in the sorbent. Initial work in this area started with an impregnated PEI-silica sorbent (35-40 wt.%) followed by incipient wetness impregnation of the sorbent with a methanolic solution of TEOS (10 wt.% based on the sorbent). The cyclic CO_2 capacity of this type of TEOS-treated sorbent is exhibited in **Figure 32**, compared to an equivalent sorbent sample prepared without TEOS-treatment. The CO_2 capacity of this sorbent was found to increase substantially over the untreated sample (~ 11 wt.% from 8 wt.% respectively). The reason for this improvement in CO_2 capacity was not immediately identified, so work in this area continued into the project's BP3.

Subtask 6.2: Fluidized-bed Sorbent Optimization and Scale-up

The goal of Subtask 6.2 was to make further progress in the development of a fluidizable, attrition-resistant supported-PEI CO_2 capture sorbent by building upon advancements made in BP1. This included further investigation of the optimal silica support, integration of PEI-tethering advancements made in BP1 and BP2 (as part of Subtask 6.1) into the production procedure, and scaling up production of the most-promising sorbent for use in bench-scale testing. This Subtask was performed as a series of two scale-up efforts with the subsequent scale-up integrating the lessons learned from the previous effort and the advancements made in improving sorbent stability (Subtask 6.1). Ultimately, these sorbent improvement and optimization efforts led to the selection of a single sorbent candidate suitable for scale-up to ~ 150kg and use in the bench-scale contactor evaluation unit. Guiding this work, and the subsequent selection of the most promising sorbent candidate, were additional (and more aggressive) physical property and performance targets by which the sorbents were screened:

- CO_2 loading of > 6.5 wt.%
- Density of > 0.5 g/cm3
- Particle size average of between 75 to 120 µm or higher
- Fluidizability that exhibits a “passing” grade in all vFBR test conditions

Narrowing of Silica Supports for PEI-Impregnated CO_2 Capture Sorbent (“Generation 1” Sorbent)

Several new formulations of fluidizable supports and sorbents were prepared. PEI-based sorbents were prepared, loaded with different weight percentages of PEI in order to optimize the PEI loading amount relative to optimized CO_2 capture performance. The silica materials used as supports in these sorbent candidates were both commercially-available fluidizable silicas and in-house prepared materials formed by spray drying silica and various binders and enhancers together.

Table 10. Comparison of the CO_2 capture performance and physical properties of RTI’s most promising sorbents

Sorbent	Support	Solvent	CO_2 Capacity	Particle size
Sorbent 1	In-house (RTI)	Ethanol	9.3 wt.%	25 – 110 um
Sorbent 2	Grace Davison A	Ethanol	11.4 wt.%	75 – 150 um
Sorbent 3	SiliCycle A	Ethanol	11.8 wt.%	200 – 500 um
Sorbent 4	SiliCycle B	Ethanol	11.7 wt.%	75 – 250 um

Prior to extensive vFBR testing, RTI was able to narrow the sorbent candidate field to four candidates – three made from commercial silica supports (supplied by Grace Davison and SiliCycle Inc.) and one from a spray-dried support material prepared by RTI (**Table 10**). The commercially-available supports were particularly attractive since they had already been proven to be scalable and available in significant quantity. All four candidates were able to achieve reasonable CO_2 loading capacities – with all four exhibiting capacities well above the target of > 6.5 wt.%. More extensive CO_2 capture testing of the sorbent prepared using commercial support “Grace Davison A” exhibited behavior unlike the others as it rapidly lost CO_2 loading capacity over just a few adsorption/regeneration cycles. Given this negative result, this particular support material was discarded and not prepared in sufficient quantities for testing in the vFBR system.

The remaining three sorbent candidates showed acceptable densities, with the highest density being observed on "SiliCycle B" of ~ 0.65 g/cc. As for particle size distribution, two of the three commercial support-based sorbents (Grace Davison A and SiliCycle B) showed particle size distributions within a desired range. RTI's in-house support and the sorbent prepared with SiliCycle A exhibited lower and higher particle size average (respectively) than the desired range. Subsequently, the three remaining sorbent candidates were evaluated in the vFBR and observations were made pertaining to fluidizability and potential for PEI leaching. In general, at optimal loadings of PEI, it was observed that all sorbent samples remained fluidized under the four sets of testing conditions and thus the remaining three candidates were given a "passing" grade.

PBR testing of the sorbent candidates revealed that the optimal PEI loading ranged between 30 to 40 wt.% PEI and that by increasing the PEI loading to 40 to 50 wt.%, it does not increase CO_2 loading capacity. Results from this work are exhibited in **Figure 33**. It was theorized that this result is due to superior PEI dispersion on the support and is consistent with higher amine utilization compared to impregnated materials with higher PEI loadings. Other advantages of using less PEI in sorbent impregnation include potentially lower costs and avoidance of agglomeration due to having less PEI on the external surfaces of the silica support.

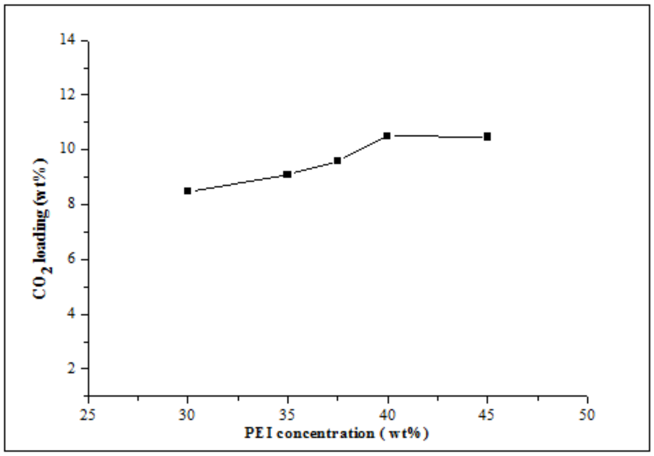


Figure 33. Effect of PEI loading percentage on a sorbent's CO_2 loading (tested at 65 °C, simulated coal-fired flue gas).

Given that these sorbent candidates were all able to meet initial screening criteria, secondary criteria were used to down-select to one candidate for scale-up. Considerations such as level of effort in preparing large quantities, schedule for delivery of large support quantities, and cost were used to evaluate the remaining candidates. RTI's in-house spray dried support was eliminated from consideration. Even though this support material exhibited potential for better attrition-resistance and had sufficient CO_2 loading potential, it was determined that this pathway would be much more expensive and time-consuming to make a scaled-up version rather than moving forward with a commercial support. The final two support candidates were contrasted based on cost and schedule of delivery and ultimately SiliCycle B was selected to be used for sorbent scale-up. The stability of these sorbents prepared using commercial silica supports is shown through their retention of high CO_2 loading capacities over 200+ cycles, as exhibited in **Figure 34**.

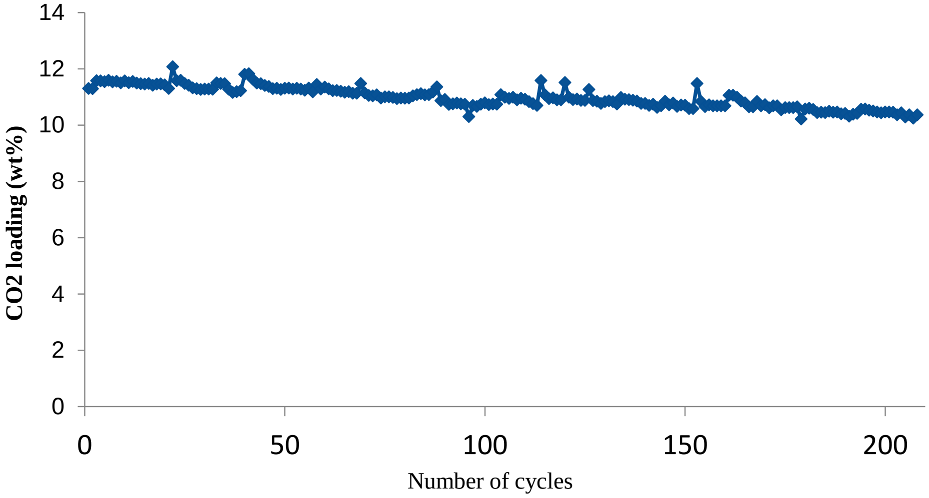


Figure 34. Multi-cycle performance stability of PEI-impregnated commercials support

Sorbent Scale-up (“Generation 1” Sorbent)

The objective of the sorbent scale-up effort was to manufacture a sufficient quantity of sorbent to initially fill the BsCEU and have a 1x inventory available as make-up sorbent to the system. The bench-scale system requires ~75 kg initial fill, therefore, 150 kg of scale-up sorbent was targeted in this effort.

The first step in the sorbent scale-up effort was to finalize the manufacturing procedure to be used by a commercial manufacturing partner. This step included the final selection of the silica support source (SiliCycle B, as described above), the PEI type and source (MW = 600; Aldrich, as identified in previous sorbent optimization efforts), the solvent to be used in the sorbent preparation (Ethanol), and the PEI loading target for the prepared sorbent (30 wt.%, slightly lower than the optimum identified in **Figure 33**, to ensure that PEI deposition on the silica surface was completely avoided). In addition, roughly 15 toll manufacturing companies were evaluated before selecting a manufacturing partner which was uniquely capable of providing the sorbent scale-up service. The commercial manufacturing partner first performed a small-batch trial preparation run for the sorbent, we evaluated the trial batch performance and properties (confirming that they met the desired targets), and then the full production run (150 kg) was authorized and executed for the CO_2 capture sorbent. A photo of the sorbent received by the commercial manufacturing partner is exhibited in **Figure 35**.

Figure 35. Scaled-up sorbent delivered by commercial sorbent manufacturing partner

RTI's analyses of the scaled-up sorbent suggested that it is near to exactly the same composition as the sorbent prepared in RTI's laboratory. The CO_2 capture performance, fluidization performance, and physical properties were all nearly identical to the lab-scale sorbent and met the desired targets. **Table 11** exhibits a comparison of the CO_2 capture performance and properties between the lab-scale and scaled-up sorbent. RTI performed fluidized-bed testing on the scaled-up sorbent under multiple process conditions. The sorbent passed these tests and exhibited no agglomeration or PEI leaching under the conditions tested. The vFBR tests, coupled with the physical property measurements, confirm that the scaled-up sorbent is suitable for bench-scale testing and thus the initial fill of ~75 kg was loaded in the BsCEU for parametric testing.

Table 11. Comparison of sorbent performance and physical properties of lab-scale and scaled-up sorbents

Silica	Support	Amount	PEI loading	CO_2 Capacity	FBR test	Density	PSD
Lab Sorbent	SiliCycle B	100+ g	30 %	8.5 wt.%	Pass	0.6 g/cc	75 – 250 um
Scaled-up Sorbent	SiliCycle B	150 kg	30 %	8.9 wt.%	Pass	0.6 g/cc	80 – 250 um

Based on discussions with the commercial manufacturing partner, they have capabilities to confidently scale production to at least an order of magnitude larger (1000+ kg) and SiliCycle, which produces the commercial silica support, can easily meet the silica demand at that scale also. Additional sorbent scale-up was required later in this project to provide additional inventory for the BsCEU and refresh sorbent that had deactivated due to oxidative degradation.

4.2.3 Sorbent Improvement and Optimization (Subtasks 7.2, 7.5)

Additional lab-scale sorbent improvement and optimization, in addition to sorbent scale-up, was carried out in Task 7 (i.e. Subtasks 7.2 and 7.5). It was expected that bench-scale testing would provide a wealth of performance insights related to the PEI-based sorbent. All of these insights, as well as additional insights through lab-scale testing, acted as a roadmap pointing to specific improvements needed in the sorbent formulation and provided the framework for sorbent development efforts carried out in Task 7. The main emphasis of these sorbent improvement activities was to further improve performance stability, critical physical properties, optimize the scale-up procedure for the PEI-impregnated sorbent ("Generation 1"), and evaluate modification to the novel water-stable sorbent ("Generation 2") preparation. Specific objectives included:

- Develop a systematic study of new sorbent preparation variables that would affect the CO_2 sorption capacity of the prepared sorbent
- Revisit scaling up the production of the PEI-based sorbent and produce a new BsCEU inventory while retaining all physical and performance metrics as well as chemical, thermal, and physical stability exhibited in the lab-scale sorbent
- Modify the new water-stable sorbent ("Generation 2") and further improve physical and performance metrics, in particular the density and particle size distribution.

Subtask 7.2: Additional Sorbent Scale-up for Bench-scale Testing

The objective of subtask 7.2 was to manufacture, at kilogram-scale, any additional fresh batches of CO_2 capture sorbent needed to carry out the bench-scale testing campaigns that had been planned for Tasks 7.1, 7.3, and 7.4. Two key areas for improvement in the sorbent scale-up were the silica support choice and PEI loading amount. Silica support selection, which was guided by previous support selections, again focused on the pore volume and pore size of the support. The necessity for new silica support selection was driven by discontinuation of certain silicas, and improvement of other products, by the commercial manufacturers targeted in our study. Several highly-promising silica supports were evaluated for overall CO_2 capture performance and adherence to targets for physical properties. In total, five new lab-scale sorbents were prepared exhibiting different physio-chemical properties (**Table 12**).

Table 12. Physio-chemical properties of new lab-scale sorbent candidates considered for scale-up

Silica	Surface Area (m^2/g)	Pore size (nm)	Pore Volume (ml/g)	Density (g/cc)	wt.% CO_2 Loading[a]
Silica-1	**290**	**15.5**	**1.12**	**0.66**	**10.0**
Silica-2	400	8.5	0.85	-	7.3
Silica-3	377	9.1	0.86	-	7.0
Silica-4	57	48.7	0.79	0.60	7.1
Silica-5	72	46.9	1.15	0.59	12.0

a) All samples were prepared with 35% PEI on and were tested for CO_2 capture by PBR testing over 10 cycles.

Several of these new silica samples exhibited promising results for certain properties, however, “Silica-1” was chosen for scale-up for the following reasons:

- Good pore volume
- Improved density
- Reasonable list price
- Commercial availability for larger scale manufacture.

The sorbent scale-up (~100 kg) was carried out in three batches at the commercial manufacturing partner site. CO_2 capture performance data collected on samples extracted from three separate batches are exhibited in **Figure 36**.

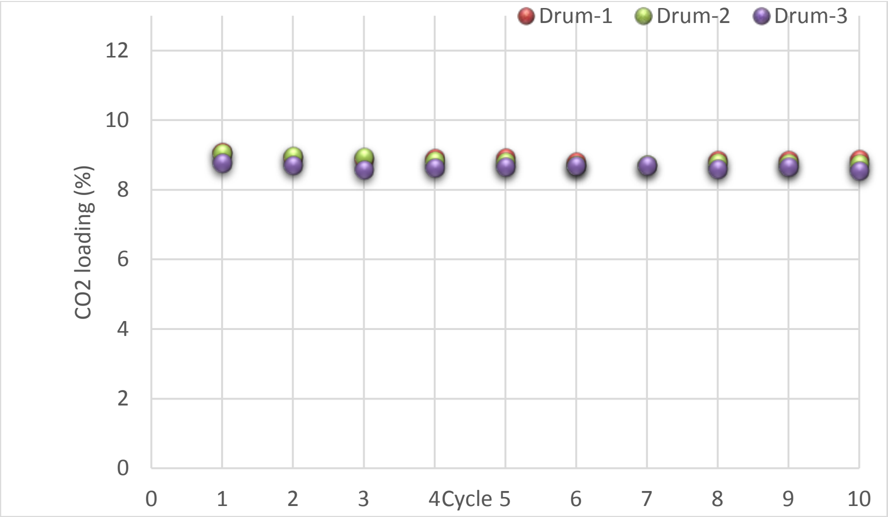


Figure 36. CO_2 capacity (wt.%) of three sorbent samples (different batches) tested over 10 cycles.

As shown in **Figure 36**, the CO_2 loading (9 wt.%) is consistent for all three sorbent batches. Physical property measurements also confirmed that the sorbent batches were nearly identical in density (~0.68 g/cc) and particle size distribution (80-275 µm). These data confirmed the consistency and reliability of the sorbent manufacturing procedure. After full characterization and testing of these new sorbent batches, they have been combined and tested in RTI’s BsCEU.

Subtask 7.5: Next Generation Sorbent Improvement

Further Improvement of the PEI-Impregnated CO_2 Capture Sorbent ("Generation 1" Sorbent)

The reliability and attractiveness of RTI's "Generation 1" sorbent had been confirmed through extensive lab- and bench-scale testing. Although this sorbent has no PEI tethering mechanism, testing prior to the beginning of BP3 had met many of the desired performance targets, so this sorbent remained a good candidate for further improvement and optimization. To this end, the project team developed and executed a detailed sorbent optimization plan for this "Generation 1" sorbent. Several parameters that affect the sorbent CO_2 sorption capacity were studied, including the effect of different PEI polymers, blended amines, different solvents, and modifications to the evaporation process.

Effect of PEI polymer choice at different loadings: The effect of different PEI polymer types were examined within the optimal loading range identified in the project team's previous work (i.e. three loadings were attempted: 35, 37, and 40wt.% PEI).

Table 13. CO_2 sorption capacity of sorbents prepared with different PEI polymers and varied PEI loadings.

Sample	PEI type	CO_2 capacity at different PEI loading (%)		
		35%	37%	40%
PEI Polymer 1	B-PEI[a]	9.2	9.7	9.5
PEI Polymer 2	EDEC-PEI[b]	9.5	10.6	10.4

a) B-PEI: branched-PEI;
b) EDEC-PEI: ethylenediamine-end-capped-PEI.

As shown in **Table 13**, the CO_2 sorption capacity of the sorbents prepared using "PEI Polymer 1" with PEI loadings of 35, 37, and 40 wt.% is quite similar to the sorption capacity of the sorbents prepared using "PEI Polymer 2" at these same PEI loadings. These data indicate that "PEI Polymer 2", which has a much lower "catalog price", does not cause a significant difference in terms of CO_2 sorption capacity. The beneficial impact "PEI Polymer 2" has on the final cost of sorbent manufacturing, makes it a good choice for further exploration. In addition, the data exhibited in **Table 13** confirms the PEI loading trend found in previous work – i.e. there appears to be a performance optimum between 35 and 40 wt.% loading PEI. This is the final confirmation the project team needed to determine that all PEI-impregnated sorbents should only be prepared with a PEI amount that makes up between 35 to 40 wt.% of the final sorbent.

Effect of blended amines: The project team theorized that the use of additional amines, besides PEI, may have a synergistic benefit on prepared sorbents and/or lead to better thermal and chemical stability. Two additional amines, having a chemical affinity for CO_2, were selected and blended with different ratios PEI prior to impregnation on a silica support. The effect of these new amine on the overall sorbent CO_2 sorption capacity was studied and the data are exhibited in **Table 14**.

Table 14. CO_2 sorption capacity of sorbents prepared using a blend of PEI and two new amines.

Amine Choice	Ratio (wt. %)		
PEI standard	20	20	20
Amine 2 (A2)	10	15	20
Amine 3 (A3)	10	15	20
Total Amine Loading (wt.%)	30	35	40
Sorbent 2 (A2)- CO_2 Capacity (%)	**8.2**	**8.9**	**11**
Sorbent 3 (A3) – CO_2 Capacity (%)	**5.1**	**5.9**	**6.9**

As show in **Table 14**, with the increase of “Amine 2” loading from 10 to 20 wt.%, the CO_2 sorption capacity of these sorbents increase from 8.2 to 11 wt.%. – a 34% improvement in CO_2 sorption capacity. A similar pattern of CO_2 capacity improvement is found when using “Amine 3” blended with PEI – overall a ~35% improvement – however, “Amine 2” leads to a much higher overall CO_2 loading capacity within the prepared sorbents and thus is a much more attractive candidate for additional evaluation.

Sorbents were also prepared by blending both new amines with PEI and then impregnating on a silica support. The CO_2 sorption data exhibited in **Table 15**, further confirms that blending “Amine 2” with PEI is more effective than “Amine 3” to elicit sorption capacity improvement within the PEI-impregnated sorbents. The highest CO_2 sorption capacity (8.9 wt.% CO_2) of the sorbents prepared was observed within the sorbent having the highest amount of “Amine 2” (10 wt.%) and the lowest amount of “Amine 3” (5 wt.%) 8.8%.

Table 15. CO_2 sorption capacity of the sorbents prepared by blending PEI with two new amines.

Amines	Ratio (wt. %)		
PEI	20	20	20
Amine 2	5	10	10
Amine 3	5	5	10
Total Amine loading (wt.%)	30	35	40
Capacity (%)	**8.3**	**8.9**	**8.8**

Effect of using polar solvents at different PEI loadings: Upon evaluating all preparation variables that can be tailored for sorbent performance optimization, the project team identified one that had not yet been studied, i.e. the use of different solvent types in the impregnation process. Since the polarity of a solvent may influence the interaction between PEI and the silica support, possibly affecting the distribution of PEI on the support, the project team identified solvents with different polarities for use in trying to optimize the “Generation 1” sorbent preparation procedure. **Table 16** lists the CO_2 sorption capacities measured for sorbents prepared using different solvents as well as different PEI loadings (35 and 40 wt.%).

Table 16. CO_2 sorption capacities of sorbents prepared with different solvents at different PEI loadings.

Sample	Solvent	PEI loading (%)	CO_2 Capacity (%)
35% PEI/Silica	Solvent 1	35	9.4
	Solvent 2	35	9.5
	Solvent 3	35	10.4
	Solvent 4	35	10
40% PEI/Silica	Solvent 1	40	10.6
	Solvent 2	40	8.2
	Solvent 3	40	9.5
	Solvent 4	40	8.2

The sorption capacities of all sorbents prepared with different solvents were quite similar. The sorbents prepared using “Solvent 3” showed a tendency for slightly higher CO_2 sorption capacity, however, no clear trend can be identified where one type of solvent is better than the others and is consistent across the two PEI loadings. It was theorized that the pattern for CO_2 sorption performance would be consistent between the two PEI loadings, but this theory is no yet confirmed through the data collected to date.

Effect of modified solvent evaporation process: The dispersion of PEI on the silica support is an important factor determining a sorbent’s CO_2 sorption performance. It was theorized that the solvent evaporation process carried out as an early step in the sorbent preparation may impact how well the PEI is dispersed among the support material. Two evaporation processes – fast evaporation (rotary evaporator) and slow evaporation (under N_2 flow) – were examined to help clarify how different evaporation speeds may impact the PEI dispersion and associated CO_2 capture capacity within prepared sorbents (See **Table 17**).

Table 17. CO_2 sorption capacities of sorbents prepared using different solvents and solvent evaporation speeds.

Sample	Solvent	CO_2 sorption capacity (%)	
		Slow evaporation	Fast evaporation
35% PEI/Silica	Solvent 1	9.4	9.9
35% PEI/Silica	Solvent 2	9.5	10.1
35% PEI/Silica	Solvent 3	10.4	10.4
35% PEI/Silica	Solvent 4	10	10.2

As exhibited in **Table 17**, it can be expected that CO_2 sorption capacity can be slightly improved when using a fast solvent evaporation in the preparation of "Generation 1" sorbents. Although the sorption capacity improvement may only be modest – up to 6% improvement – the methods and speed of evaporation are worth exploring further for both the lab and scaled-up versions of this PEI-impregnated sorbent.

Stability of RTI's PEI-Impregnated CO_2 Capture Sorbent during Bench-scale Testing

As discussed previously in this report, RTI's PEI-based sorbent was scaled-up to ~150 kg for use in RTI's bench-scale prototype system. Lab characterization of the scaled-up sorbent confirmed that it had retained all of the desired performance and properties exhibited in the lab-scale version of the sorbent. During bench-scale testing (described in Section 4.3), the project team observed a steady decline in the sorbent's CO_2 capacity over several hundred hours of testing. The sorbent's CO_2 sorption capacity was impacted while fluidizability and other key physical parameters remained unaffected. The reduced CO_2 capacity exhibited by the sorbent made certain goals of our parametric testing campaign difficult to achieve. In order to achieve these goals, a new batch of high-CO_2 loading sorbent would be needed. Prior to procuring a fresh batch of sorbent, it was important to understand why the sorbent capacity had degraded during BsCEU testing and what mitigation strategy was needed to eliminate (or at least limit) the deactivation of a new, fresh batch of sorbent.

***Potential Methods of Degradation*:** Given that the sorbent degradation pathway of our scaled-up sorbent was not immediately obvious, RTI closely examined several operating scenarios encountered during BsCEU operation to determine whether they could be pathways to sorbent degradation. These operating conditions were as follows:

- PEI-leaching
- Dry flue gas
- Dry stripping gas
- Exposure to oxygen
- Combination of the conditions listed above.

Various spent sorbent samples from the BsCEU were submitted for CHN analysis to quantify the amount of nitrogen (present in PEI) in the sorbent. This analysis is a good measure of the amount of retained PEI on the sorbent. The results from CHN analysis suggested that the PEI loading on the spent sorbent was similar to the fresh sorbent received from the commercial manufacturer. For this reason, PEI leaching was eliminated as one of the potential causes for sorbent degradation.

***Design of Experiments Statistical Analysis*:** In order to efficiently screen through the remaining operating conditions, and determine their potential contribution to sorbent degradation, a Design of Experiments (DoE) study was implemented and a half factorial test campaign for the five parameters below was conducted.

- Flue gas moisture
- Stripping gas moisture
- Oxygen in flue gas
- Oxygen in stripping gas
- Regeneration temperature

A half-factorial design for a 5-parameter study results in an evaluation of 16 test conditions. These test conditions were evaluated and results confirmed through two different experiments, using two PBRs and running through the test conditions in random sequence. To ensure that no error or bias was introduced in one experiment over the other, each of the two test runs was started with three cycles of standard capacity test conditions to ensure similar capacity and behavior was observed. This sequence was then followed by the test conditions to be studied. Three standard capacity measurement cycles were then run between the two test condition sets to observe any irreversible drop in CO_2 capacity – which would have been caused by the prior test condition.

Statistical analysis was applied to the results collected through PBR testing. The resulting half-normal % probability plot is shown in **Figure 37**. These results clearly indicate the two most important factors affecting sorbent stability: oxygen concentration (i.e. exposure to oxygen) and the temperature at which oxygen exposure occurs. A third factor, absence of steam in the stripping gas, also has a significant effect, however, that impact is reversible and in a commercial embodiment of this technology, steam will always be utilized in the stripping gas.

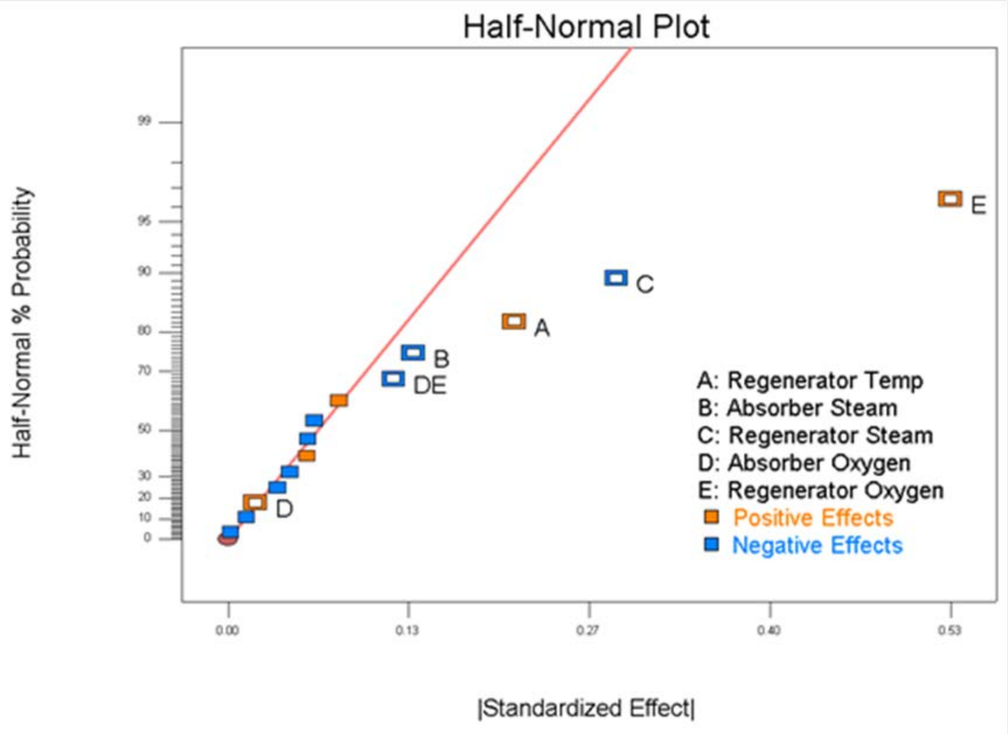


Figure 37. Half-normal probability plot from DoE study identifying most impactful parameters leading to sorbent degradation – O_2 exposure, O_2 concentration, and the temperature at which O_2 exposure occurs.

Extended Exposure to Oxygen: In order to further explore the effect of oxygen exposure on sorbent deactivation, a PBR test was set up to expose the sorbent to various oxygen concentrations at three temperatures: 40°C, 70°C and 110°C. The results from this test are shown in **Figure 38**. The test was started with four cycles of standard CO_2 capacity measurement conditions, followed by a soak condition of exposure to 4.5 vol% O_2 at 40 °C for 1 hour, and finished with four cycles of standard CO_2 capacity measurement conditions. The results show that exposure to O_2 at 40°C and 70°C does not affect sorbent capacity, however, exposure at 110°C does and leads to a significant decrease in sorbent capacity, with the extent of the degradation proportional to O_2 concentration. This test was continued as the sorbent was exposed to air at 110 °C for 1 hour. The exposure time was then increased to 6 hours and led to the most substantial decrease in sorbent capacity.

Other tests were planned and executed in order to identify the critical temperature at which the sorbent starts to deactivate under oxygen exposure. Similar to previous experiments, these tests started with four cycles of standard CO_2 capacity measurement conditions followed by exposure to 21 vol% O_2 for 72 hours at a) 70 °C, and b) 90 °C.

Sorbent capacity was unaffected at 70 °C., however, upon exposure to oxygen at 90 °C the sorbent capacity dropped over 50% from 5.8 wt.% to 2.5 wt.%. It is clear from this study that PEI-based sorbents should avoid exposure to O_2 at temperatures above 70°C. It appears that even extended exposure to O_2 at 70°C and below has no detrimental impact on the sorbent's CO_2 capture performance.

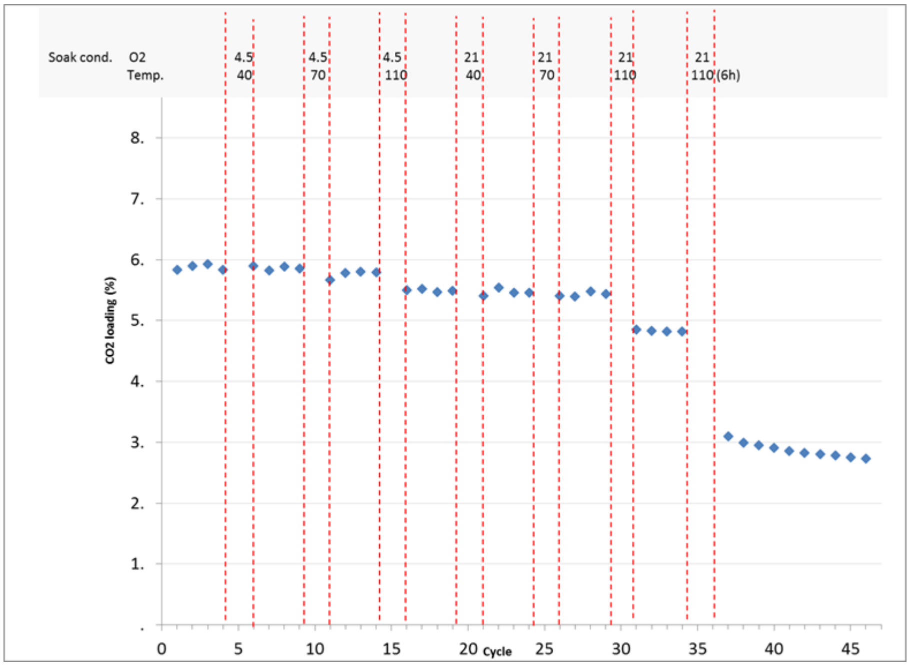


Figure 38. Sorbent exposure to various O_2 concentrations at 40°C, 70°C and 110°C.

Impact on BsCEU Design and Operation: In the original configuration of the BsCEU, air was used as the lift gas to move the sorbent from the bottom of the Regenerator to the top of the Adsorber. Sorbent from the Regenerator, operating at ≥110 °C, was transferred to the lift line via a vertical standpipe. The hot sorbent contacts the ambient temperature air and the mixture moves up through the lift line. Thus, it was theorized that the primary source (if not the only source) of sorbent deactivation during BsCEU testing occurred at this location – where the hottest sorbent was exposed to ~21 vol% oxygen (in the air lift gas). During a modification of the BsCEU, a thermocouple was installed at the bottom of the Regenerator standpipe in order to monitor the solids temperature at this location. The thermocouple confirmed that the sorbent leaving the Regenerator standpipe was essentially at the same temperature as the Regenerator (110 - 120 °C).

This problem of sorbent degradation at the standpipe location could be resolved by either avoiding the use of air as a lift gas or by lowering the temperature of the sorbent prior to exposure to air. We first attempted to lower the temperature of the sorbent prior to air exposure. Removing insulation from the standpipe only dropped the sorbent temperature by 1 to 2 °C. In order to induce the more extensive sorbent cooling, without undergoing a significant system modification, we replaced the standpipe with a jacketed pipe that could be cooled with cooling water flowing through the jacket. This "jacketed" standpipe was sized assuming an internal heat transfer coefficient often observed with fluidized materials and an external heat transfer coefficient based on turbulent flow of cooling water (using baffles and cross-current flow). In operation, the jacketed standpipe did not work as well as planned, only reducing the sorbent temperature by about 10°C. It was determined that a much more extensive sorbent cooler, mimicking the design of an Adsorber or Renenerator stage would be required to enact the level of sorbent cooling required. This would have been a costly and time-consuming modification, so the project team turned to the use of pure nitrogen in the riser supplied by existing liquid bulk and microbulk dewers at the RTI test facility. Over several hundred hours of testing there was no noticeable drop in CO_2 capacity in the scaled-up sorbent, thus confirming that oxidative degradation at higher temperatures (i.e. >70°C) was the source of capacity loss in the previous testing campaign.

<u>Further Improvement of the Novel Water-Stable CO_2 Capture Sorbent ("Generation 2" Sorbent)</u>

As discussed previously in this report section, several pathways for the simple preparation and synthesis of new water-stable sorbents have been investigated. Water-stable sorbents (WSS) were sought due to concerns that PEI may leach out of "Generation 1" sorbent materials in which the PEI is not bound in any way to the surface of the silica support. The leaching could also be exasperated by condensation of water on the sorbent within the process system due to any non-typical operating conditions. Thus, the novel PEI-tethering method was developed to create a water-stable, PEI-based solid sorbent (*Patent application: 62/024,705 filed on July 15, 2014 for the method of manufacturing and material composition and use*). This novel method to immobilize PEI in a solid form by reaction with silica precursors has proven to be a very promising and attractive candidate for a "Generation 2" PEI-based sorbent. The immobilized PEI withstands rigorous contact with water without being completely removed from the support and thus is a good candidate for acid gas separation from humid gas mixtures. Further optimization of this "Generation 2" sorbent was carried out in BP3 with the goal to improve and optimize CO_2 capacity, density, fluidizibility, and other physical properties.

***Impact of water-stable sorbent preparation conditions*:** It was theorized that by modifying WSS preparation conditions, the WSS CO_2 capture performance would be optimized. The project team explored this pathway by varying conditions such as reaction temperature, solvent type, speed of reagent addition, and the use of a catalyst in various concentrations. The reaction temperature was varied between 0 - 60 °C to study the impact it CO_2 sorption capacity and PEI retention. Water was used as a solvent to replace methanol and sorbent prepared by this method were studied at different sorption temperatures. An NH_4OH catalyst was also studied at different concentrations to observe whether this catalyst would impact CO_2 sorption, sorbent density, and/or PEI retention in the sorbent. Results from CO_2 sorption and physical property measurements on these samples are summarized in **Table 18.**

Table 18. Sorption capacity and physical property measurements of WSSs prepared at different conditions

Preparation Condition	Sorption Capacity (wt.%) at different Temp.				PEI content (%)	Density (g/ml)
	75 °C	95 °C	115 °C	125 °C		
WSS-room temperature	8.2	10.3	13.4	13.2	64	0.48
WSS-0°C	5.9, 6.05	8.33	9.29	7.83	51	0.43
WSS-60°C	4.57, 4.28	5.87	7.84	8.48	65	0.51
WSS-all-water	8.88, 9.26	11.7	14.95	14.66	75	0.68
WSS-dropwise (92 min)	10.59, 10.38	13.52	14.9	13.06	67	0.39
WSS-0.05N NH_4OH	9.62	-	-	-	70	0.41
WSS-0.1N NH_4OH	9.79	-	-	-	72	0.41
WSS-1N NH_4OH	10.48	-	-	-	73	0.45
WSS-5N NH_4OH	7.34, 7.64	10.03	12.93	12.46	76	0.43
WSS-5 mL NH_4OH	9.49	-	-	-	72	0.42
WSS- 15 mL NH_4OH	10.19	-	-	-	74	0.38
WSS-20 mL NH_4OH	9.88	-	-	-	75	0.50

In comparison to the conditions used to create the "original" WSS, this evaluation of preparation conditions resulted in the following:

- An increase in reaction temperature (0°C and 60°C) decreases the CO_2 sorption capacity and PEI content. This suggests that the optimal preparation temperature is room temperature.
- WSSs samples prepared using a water solvent exhibit good performance and promising physical properties. The "WSS-all-water" sample showed higher CO_2 sorption capacity (~10 wt.%), PEI content (~75 wt.%), and density (~ 0.68 g/mL) compared to the original WSS. CO_2 capacity increased with an increase in sorption temperature and reaches a maximum of 14.9 wt.% at115 ºC.
- An increase in ammonium hydroxide concentration, only results in a slight increase in the CO_2 sorption capacity. In these samples, PEI content ranged from 70 to 76 wt.% and density varied between 0.40 to 0.41 g/mL, so, in

conclusion, the NH_4OH concentration appears to have a negligible effect on the PEI content, sorbent density, and CO_2 sorption capacity.

Impact of surfactants in water-stable sorbent preparation: It was theorized that nonionic surfactants and templates may improve the properties of WSSs and generate a different type of porous structure within these prepared sorbents. **Table 19** exhibits the sorption capacities measured for WSSs modified with various surfactants and template (in molar ratios of 1 : 0.02 and 1 : 0.04; silica : surfactant/template).

Table 19. Sorption capacity (wt.%) of WSS modified with Template1, Surfactant1, and Surfactant2 in different molar ratios.

Temp (°C)	WSS-T1 (0.02)	WSS-T1 (0.04)	WSS-S1 (0.02)	WSS-S2 (0.02)	WSS-S2 (0.04)
75	10.9	9.1	9.1	7.3	6.3
95	14.2	12.5	12.5	9.6	8.3
115	17.4	15.3	15.3	12.7	11.7
125	16.1	13.9	13.9	12.8	11.6

In modifying the WSS preparation procedure, the use of Surfactant 1 (S1) is a better choice than Surfactant 2 (S2) as it leads to ~25% increase in CO_2 sorption capacity at 75°C. However, use of Template 1 (T1) is the best choice and results in a WSS having 10.9 wt.% CO_2 sorption capacity (~50% higher than the S1-modifed sorbent). In terms of silica-to-surfactant/template ratio, increasing this molar ratio results in decreased sorption capacity for both T1 and S2 and thus a lower amount of surfactant/template is preferred in the WSS preparation.

The investigation of surfactants for WSS preparation was expanded to a whole host of other surfactants, all prepared in the ideal 1 : 0.02 silica : surfactant molar ratio. Detailed characterizations on these sorbents were performed, including N_2-physisorption analysis for surface area and pore property measurement, TGA analysis for PEI content measurement, SEM for surface morphology characterization, and FTIR to evaluate potential chemical bonding in the sorbent samples. **Table 20** summarizes the main properties measured for these sorbent samples. WSSs which were modified using T1, S1, and S2 are included for comparison.

Table 20. CO_2 sorption capacity, density, and pore properties of various surfactant-modified WSSs

Sample	PEI cont. (%)	CO_2 capacity (%)				Density (g/ml)	Pore Property		
		75°C	95°C	115°C	125°C		BET (m^2/g)	P.S (A)	P.V. (cm^3/g)
WSS (Original)	64	8.2	10.3	13.4	13.2	0.48	-	-	-
T1-WSS	71	10.9	14.2	17.4	16.1	0.52	2	-	0.0006
S1-WSS	69	9.1	12.5	15.3	13.9	0.45	2.1		0.001
S2-WSS	-	7.3	9.6	12.7	12.8	0.54	n.d.	-	n.d.
S3-WSS	36	4.0	-	5.9	-	-	6.7	82	0.02
S4-WSS	45	9.6	9.8	9.3		-	1.0	-	-
S5-WSS	61	7.3	-	11.9	-	-	0.83	-	0.002
S6-WSS	75	10.1	13.3	16.4	14.9	0.42	n.d.	-	n.d.
S7-WSS	75	8.0	10.2	13.2	13.4	-	n.d.	-	n.d.
S8-WSS	72	8.0	10.4	13.2	12.9	-	n.d.	-	n.d.
S9-WSS	-	9.0	11.8	15.2	14.5	-	n.d.	-	n.d.
S10-WSS	-	8.7	11.1	14.3	14.2	0.60	n.d.	-	n.d.
S11-WSS	-	9.0	10.5	13.6	12.7	0.57	n.d.	-	n.d.

Through the use of different surfactants, a wide range of CO_2 sorption capacities and sorbent densities were observed in the modified-WSS samples (4.0 to 10.9 wt.% CO_2, and 0.42 to 0.60 g/ml, respectively). The T1-modified WSS exhibited the best combination of CO_2 sorption capacity and density. All sorbent samples measured very low surface area (< 10 m^2/g) with almost no pore volume detectable (it should be noted however that these measurements were conducted at liquid N_2 temperature, which could freeze all PEI inside the sorbents). In evaluating the images attained through SEM, it was observed that the sorbent surface morphology changed with the addition of different surfactants. WSS samples modified with ammonium-based surfactants showed a similar morphology to the original WSS, while those modified with phosphonium-based surfactants exhibited a vastly different morphology. In general, the use of ammonium-based surfactants appear to produce sorbents with more attractive sorption capacity and physical properties.

A key feature of WSSs is their capability to retain CO_2 sorption capacity even in the presence of liquid water. Throughout the project, WSSs have been subjected to robust water washing to determine whether they are able to retain a critical amount of reagent on the support structure even after a water condensation event. Surfactant- and Template-modified WSSs were also subjected to this deep water wash and then CO_2 sorption measurements performed (shown in **Table 21**). The results are promising for the S- and T-modified sorbents, because even after robust water washing these sorbent exhibit a significant amount of PEI retention and CO_2 sorption capacity (all within a narrow range of 3.5 to 4.2 wt.% CO_2 loading).

Table 21. CO_2 sorption capacity of surfactant- and template-modified WSSs following a deep water wash step

Sample ID	Sorp. Capacity (wt.%) at 75 °C	Measured PEI content (%)
Washed WSS-T1 (0.02)	3.5	27
Washed WSS-T1 (0.04)	3.6	31
Washed WSS-S1 (0.02)	3.6	27
Washed WSS-S2 (0.02)	4.2	29

Impact of transition metals and support materials in water-stable sorbent preparation: Among the most promising features of WSSs are their high CO_2 sorption capacities and PEI retention after water washing. One of their biggest drawbacks, particularly given the perspective that these materials need to be prepared in fluidizable form, is low density in nearly all prepared WSSs. In one of our sorbent improvement efforts, the project team placed specific emphasis on improving the density of these water-stable sorbents. It was theorized that "doping" a small amount of heavy transition metal and/or an additional support material into the WSS structure may result in significantly improved densities. Nitrates of various transition metals (Zn, Fe, Cu, Co, Al, and Ni) were all used in preparing some new WSSs. In addition, new support materials such as fumed silica (FS), alumina (Al_2O_3), silica gel (SG), titania (TiO_2), ceria (CeO_2) and zirconia (ZrO_2) were used in preparing other WSS samples. Screening of these samples was done by measuring CO_2 sorption capacities at different temperatures, PEI content, and sorbent densities. Results are summarized in **Table 22** and **Table 23** respectively for WSSs prepared using transition metals and support materials**.**

Table 22. CO_2 sorption capacity, PEI content and density of metal-doped WSSs

Samples	CO_2 sorption capacity (wt.%)				PEI content (%)	Density (g/ml)
	75 °C	95 °C	115 °C	125 °C		
5%Ni-WSS	10.7	13.8	17.2	15.8	74.6	0.58
5%Zn-WSS	9.3	11.9	15.7	15.5	70.8	0.39
5%Cu-WSS	4.7	7.6	9.2	8.3	-	0.41
5%Fe-WSS	7.9	10.4	13.6	13.0	-	0.47
5%Co-WSS	-	-	-	-	55	0.38
5%Al-WSS	7.4	9.6	12.9	13.2	-	0.50
WSS	8.2	10.3	13.4	13.2	64	0.48

Table 23. Sorption capacity and physical property of WSS samples prepared with addition of supports including fumed silica (FS), alumina (Al_2O_3), silica gel (SG), titania (TiO_2), ceria (CeO_2) and zirconia (ZrO_2).

Sample ID	CO_2 Sorption Capacity (%)				PEI content (%)	Density (g/ml)
	75 °C	90 °C	115 °C	125 °C		
2%FS-WSS	8.0, 8.5	11.3	14.9	15.0	66	0.57
5%FS-WSS	9.5, 9.4	11.3	14.0	13.4	57	0.60
1%Al_2O_3-WSS	7.04	-	-	-	63	0.44

2%Al_2O_3-WSS	4.59	-	-	-	47	0.39
5%Al_2O_3-WSS	8.04	-	-	-	56	0.42
1%SG-WSS	7.03	-	-	-	58	0.41
2%SG-WSS	7.55	-	-	-	14	0.46
5%SG-WSS	7.71	-	-	-	61	0.47
10%SG-WSS	7.33	9.44	12.02	11.73	-	0.58
2%TiO_2-WSS	6.86	-	-	-	-	0.53
5%TiO_2-WSS	9.38, 9.29	12.28	13.6	11.7	54	0.58
10%TiO_2-WSS	8.17	11	12.5	10.91	-	0.62
5%TiO_2-WSS[a]	5.07	6.76	9.11	9.51	-	0.48
5%CeO_2-WSS[b]	2.84	-	-	-	-	0.56
5%ZrO_2-WSS[c]	6.71	-	-	-	-	0.35

[a] $TiOSO_4$ as the TiO_2 source; [b] $(NH_4)_2Ce(NO_3)_6)$ as the CeO_2 source; and [c] $ZrO(NO_3)_2$ as the ZrO_2 source.

Table 22 shows that a WSS doped with 5 wt.% Ni results in the best CO_2 sorption performance – 10.7 wt.% at 75 °C and >17 wt.% at 115 °C. This observation correlates well with the high organic content observed in the Ni-WSS (74.6 %) compared to the original WSS (64%). In addition, the bulk density of metal-doped WSSs varied from 0.38 to 0.58 g/ml and the Ni-WSS again shows the best result (0.58 g/ml). These data indicate that using Ni during WSS preparation may help in the retention and better dispersion of PEI within the WSS. It should be noted, however that increasing the amount of Ni to 10 wt% in the WSS does not improve either the CO_2 sorption capacity (7.8 wt.% at 75 °C) or the sorbent density (0.42 g/ml). This is a positive result given that the use of transition metals are expected to only increase the WSS preparation costs. The project team stopped short of being able to fully evaluate transition metal interaction with WSSs, but this pathway has exhibited exciting results and further exploration is warranted, particularly for Ni-doped WSSs.

In terms of density impact when using new support materials, **Table 23** shows that WSSs loaded with fumed silica and/or titanium dioxide lead to the greatest density improvements. Specifically, using 5 wt.% fumed silica results in a WSS density of 0.60 g/ml and 10 wt.% TiO_2 leads to a density of 0.62 g/ml. Both of these sorbents exhibited a promising CO_2 sorption capacity also – 9.5 and 8.17 wt.%, respectively. The remainder of the WSSs prepared with different supports showed very little (if any) improvement over the original WSS. Detailed investigations are needed to fully understand the PEI/silica/new support interactions within these new WSSs. Extending this study to other solid oxides (e.g. CeO_2 and ZrO_2) would also be beneficial and insightful as well as an investigation of mixing all promising sorbent preparation pathways (i.e. the combined impact of using desired templates, ammonium-based surfactants, Ni transition metal, FS, and TiO_2).

4.3 Process Development (Tasks 4, 5, and 7)

One of the objectives of this project was to transition RTI's solid sorbent-based CO_2 capture technology from the lab to bench-scale testing in a representative process at realistic process conditions. As described earlier, RTI's technology is a solid sorbent-based process which selectively removes CO_2 from gas streams through a cyclic, thermal-swing, adsorption-desorption process, generating a high-purity CO_2 product gas that is "sequestration-ready". The process shows promise for being a lower cost alternative to conventional aqueous amine CO_2 scrubbing. Prior to this project, the process development had only advanced to lab-scale evaluations and the process configuration had not yet been proven experimentally at sufficient scale. The focus of the project team was to demonstrate the advantages of RTI's process design through detailed fluidized-bed modeling and bench-scale evaluations of a process prototype. Following 4 years of R&D on the CO_2 capture process, RTI and the project team have achieved the following:

- Identified commercially feasible and scalable process for continuous capture and release of CO_2.
- Proved need for heat management and use of fluidized-bed reactors and staged configuration.
- Developed a multi-physics based fluidized-bed reactor model to analyze the effectiveness of proposed CO_2 capture process configurations.

- Successfully designed and commissioned a bench-scale, multi-stage, fluidized bed CO_2 capture system with a flue gas processing capacity of 13 SCFM, equivalent to ~7 kW_t.
- The multi-stage CO_2 Adsorber was able to achieve 90% capture from simulated flue gas.
- Experimental results clearly demonstrated the need for heat management and staged design.
- Full regeneration (i.e. 0 wt.% CO_2 on the regenerated sorbent) was achieved in the single-stage regenerator. While this clearly demonstrates that sorbent is capable of full regeneration in single stage, we are evaluating staged design to reduce the steam consumption.

Background on Process Engineering and Design

In considering how to optimally design the configuration of a solid sorbent CO_2 capture process, it was observed that PEI-based sorbents can feasibly be used in multiple process reactor environments – fixed-bed, fluidized-bed, and transport reactors. This engineering evaluation focused on the effect of sorbent characteristics, such as the heat of CO_2 adsorption and CO_2 loading capacity on the initial sorbent load requirement, the thermal regeneration energy, the necessity for a heat management system to maintain a heat balance throughout the process, the necessary overall heat transfer coefficient to effectively manage heat movement into or out of the sorbent bed, and the commercial viability and availability of the process components. A main finding of RTI's analysis was that to adequately manage the heat generated by the adsorption of CO_2, a fluidized-bed reactor design must be used due to the need for high overall heat transfer coefficients in the system. Heat management is extremely critical in sorbent-based CO_2 capture processes, especially in the Adsorber, since CO_2 adsorption is an exothermic, self-extinguishing reaction. In addition, from this analysis, RTI identified the following necessary and desirable characteristics of a solid sorbent-based CO_2 capture process:

- sorbent circulation between adsorption and regeneration process vessels
- internal heat management system to avoid the accumulation of heat during adsorption or inadequate heat delivery during regeneration
- fluidized-bed operation to achieve sufficiently high overall heat transfer coefficient

This engineering analysis has led to the determination that the most promising reactor environment for thermal-swing solid sorbent-based CO_2 capture is dual fluidized, moving-bed reactors (FMBRs) in which the sorbent is continuously circulated between a CO_2 Adsorber (for CO_2 capture) and a Sorbent Regenerator (for CO_2 release and concentration). This circulating, FMBR design concept addresses the major process-related challenges associated with solid sorbent-based CO_2 capture and achieves the following:

- process intensification by minimizing the number of process vessels and sorbent load
- minimization of thermal regeneration energy load by enabling the use of high CO_2 capacity solid sorbents and eliminating the cyclic thermal load of associated process equipment
- superior gas-solid heat and mass transfer characteristics compared to fixed-bed reactors
- an effective means of ensuring counter-current flow of gas and solids via bed staging, and
- utilization of process equipment that are commercially available at the scale required.

Despite these advantages, the primary challenge in terms of process development at the start of the project was that it had not been proven experimentally at a reasonable scale. The goal of the process development effort within this project was to address any remaining process challenges – leading to a high-fidelity bench-scale prototype and testing campaign of the favored process design.

4.3.1 Fluidized-bed Modeling & Contactor Design (Task 4)

Task 4 was set-up early in the project to develop a process model which could be used for design and optimization of future iterations of RTI's process technology (bench, pilot, and commercial). Task 4 was broken up into two main efforts:

1. development of a modeling tool to evaluate proposed FMBR design concepts specifically for the CO_2 Adsorber and Sorbent Regenerator
2. development of a design package for a bench-scale contactor evaluation unit to evaluate/verify the effect of key parameters on the performance of the proposed FMBR designs.

Subtask 4.1: CFD Modeling of PEI-based Sorbent Process

The overall objective of this Subtask 4.1 was to develop a multi-physics based model of a FMBR to be used in support of designing various future prototypes of our CO_2 capture process. Specifically, the project team focused on developing a detailed mathematical model of a fluidized-bed reactor including momentum, mass, and energy balances for both gas and solid phases and use this model to support the design of a FMBR process. This modeling tool was developed to aid future process development efforts by providing a means of evaluating numerous proposed FMBR designs without significant investment in capital equipment while providing detailed insights into the effect of key process and sorbent parameters on the performance of proposed FMBR designs. The model was intended for the following end uses:

1. Evaluate numerous reactor design concepts that:
    a. create a counter-current, ‘plug-flow’ process with respect to the sorbent (e.g. bed staging)
    b. increase gas throughput through the CO_2 Adsorber to reduce reactor diameter and sorbent holdup without ejecting the sorbent from the bed
    c. reduce pressure drop across the CO_2 Adsorber to minimize energy consumption
    d. minimize heat transfer internal area.
2. Evaluate the effect of physical and chemical properties of the sorbent including
    a. Geldart Group type (related to the particle diameter and density)
    b. reaction rate (a function of particle diameter and loading capacity)
    c. reactor dimensions (diameter, bed height) to achieve 90% CO_2 capture
    d. pressure drop across the reactor
    e. heat transfer coefficient and ultimately the amount of heat transfer area required.
3. Optimize the design of heat transfer internals in both the CO_2 Adsorber and Sorbent Regenerator

Process Model Development

At the project start, RTI had proposed the development of a multi-physics based computational fluid dynamics (CFD) model to simulate the CO_2 Adsorber and Sorbent Regenerator. However, upon further evaluation and consultation with leading experts in the modeling of fluidized-bed reactors, it was decided that development of reliable and accurate CFD models would be a much more burdensome effort than originally anticipated and was not warranted at this early stage of reactor design. Reliable CFD models of fluidized-bed reactors require rigorous experimental verification and validation of gas-solid hydrodynamics, heat transfer, mass transfer, and reaction kinetics which can be complex and intensive and therefore require significant investment. Instead of making the significant investment in the development of a CFD modeling platform for FMBRs that could not be verified or validated as part of this project, we refocused the modeling effort to build upon the extensively validated 1-dimensional, semi-empirical, two-phase fluidized-bed reactor model developed by Werther and Hartge (2003)[i]. This model was developed with the explicit purpose of designing and scaling-up industrial fluidized-bed processes. The modifications/additions to the Werther-Hartge model made by our project team for this application included:

- a convective term to the continuity equations accounting for the continuous addition and removal of sorbent to the fluidized bed to describe the moving bed aspect of our proposed designs
- an accumulation term to the continuity equations to account for the buildup or release of CO_2 from the sorbent. The sorbent accumulates CO_2 whereas most fluidized-bed reactor systems use catalysts in which the accumulation of any species on the solids is ignored
- a convective term in the energy balance to account for heat transfer between the fluid bed and internals (e.g. banks of heat transfer tubes)

The process- and sorbent-related inputs that can be delivered to the model include sorbent physical properties (e.g. particle size, density, particle shape, etc.), process operating conditions, and reactor configuration. The model uses a Geldart particle classification to classify the sorbent materials into either Group A, B, C, or D types. Based on the classification, the model uses appropriate correlations to estimate additional properties such as minimum fluidization velocity, terminal velocity, bubble rise velocity, bubble diameter as a function of bed height, etc. The model also predicts the heat and mass transfer coefficient using correlations specific to the sorbent classification and fluidized bed operation regime. In the current state of development, the kinetics of CO_2 adsorption within the model are described using a fractional order kinetic model based on Avrami's kinetic model[ii,iii] and the equilibrium adsorbed amount of CO_2 is described by a temperature-dependent isotherm model[i]. Overall, this steady-state process model is able to accommodate the following inputs:

- Sorbent physical properties
- Process operating conditions
- Continuous addition and removal of sorbent from the fluidized bed reactor
- Heterogeneous reactions with adsorption or regeneration
- Kinetics, heat and mass transfer correlations developed in-house
- Configuration of multiple beds in series (staged with co- or counter-current gas-solid flow)

And is able to provide the following information for process design efforts:

- Gas-solid hydrodynamics based on changing operating conditions
- Performance based on selected sorbent properties: particle size, density, and shape factor
- Effect of changing gas flow rate and superficial velocity along the bed
- Heat transfer rates across bed internals
- The combined effect of mass transfer, heat transfer, and kinetics
- Design simulations of reactors with varying size from bench-scale to industrial scale

RTI enlisted the services of Particulate Solid Research, Inc. (PSRI), a non-profit institute, dedicated to the study and development of fluidization, solid transport and other fluid-particle areas to write the simulation code and ordinary differential equation (ODE) solver routines and develop a user-friendly graphical user interface (GUI). Mathematica 8 was used as the programming language. Being the leading research institute in solid materials fluidization modeling and evaluation, PSRI has particularly unique prior experience, expertise, professional stature, industrial knowledge of fluidized-bed processes, and extensive expertise in modeling fluidized-bed reactors. An intangible benefit of our engagement with PSRI has been the value-added design and engineering suggestions that they have made to improve our proposed FMBR designs.

RTI and PSRI worked together to complete and validate the fluidized-bed reactor modeling program. The solver routine for this model is presented in a block flow diagram (BFD) in **Figure 39**. Several graphical plots exemplifying typical results are provided in **Figure 40**.

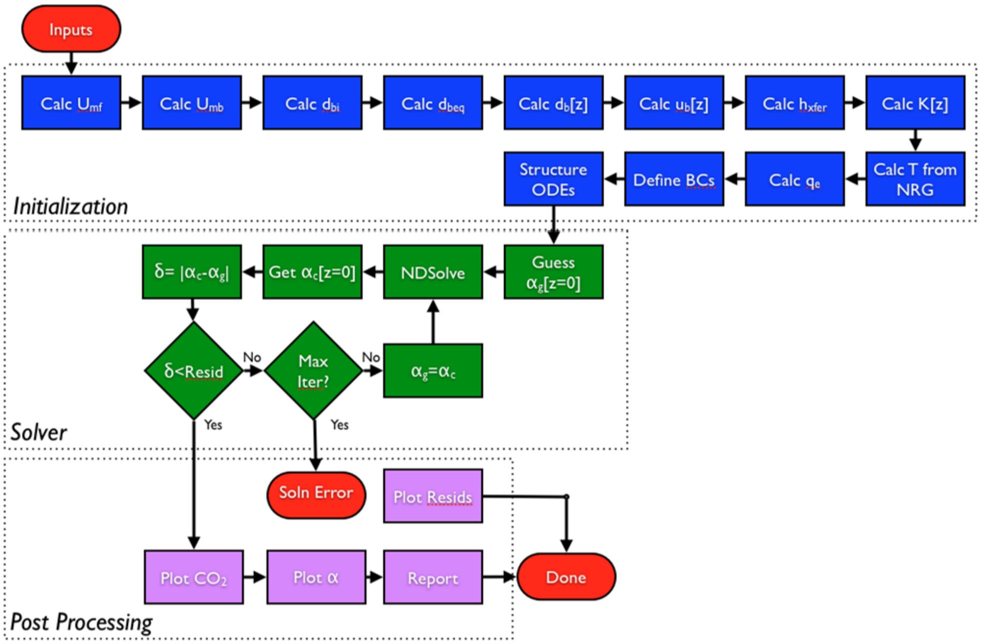


Figure 39. BFD of fluidized, moving-bed reactor model solver routine.

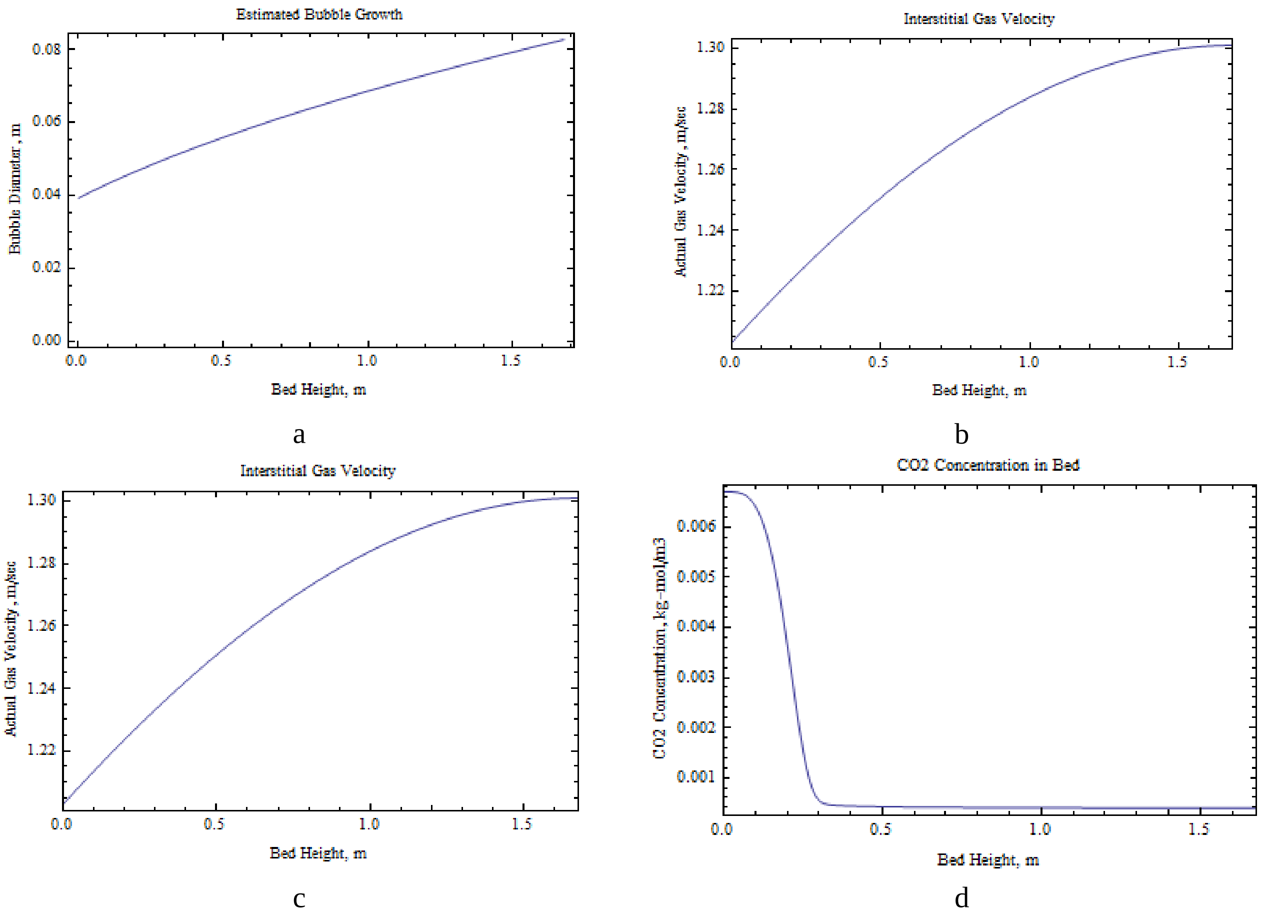


Figure 40. Examples of fluidized, moving-bed reactor model results in graphical form.

The process model developed by RTI and PSRI can be used to guide engineering and design considerations for most solid sorbent-based CO_2 capture systems employing a fluidized-bed design. In particular, RTI will use this model to assist in designing the process reactors needed in subsequent scale-up steps for the RTI technology (e.g. small and large pilot system, pre-commercial demonstration systems).

Subtask 4.2: Design of a Bench-scale, Single-stage Fluidized, Moving-bed Reactor

The work undertaken in Subtask 4.2 represented the first step leading to the larger development goal of realizing a continuously circulating prototype of the advanced sorbent-based CO_2 capture process. The goal of Subtask 4.2 was to develop a detailed engineering design package of a bench-scale contactor evaluation unit (BsCEU) to be built in BP2 of the project. The BsCEU represented a major step forward from RTI's previous capability of only using fixed-bed sorbent testing and reactor modeling to evaluate the design and performance of solid sorbent-based CO_2 capture systems. As a cost- and time-savings measure, and to hedge against any major design modifications, the initial bench-scale system was intended to be a "single-stage" moving-bed reactor and would not be capable of providing high-fidelity data representative of a continuously circulating, fluidized-bed process.

Design and Engineering

At the end of the project's BP1 period, a detailed engineering design package of the single-stage BsCEU was delivered to DOE. This engineering design package included a detailed process description, piping & instrumentation diagrams, bill of materials, detailed cost estimates, and completion schedule estimates. In developing the engineering design package, we worked very closely with PSRI to finalize the design of the FMBR design and all solids handling equipment.

In expanding our original engineering evaluation of solid sorbent-based processes, we identified that the CO_2 Adsorber may take on the form of two promising commercially-relevant designs while we theorized the Sorbent Regenerator only had one commercially-relevant design. Each CO_2 Adsorber design was capable of addressing the specific challenges facing a solid sorbent-based CO_2 capture process for commercial application. These capabilities included:

- Handling very large volumetric gas flow rates (~450 m^3/s for a ~550 MW_e plant) while minimizing pressure drop and process footprint
- Continuously circulating sorbent between adsorption and regeneration (minimizing sorbent inventory and the number of process vessels as compared to fixed-bed systems)
- Achieving effective fluidization to maximize heat transfer between the sorbent and heat transfer internals
- Flowing gas and sorbent counter-current to each other to maximize the concentration driving force and thus CO_2 removal
- Adding and removing large heat loads during adsorption and regeneration respectively with internal/integrated process heat management
- Minimizing sorbent degradation via attrition and/or side reactions with flue gas contaminants.

The two proposed designs for the CO_2 Adsorber are described in **Table 25** including a list of benefits and challenges associated with each design. A single-stage design was originally proposed as a cost-savings measure to reduce the capital investment for the process system; however, based on expanded engineering evaluations, it was determined that it was critical that the project team understand the effect of bed staging not only on capture/regeneration efficiency but also on reactor operation and overall pressure drop. The BsCEU was designed to evaluate the effectiveness of both of these designs for CO_2 removal from flue gas, however, "Design A" gained favor as the primary design to be evaluated within this project for several reasons:

- The complexity and initial cost of "Design B" was seen as prohibitive at that stage in the project
- The benefits of "Design a" outweighed those of "Design B"

- A Sorbent Regenerator design would be based on “Design A”. Given the lower superficial gas velocity and stripping gas composition expected in the Regenerator, “Design A” would be the most viable design for a Sorbent Regenerator in a commercial process.

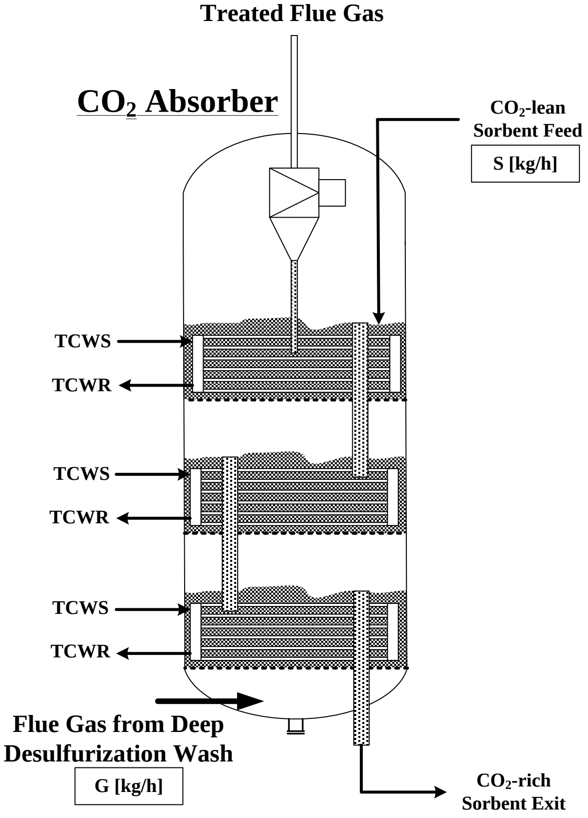
The bench-scale contactor evaluation unit was designed to be a versatile experimental system able to support the evaluation of variations in process arrangement and is instrumented and controlled well enough to accurately measure the effect of process parameters on CO_2 capture performance. The unit was intended to be housed in (and was eventually built in) RTI’s Energy Technology Development Facility (ETDF). **Figure 41** exhibits a simple P&ID of the bench-scale contactor evaluation unit. As displayed in **Figure 41** the BsCEU consists of five sections including:

1. flue gas generation
2. a reactor column
3. a sorbent reservoir
4. process gases, instrumentation and control, and
5. analytical equipment.

Simulated flue gas was used for testing the CO_2 adsorbent in the BsCEU. The flue gas will be delivered from gas cylinders or tanks and the composition can be adjusted to represent coal-fired and NG-fired flue gases by blending in various gases (air, moisture, CO_2, contaminants) as needed. The scale of the bench-scale unit was selected based on the minimum column diameters recommended by PSRI. A column diameter of 6” was selected for the staged, FMBR design (“Design A”) to avoid issues related to bed slugging that would lead to poor CO_2 capture performance and could possibly damage the reactor column. Based on the column diameter and the range of gas velocities expected, the system was designed to process between 300 and 900 SLPM of flue gas, process ~150 kg-CO_2/day, have a solids circulation rate of 75 to 450 kg/h, and has a sorbent fill inventory of ~75 kg.

Table 24. Description of two staged, FMBR designs evaluated in BP1 of RTI's project

A. Staged, Moving Fluidized Bed with Internal Heat Management – Adsorber & Regenerator –



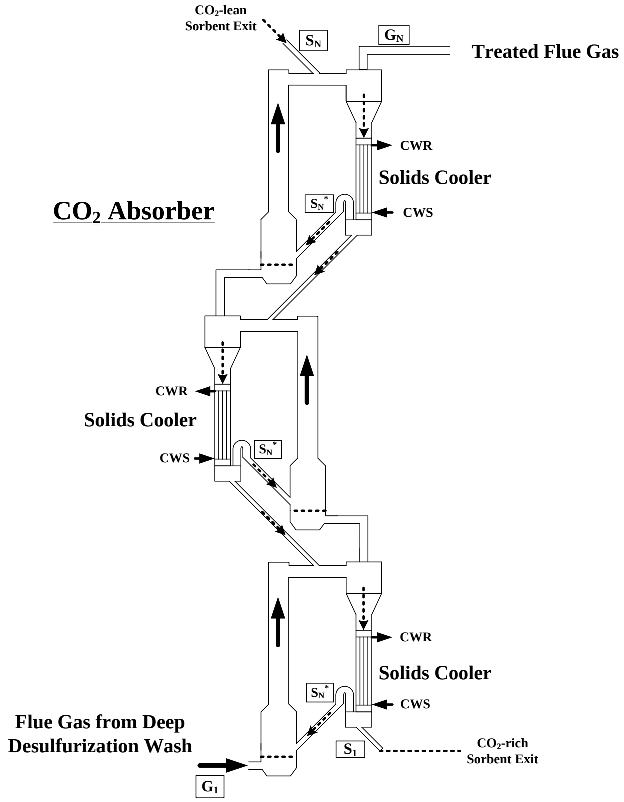
BENEFITS

- Simple design analogous to trayed columns used in gas-liquid adsorption processes
- Demonstrated at commercial-scale for capture of solvent vapors / trace contaminants from industrial gases using activated carbon
- Suitable for Group A and B fluidizable particles
- Provides counter-current flow of gas and solids and internal heat management in one process vessel

CHALLENGES

- Tempered (warm) cooling water must be used to reduce risk of fouling/plugging bed due to water condensation from saturated flue gas
- Large heat transfer area due to small temperature difference between tempered cooling water and bed
- Large cross-section footprint to reduce gas flow rate to reduce back-mixing between stages and entrainment

B. Staged, Circulating Fluidized Bed with Integrated Heat Management – Adsorber Only –



BENEFITS

- CFBs are used in many industrial processes including fluid catalytic cracking (FCC), fluidized-bed combustors, etc.
- Suitable for Group A particles; easily produced commercially in an attrition-resistant form
- Separates heat management and reactor sections so that each can be performed optimally
- Enables the use of cold cooling water to cool solids
- Reduced capital by reducing vessel dimensions, primarily footprint, and heat transfer area by ~50%
- Improved CO$_2$ capture rates due to high heat and mass transfer rates and small particle sizes

CHALLENGES

- Increased sorbent attrition rate due to the number of gas-solid separation devices
- Complex balancing of multiple solids circulation loops
- More complex than "Design a"

To maximize resources, the BsCEU reactor column was designed in such a way to allow it to operate in both Adsorber and Regenerator mode without modification to peripheral equipment. To convert between Adsorber and Regenerator mode, only the process fluids (i.e., feed gas to contactor and reservoir and heat transfer media) would be changed. Ultimately, the BsCEU was a flexible and valuable tool for evaluating sorbent performance and process design at a relatively modest cost and could be modified without the need to build a completely new system.

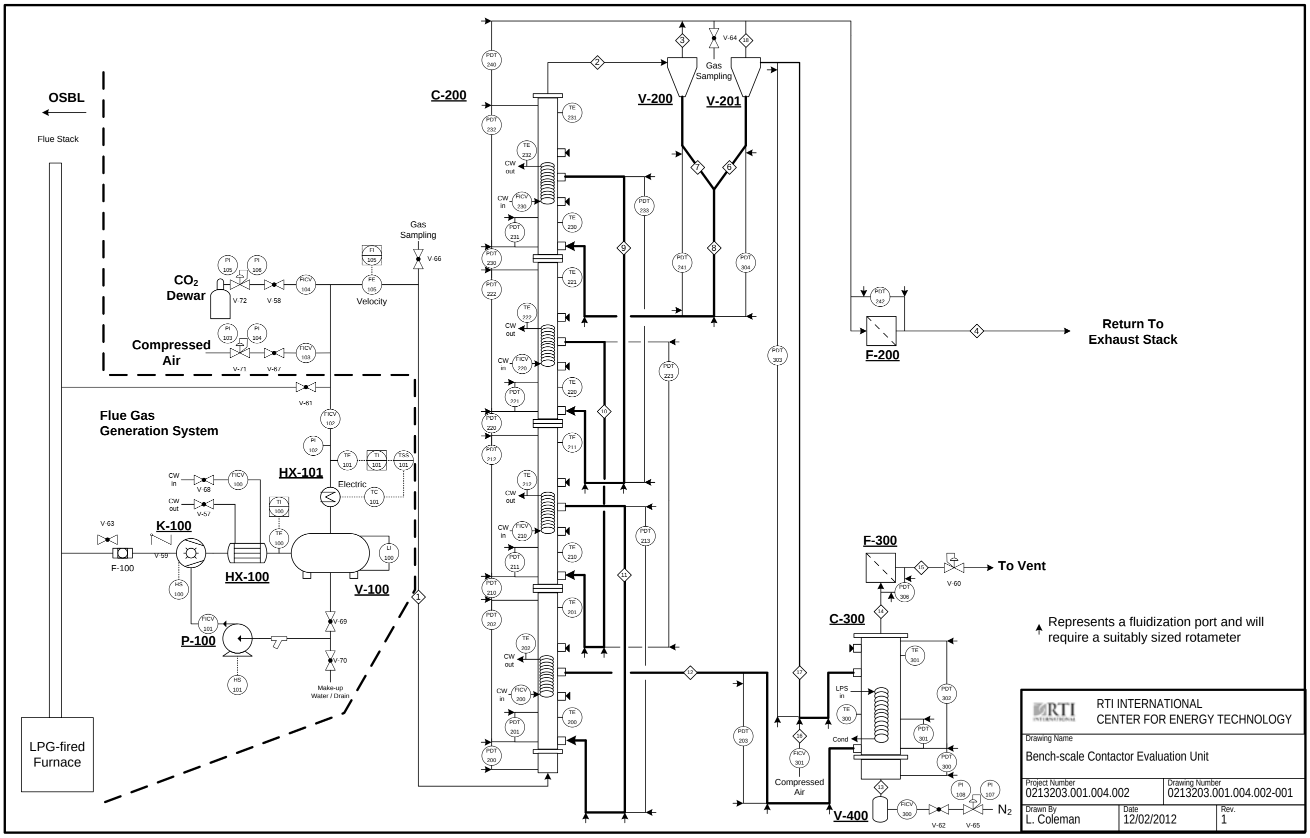


Figure 41. P&ID of RTI's BsCEU – a staged, fluidized, moving-bed system with internal heat management

4.3.2 Fluidized, Moving-bed Reactor Process Build and Testing (Subtasks 5.1, 5.2, 5.3)

The overall objective of Task 5 was to experimentally evaluate the performance and efficiency of a staged FMBR design by building the BsCEU (based on the design developed in BP1) and testing it using a scaled-up sorbent based on RTI's optimal procedure for making a "Generation 1" sorbent. Lessons learned and data collected from the BP2 build and testing were expected to lead to system design modifications which would involve adding to and modifying the BsCEU to realize a more accurate (i.e. high-fidelity) representation of a prototype system. Our approach in Task 5 focused on addressing specific reactor design uncertainties and evaluating the effect of key parameters on the performance of the CO_2 capture process. The BsCEU was used as a testing platform to advance our technical understanding of fluidized-bed sorbent-based CO_2 capture processes, building on the work already done on fixed-bed sorbent screening and reactor modeling. Specific goals of this bench-scale testing Task were to:

- determine the optimal CO_2 Adsorber and Sorbent Regenerator design specifications
- demonstrate that effective heat management is necessary to achieve optimal CO_2 capture and sorbent regeneration performance
- demonstrate that the PEI-impregnated sorbent is fluidizable, can achieve target CO_2 loading capacity and capture rates, and exhibits reasonable attrition resistance, and
- collect critical process data to support the design of a high-fidelity, bench-scale prototype system.

Subtask 5.1: Procurement, Fabrication, and Shakedown of Bench-scale Contactor Evaluation Unit

BsCEU Procurement and Fabrication

A final engineering/design package for the BsCEU was completed in November 2013 and equipment procurement completed in December 2013. Fabrication and construction was initiated in early 2014. A process hazard analysis (PHA) was completed in November 2013 between RTI staff and a 3rd party engineering company and all safety recommendations were implemented within the final engineering/design prior to system fabrication and construction.

Figure 42. RTI's bench-scale contactor evaluation unit

The bench-scale contactor evaluation unit, shown in **Figure 42**, was fabricated and constructed within RTI's ETDF. RTI worked with a multitude of vendors to acquire the appropriate support to deliver, install, and commission the BsCEU. RTI managed and coordinated all aspects of the BsCEU fabrication and build which, in general, followed this sequence (working with the appropriate support vendors at each step):

- Development of 3D design drawings from the detailed design/engineering package
- Development of detailed electrical system design
- Selection and preparation of the specific test site, including utility connections and safety preparations
- Structural analysis and engineering for the existing support structure
- Make required modifications in existing support structure to accommodate the BsCEU
- Procure required equipment and materials based on the detailed bill of materials

- Fabricate process sub-systems, including electrical control panel
- Rig reactor column and other large equipment into designated locations, coupled with structural support welding
- Complete the mechanical and piping layout of the system components
- Make all physical connections, including installation and connection of electrical control panel and process piping
- Pressure and leak test reactor and process piping
- Validate functionality of process control and data acquisition mechanisms
- Insulate reactors and process piping, and

BsCEU Shakedown

Following fabrication and construction activities, the BsCEU went through an extensive 'shakedown' period in early May 2014 to calibrate each instrument and control device and verify that each sub-system operated as designed. These individual shakedown tests were followed by sub-system testing and verification, including the execution of cold and hot gas flow verification and verification of gas composition control.

Following a comprehensive shake-down, the BsCEU was operationally commissioned using a fluidizable alumina with the objective of:

- demonstrating stable/controllable solids flow and circulation between the Adsorber and Regenerator
- calibrating valves and other control mechanisms, and
- verifying cooling/heating control within the Adsorber and Regenerator.

In the alumina flow and circulation tests, RTI demonstrated stable and controllable alumina flow and circulation between the Adsorber and Regenerator and between stages within the Adsorber. In addition, the team was able to calibrate all slide valves and other mechanical control mechanisms and heating/cooling control within the Adsorber and Regenerator.

BsCEU Configuration (i.e. original configuration for parametric testing)

The following is a summary of the system components, set-up, and operational strategy associated with RTI's BsCEU in the original configuration (i.e. prior to reconfiguration executed in BP3):

- Gas and utilities
    - N_2 and CO_2 were supplied to the BsCEU skid from liquid bulk and microbulk dewers, respectively
    - Air was supplied to the BsCEU from a compressor with an accompanied dryer
    - Cooling water was supplied from a 20 ton chiller
    - Steam was supplied from a 310 kW electric steam boiler.

- Adsorber
    - The Adsorber was comprised of four equivalent stages (6" Sch. 10 pipe, ~2 m long per stage) which are separated by Teflon distributor plates
    - Adsorber stages were connected by loop seals which provide gas seals between each of the stages
    - Cooling water was used for removing heat from the Adsorber stages. During operation cooling water was fed through each Adsorber stage's internal heat transfer coils
    - Simulated flue gas was fed to the Adsorber column via mass flow controllers (N_2 and CO_2). The flue gas could also be humidified by direct steam injection.

- Regenerator
    - The Regenerator was comprised of 12" Sch. 10 pipe, ~3 m long
    - An indirect steam contactor within the Regenerator was used to heat the fluidized sorbent and desorb CO_2
    - Simulated stripping gas was fed to the Regenerator via mass flow controllers (N_2 and/or CO_2). The stripping gas was also humidified by direct steam injection

  - Electric heaters were used to preheat the dry flue and stripping gases. Heating tapes were used to ensure the flue and stripping gas lines remain heated into the Adsorber and desorber columns, respectively.

- Solids Circulation and Control
  - The solids circulation rate was controlled by the combination of Regenerator standpipe aeration gas and a slide valve. The Regenerator standpipe aeration flow and slide valve opening were adjusted to obtain a desired riser differential pressure, which correlated to solids circulation rate
  - Cyclones were used to remove solids from the Adsorber and Regenerator effluents. The Adsorber had two cyclones (primary and secondary) while the Regenerator had a single cyclone for collecting fines generated during operation
  - Coalescing filters were used to remove any cyclone inefficiencies (i.e. mostly fines) from the gas streams prior to being vented (Adsorber effluent) or sent to the pressure control valve (Regenerator effluent)
  - A back pressure control valve was used on the Regenerator effluent to maintain the system pressure balance required for solids circulation.

- Gas Analysis
  - Gas compositions of the simulated flue gas, stripping gas, Regenerator effluent, and the effluent from each Adsorber stage were measured online. Detcon analyzers were used to determine CO_2 content, while a MKS (FTIR) analyzer was also used to verify CO_2 and water content.

BsCEU Operation Philosophy

As mentioned previously, the overall design and layout of the BsCEU is not too different from what would be expected in a commercial process. The flue gas generation system for the BsCEU has the commercial equivalent of the actual flue gas at a coal-fired power plant. The CO_2 Adsorber and Sorbent Regenerator are designed in such a way as to mimic the expected design of commercial reactors. The system delivering the process gases, utilities, and operating and controlling the instrumentation are expected to have commercial equivalents. Finally, in a commercial system, it is expected that most process and product gas streams will be analyzed continuously to evaluate performance, thus the BsCEU has been outfitted with a robust analytical system.

In its original configuration of the BsCEU (shown in **Figure 42**) operated as such: flue gas (blended from on-site gas cylinders) was delivered to the bottom of the CO_2 Adsorber – which consists of several, staged contactors. The flue gas passed through a gas distributor into the first staged contactor and came into contact with, and fluidized, the solid sorbent. The sorbent selectively removed CO_2 from the flue gas as the gas continued to flow upward prior to exiting Stage 1. The gas then passed through another gas distributor and entered a second stage within the Adsorber. This flow path repeated for the remaining stages within the Adsorber. The system was designed such that the number of stages could be adjusted by removing gas distributors. The gas then exited the final stage, having a reduced CO_2 content, and passed through a disengagement zone and cyclone to remove a large fraction of the particulates in the gas stream prior to entering a fines filter which removed fine powders. The CO_2-lean, solids-free gas was then sent to an analyzer to quantify the CO_2 content prior to being vented. CO_2 -lean sorbent was continuously fed to the top of the Adsorber. The sorbent mixed into the fluidized bed and reacted with CO_2 in the gas phase. The sorbent then exited that stage of the Adsorber via an overflow downcomer and was sent to the stage below, repeating the process until the sorbent exited the Adsorber. Upon exiting, the sorbent was fed to the Sorbent Regenerator. In this original BsCEU configuration, the Regenerator simply acted as a sorbent inventory vessel with heating capability to regenerate the sorbent. Improvements to the Regenerator design were planned for and executed in BP3 of this project, as originally proposed).

Each stage of the CO_2 Adsorber was equipped with heat transfer internals to remove the heat of CO_2 adsorption and maintain the desired bed temperature. The CO_2 and H_2O loading of the sorbent was varied by controlling the bed temperature and concentration of the feed gas. Being able to change the solids circulation rate, and effectively the solids-to-gas (S/G) ratio, was pivotal to the successful operation of the BsCEU.

Subtask 5.2: Process Evaluation using the Bench-scale Contactor Evaluation Unit

With the completion of Subtask 5.1, approximately 75 kg of our PEI-based sorbent was loaded in to the BsCEU and the system valves, mechanical control, and heating/cooling were recalibrated with the PEI-based sorbent. The primary goals of Subtask 5.2 were to:

- demonstrate stable, continuous operation of the system while achieving ~90% CO_2 capture
- demonstrate that heat management in the CO_2 Adsorber, particularly the removal of heat with immersed internals, is necessary for achieving 90% CO_2 capture, and
- demonstrate that the PEI-based sorbent can achieve sufficient regeneration in a continuous flow, circulating system.

Following shakedown and commissioning, BsCEU operation went right into demonstrating these critical process concepts to help the team better understand how to operate a FMBR system most effectively. The PEI-based sorbent, discussed in section 4.2, was found to fluidize and circulate well in the BsCEU. Stable sorbent circulation was achieved at various sorbent circulation rates spanning 75 to 300 kg/h with over 100 hours of stable circulation and fluidization achieved. These solids circulation rates closely matched the design specifications. CO_2 capture experiments using simulated flue gas were performed to demonstrate that the bench-scale FMBR unit was capable of continuous, stable CO_2 removal in the Adsorber and sufficient desorption in the Regenerator. These preliminary experiments proved the BsCEU capacity to operate continuously, achieve stable sorbent circulation, complete adsorption / desorption cycles, and achieve rapid removal of CO_2 (up to 99+%) from the flue gas.

90% CO_2 Capture Tests

CO_2 capture experiments using simulated flue gas were performed to demonstrate that the BsCEU was capable of continuous, stable CO_2 removal and sorbent regeneration over an extended test period. During this initial parametric testing period, the sorbent was tested in a simulated flue gas environment for 50+ hours. The following were observations from this initial parametric testing:

- the sorbent was capable of rapid removal of CO_2 from the flue gas
- during CO_2 removal, a large exotherm (i.e. increase in bed temperature) was observed starting at the bottom stage of the CO_2 Adsorber and migrating up through the other Adsorber stages,
- capture of 90% CO_2 (a desired target of DOE/NETL's Carbon Capture Program) in the simulated flue gas stream is possible as exhibited in **Figure 43**.

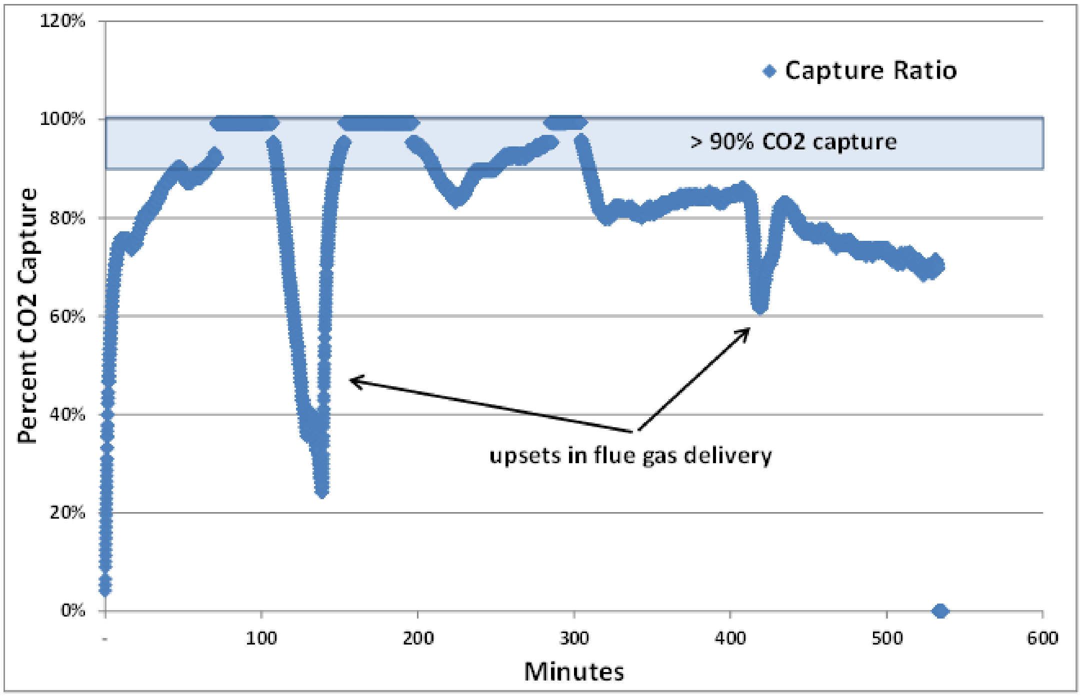


Figure 43. Initial parametric BsCEU test data exhibiting capability to achieve 90% CO_2 capture

Several other parametric tests were executed and observed the same capability of achieving 90% CO_2 capture. At the close of BP2, additional work was needed to balance the degree of CO_2 adsorption in the CO_2 Adsorber and degree of desorption in the Sorbent Regenerator such that the CO_2 capture efficiency would be maintained at >90% for longer periods. The project team carried out much more extensive parametric tests in BP3 investigating how the BsCEU performance responds to the adjustment of process variables. Long-term performance testing was also carried out in BP3.

Heat Management Tests

The main objective of performing "heat management" tests in the BsCEU was to prove a critical design assumption that heat removal in the CO_2 Adsorber is necessary for optimal performance and maximum CO_2 removal for a solid sorbent-based CO_2 capture process. Ultimately, this assumption ties to RTI's conclusion that fluidized, moving-bed processes (versus fixed-bed or transport reactors) are the optimal choice for CO_2 capture using solid sorbents. The conclusive proof for this assumption was not achievable until we had a process system of sufficient scale (e.g. the BsCEU scale) to perform heat management experiments with a sufficient quantity of sorbent.

Initially it was theorized that this "heat management" assumption could be studied by simply adding (and then removing) cooling water from the CO_2 Adsorber heat exchange internals while the sorbent bed in the Adsorber was capturing CO_2 and thus generating heat. By adding the cooling water during CO_2 adsorption, we expected to see the ideal CO_2 capture performance while the sorbent bed was maintained at an ideal temperature. By then removing the cooling water during CO_2 adsorption, we expected to see a sharp rise in sorbent bed temperature and subsequent decrease in CO_2 capture rate and performance. In an ideally insulated system (i.e. with no heat loss to the environment) we still expect this theory to hold true, however testing in BP2 has shown that the BsCEU loses a significant amount of heat to the environment – even with significant insulation throughout the BsCEU. This heat loss to the environment actually acted as the primary heat dissipation sink in the system. The scale of the BsCEU – though large for laboratory testing – was still quite small compared to a commercial process and thus the surface area by which heat can dissipate compared to the overall system volume is relatively large. At a commercial scale this ratio approaches zero and thus heat loss to the environment is insignificant compared to the amount of heat generated by the process. In order to still show the acute improvement of heat management use in the BsCEU, we set-up our heat management tests in a different way than initially proposed.

In our experiments, the importance of heat management was studied by comparing the CO_2 capture rate when no heat was allowed to escape the BsCEU Adsorber, to the CO_2 capture rate when the Adsorber was maintained at an adsorption-favored bed temperature. The "No Heat Management" case – in which no heat is allowed to escape the Adsorber – was set-up to prevent as much environmental heat loss (and sensible heat loss) as possible. To accomplish this condition, during inert N_2 flow (i.e. no CO_2 capture), heat was continuously added to the Adsorber to maintain a desired bed temperature by compensating for heat losses to the environment and the sensible heat to the process gas and the sorbent. This amount of heat required to maintain a stable bed temperature was measured and then was maintained even after the start of CO_2 capture. The objective of this method was to initiate CO_2 capture within the sorbent bed at a relatively high temperature in the Adsorber and continue with the heat addition to compensate for losses to the environment. This allowed the bed temperatures to rise solely from the exothermic heat released during CO_2 capture and prevented the bed temperature from decreasing from heat losses to the environment. After achieving steady state under these conditions, the bed temperature was then lowered by removing heat from the Adsorber (effectively mimicking heat removal through cooling water) and evaluating the effect on CO_2 capture rate.

Under "No Heat Management" conditions the measured CO_2 capture rate was ~20% CO_2 removal from the simulated flue gas. Even while adding heat to the process it was calculated that ~2.8 kW_t heat was escaping from the Adsorber stages – thus if no heat were allowed to escape, we would expect the CO_2 capture rate to be even lower.

To enact the "Heat Management" conditions, the cooling water supply temperature was lowered to effectively remove some of the heat that was being added in the "No Heat Management" conditions – allowing the heat loss to the environment to help lower the Adsorber temperature. It was observed that as the Adsorber temperature decreased the CO_2 capture rate increased. When the Adsorber bed temperature reached 85-95 °C, the CO_2 capture rate increased to ~45%. **Figure 44** exhibits a comparison of the Adsorber bed temperature coupled with CO_2 capture rate in the three test conditions: 1) Pre-adsorption, 2) "No Heat Management", and 3) "Heat Management". It was thus confirmed that higher CO_2 capture rates can be achieved through effective heat management in a solid sorbent CO_2 capture process.

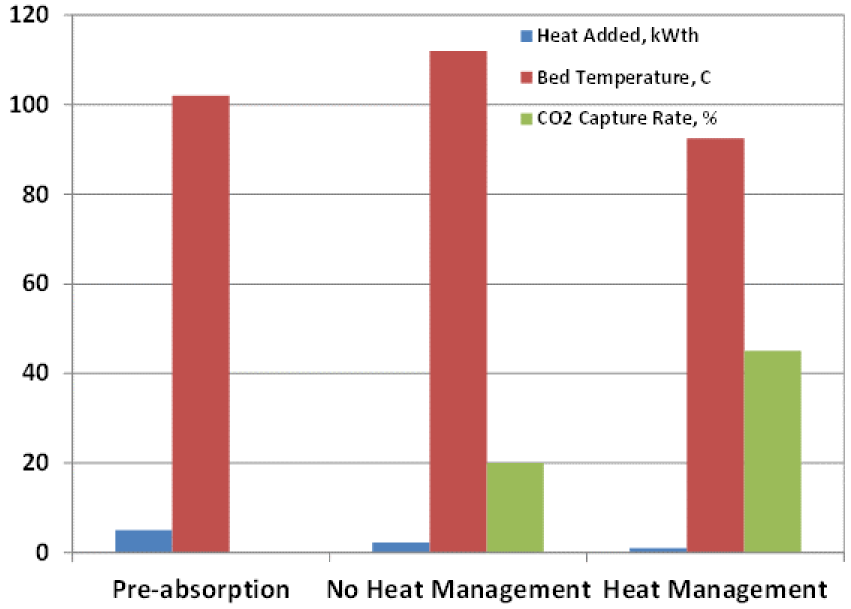


Figure 44. Comparison of steady-state Adsorber bed temperature and CO2 capture rate for No Heat Management and Heat Management case

Subtask 5.3: Design and Engineering of High-fidelity, Bench-scale Prototype

Although the original configuration of the BsCEU allowed the project team to gain significant insights into technology feasibility, operational performance, process design, etc., there was an additional step needed to develop a final proof at bench-scale that the FMBR design concept is the most technically- and commercially-viable design for our technology. The next step would require testing of a high-fidelity, continuously circulating system, which would require simultaneous operation of a high-fidelity Adsorber and Regenerator. In order to take this next step, the project team first had to engineer and design this high-fidelity system (Subtask 5.3), based entirely on how best to modify the current BsCEU configuration. Since the BsCEU was of sufficient size, was already highly instrumented and controlled, used pneumatic conveying to move its sorbent inventory, and was flexible enough to include different contactor designs, the project team proposed to simply build on to the existing bench-scale unit to complete the high-fidelity prototype. Essentially, one contactor from the original BsCEU configuration was to be used as the CO_2 Adsorber in the high-fidelity system and only one new contactor, the Sorbent Regenerator, was needed to complete the high-fidelity prototype unit. This approach was seen as a logical and effective way to mitigate the risk and expense of building a new bench-scale prototype system from scratch – as was proposed in RTI's original proposal to DOE/NETL.

The project team achieved the engineering/design milestone associated with Subtask 5.3. Based on additional engineering and design analyses and the BsCEU CO_2 capture and heat management tests conducted in BP2, the Sorbent Regenerator was designed to closely resemble the staged, fluidized-bed CO_2 Adsorber – the exception being that the heat transfer fluid in the Regenerator heat transfer internals was low pressure steam instead of tempered cooling water. The design of the staged, Sorbent Regenerator is exhibited in **Figure 45**. It was expected that the newly designed Sorbent Regenerator would allow for more efficient heat transfer within the column as compared to the original, single-stage Regenerator. This would in turn allow for more efficient and more complete regeneration of the sorbent and likely lead to better CO_2 capture performance within the CO_2 Adsorber. Additional parametric tests were planned to be conducted on the original configuration of the BsCEU prior to installing the new Sorbent Regenerator. At the completion of BP2, it was expected that the new Sorbent Regenerator would be installed roughly 6 months following the start of BP3.

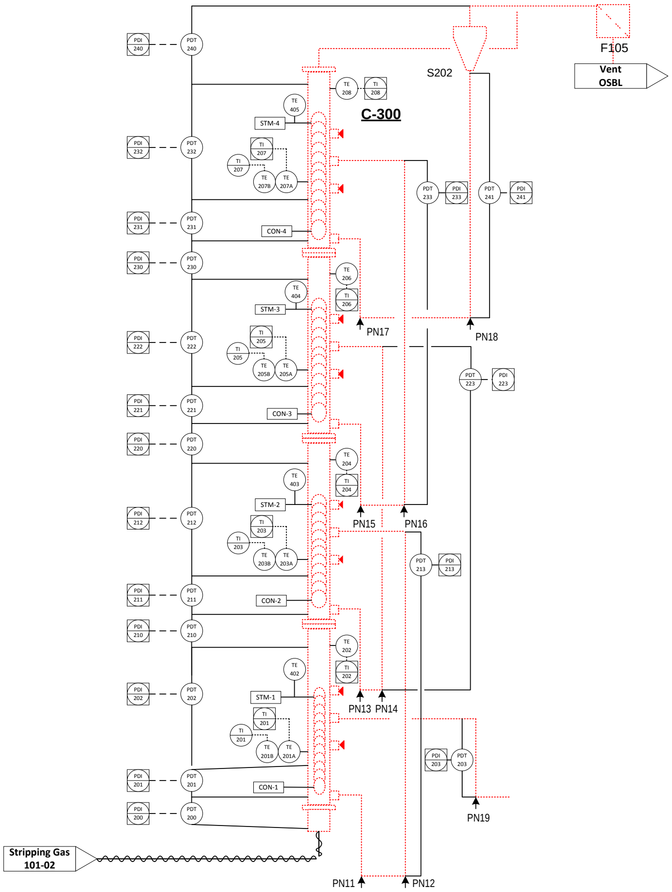


Figure 45. Design of new Sorbent Regenerator for RTI's BsCEU

4.3.3 Performance Testing of High-Fidelity Bench-scale FMBR Prototype (Subtasks 7.1, 7.3, 7.4)

Process development work in BP3 represented the defining work needed to truly evaluate RTI's approach to solid sorbent CO_2 capture – this included extended performance testing in a high-fidelity, fluidized, moving-bed reactor system. The overall objectives of BP3 process development work were:

- Demonstrating, on a bench-scale, effective and continuous CO_2 capture from flue gas using a modified prototype system designed in BP2 (i.e. conduct extensive parametric and long-term performance testing on the original and new configurations of the BsCEU).
- Proving that the CO_2 capture sorbent is chemically, thermally, and physically stable over multiple adsorption/regeneration cycles and shows significant potential to meet the DOE program targets for CO_2 capture.
- Determining the technical and economic competitiveness of the PEI-based CO_2 capture process through bench-scale test data, an updated technical feasibility study, and an environmental analysis of the process technology.

Subtask 7.1: Procurement and Fabrication of Modified Sorbent Regenerator and Integration within Existing BsCEU to Complete the High-Fidelity Bench-scale FMBR Prototype

The objective of Subtask 7.1 was to execute the necessary steps to procure, fabricate, build, and install process modifications and a new Sorbent Regenerator in order to complete the construction of a high-fidelity prototype unit. The Sorbent Regenerator was originally intended to be fabricated based on an engineering/design package developed by the project team in BP2. In order to avoid any delay in testing, and to gain additional design and performance insights, Task 7 was structured such that additional BsCEU testing was performed (in Subtask 7.3) prior to a complete reconfiguration of the system (which would be expected to shut down testing for at least 6 to 8 weeks). Subtask 7.1 started with some relatively minor upgrades to the gas flow control, the tempered cooling water delivery, the particulate filtering mechanism, the heating capability of the current Regenerator, and upgrades to the methods for process measurements. BsCEU testing campaigns were conducted to evaluate the effectiveness of the process modifications and to test the reliability of the bench-scale system prior to installation of a new Regenerator. Subtask 7.1 also included the activities related to a full bench-scale reconfiguration which ultimately involved modifying the system to a 2-stage Adsorber, 2-stage Regenerator design (as described below).

Reconfiguration of the bench-scale contactor evaluation unit (BsCEU)

The configuration of RTI's BsCEU was modified to enable the installation of a staged Regenerator to complete the bench-scale system strategy of having a multi-stage Adsorber and multi-stage Regenerator. A staged Regenerator enabled the project team to achieve a lower CO_2-lean loading within relatively high CO_2 concentrations in the regenerator off-gas (ROG). The original strategy of the project team was to mimic the 4-stage Adsorber design and replicate it for the new Regenerator. A 4-stage design was theorized to be an ideal arrangement to promote the most efficient sorbent regeneration, particularly at high CO_2 partial pressures in the ROG. The project team moved away from this initial strategy and instead reconfigured the BsCEU into multi-stage reactors by repurposing the 4-stage Adsorber and splitting it into a 2-stage Adsorber and 2-stage Regenerator. This change in approach was carefully weighed and finally decided upon due to the following factors: 1) evaluation of results obtained in parametric testing, 2) new theoretical calculations on Regenerator staging performance (**Figure 46**), and 3) time and budget considerations. In addition to the complete reconfiguration of RTI's BsCEU, various other modifications and improvements were made to the BsCEU as summarized below.

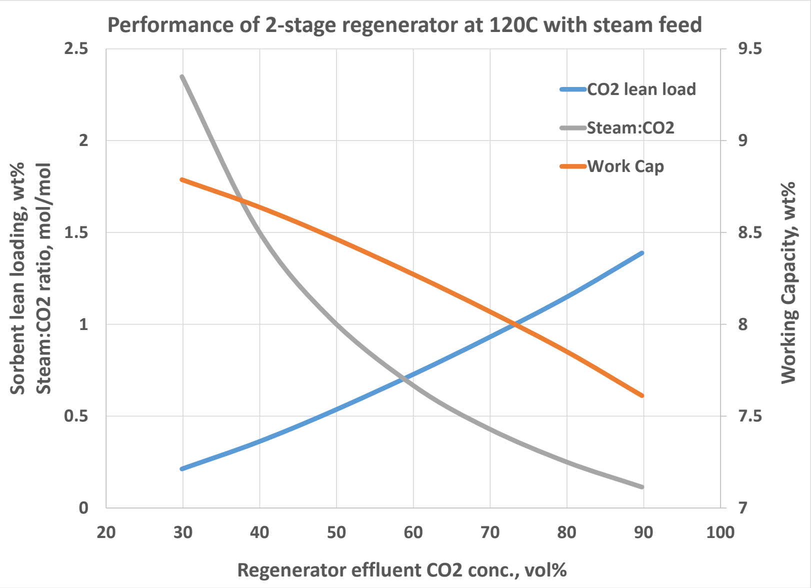


Figure 46. Theoretical CO_2 capture performance of a BsCEU system utilizing a 2-stage Regenerator

Additional steam line for top stage regenerator: Since the Regenerator was reconfigured from a single-stage to a two-stage column, it was necessary to install an additional steam supply line for the second stage with the associated instrumentation (i.e. pressure regulator, pressure gauge, pressure transmitter, etc.). The additional line provided the ability to individually control the steam supply pressure to each stage in order to control the bed temperature in each regenerator stage separately. During testing of the two-stage Regenerator, it was found that the bottom stage of the regenerator required approximately 10 psi less steam than the top stage. The lower quality steam demand in the bottom stage was a function of decreased sensible heat demand (i.e. material transferring from top stage already at temperature) and less CO_2 removal (i.e. majority of CO_2 desorbed in the top stage) and higher heat transfer area per unit volume.

New heat transfer internals for Regenerator stages: During previous testing, it was determined that there was poor heat transfer inside the previous single-stage, 12” Regenerator column. The poor heat transfer was likely due to the configuration of the heat transfer internals which were not appropriately designed for condensing steam. As a result, the single-coil heat transfer internals of the bottom two Adsorber stages were replaced with dual, helical-coils prior to being installed as the new two-stage Regenerator. The coils were arranged such that the steam supply to the heat transfer internals entered the top of each Regenerator stage and condensate was continuously pushed out the bottom of each stage. The heat transfer coils were sized to increase the heat transfer area per unit bed volume in each Regenerator. As a result of the new heat transfer coils and reconfigured Regenerator column, the indirect contact steam supply pressure required to achieve the target temperature in the Regenerator stages was reduced by approximately 15-25 psi.

Water vaporizer for stripping gas humidification: Although the stripping gas is predominantly N_2 in the BsCEU, presence of some steam is essential to prevent and/or reverse the formation of urea in the rich sorbent at desorption temperatures. In the original design, steam was directly injected to humidify stripping gas nitrogen. The amount of steam addition was controlled by varying the pressure drop across a fixed diameter orifice. This proved to be difficult and highly unreliable since the required pressure drop was on the order of approximately 1-2 psi. In the reconfigured design, since the diameter of the regenerator decreased from 12” to 6”, the stripping gas flow (and hence the required steam flow) was reduced to <50% making it further challenging to control the rate of steam addition. As a result, a water vaporizer was designed, as shown in **Figure 47**, and installed to better control the addition of steam to the stripping nitrogen.

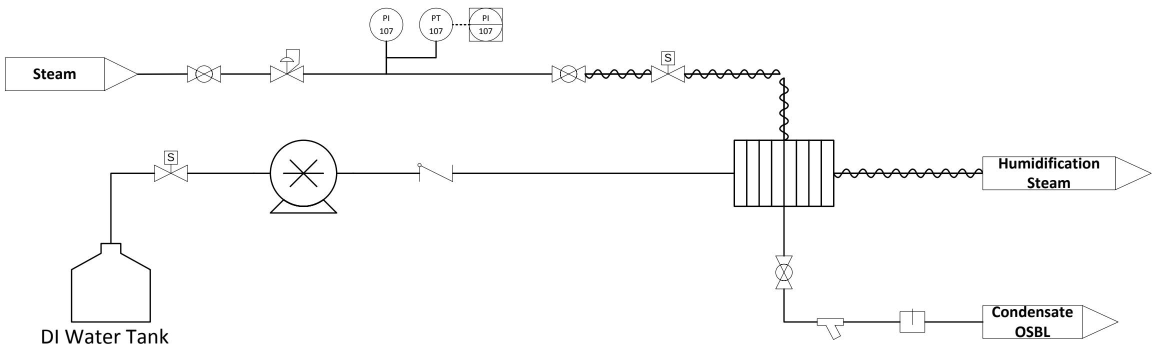


Figure 47. P&ID of a water vaporizer system installed to deliver steam to the Regenerator stripping gas for humidification

Deionized (DI) water was supplied to a brazed-plate heat exchanger by a pump at a set flow rate to achieve the desired steam addition to the SG (generally 5 to 10 vol%). On the other side of the heat exchanger, steam was supplied from the previous steam addition line to vaporize the incoming DI water. The addition of the water vaporizer, in combination with N_2 supplied from a MFC, has resulted in a very fine control of steam addition to the SG.

Regenerator condensate measurement system: In the single-stage Regenerator configuration, there was only one condensate stream that needed to be measured for thermal demand calculations. However, the new two-stage configuration has two condensate streams and required the ability to sample each stream separately and/or combined. As a result, a condensate rate measuring system was designed and installed. The condensate measuring system included a brazed-plate heat exchanger and a 3-way solenoid valve per Regenerator condensate line, as well as, a condensate collection vessel and weigh scale. Cooling water was used to remove heat from each condensate stream in the heat exchangers prior to passing through the 3-way valves, which diverted the condensate to the outide battery limits (OSBL) drain or to the condensate collection vessel. The new setup enabled system operators to select which streams were to be measured. The auto-drain, level, self-regulating collection vessel placed on the weigh scale allowed for continuous measurement of condensate collection rate.

Sorbent addition vessel: It was known that the BsCEU inherently loses solids over time due to attrition and other losses (e.g. cyclone inefficiencies). The losses were nominal and did not present a problem for short-term test campaigns (e.g. 8 to 10 hours) since those tests allowed reloading of the sorbent at the beginning of each test. However, even a slow and steady loss of solids can be damaging to the sorbent inventory during a long-term continuous testing, demanding the ability to add sorbent while running the system. As a result, a sorbent addition vessel was designed, fabricated, and installed on the BsCEU. The vessel had a capacity of approximately 4 liters and could be purged and pressurized with N_2 to load sorbent into the top Regenerator stage.

Subtask 7.3: Parametric Testing of BsCEU and Commissioning of Modified Sorbent Regenerator

Following system reconfiguration and installation of a staged Sorbent Regenerator, shakedown and commissioning of the new regenerator was started. The overall goal of shakedown testing was to confirm the accurate and sustained operation of the Regenerator, confirm that it works together with the existing BsCEU process components, and resolve any mechanical issues that arose. Subtask 7.3 was focused on parametric testing of the BsCEU which would allow the project team to collect critical sorbent performance and process design data and information. These testing efforts focused specifically on the performance of the CO_2 Adsorber and Regenerator. The team evaluated operating variables that impact CO_2 capture and optimized them for the existing BsCEU.

Operational control in the BsCEU (original configuration)

The following sections describe how, through parametric testing, the project team was able to gain significant understanding of how to optimally operate the BsCEU while also being able to gain more consistent control around the variables that impact system performance. Note that these sections refer to parametric testing performed in the original configuration of the BsCEU.

Solids circulation rate control: Within the BsCEU, the solids/sorbent circulation rate was not measured directly (e.g. measuring the mass flow over a period of time). Instead, the solids circulation rate was calculated (and calibrated) using the riser section pressure drop. To do so, a gas extraction probe was used to collect solid sample measurements recorded for a range of riser pressure drops at a constant lift gas velocity. When the BsCEU was operated with a 30 ft./s lift gas velocity in the riser, with no sorbent circulation, the average pressure drop was measured at 0.9 in.H_2O. As solids circulation was increased, and thus the riser pressure drop, the gas extraction probe was used to develop a calibration plot as seen in **Figure 48**. Riser pressure drop (and hence the sorbent circulation rate) could be tightly controlled, usually within ±0.03 in.H_2O (~0.001 psi), which was extremely important to be able to maintain a steady CO_2 capture rate.

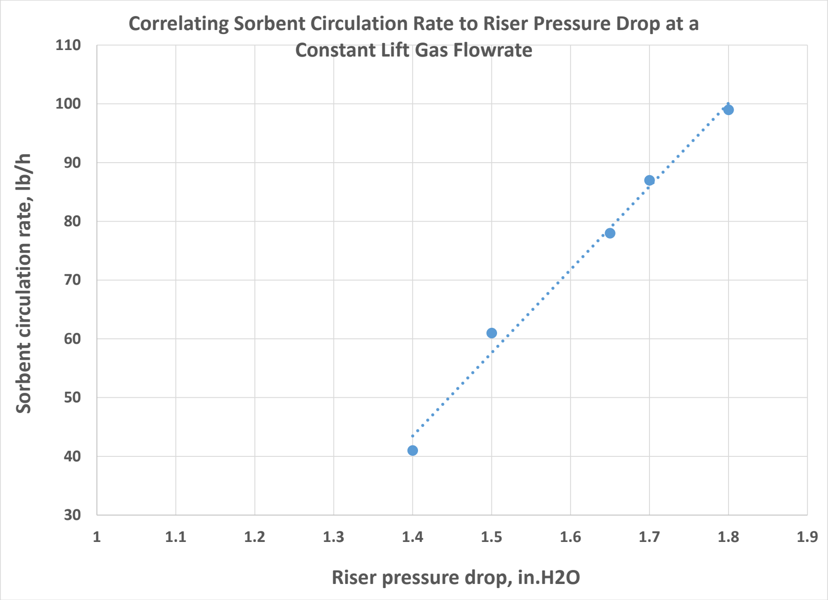


Figure 48. Correlation of BsCEU riser pressure drop to solids/sorbent circulation rate

Sorbent inventory control: Each distinct parametric experiment started with lean (i.e. low CO_2 loaded) sorbent in the Adsorber. As CO_2 was added to the simulated flue gas stream and came into contact with the lean sorbent in the Adsorber, the fixed height pressure drop in stage 1 (bottom stage) increased, followed by stage 2. The stage 3 and stage 4 (top stage) fixed height pressure drop increased gradually as the sorbent in stages 1 and 2 became saturated and CO_2 capture in the BsCEU was confined to stages 3 and 4. In addition, the fixed height pressure drop in the Regenerator was measured. The BsCEU was able to achieve steady sorbent bed pressure drop in all 4 Adsorber stages and the Regenerator (as exhibited in **Figure 49**), indicating that solids flow in and out of the stages/Regenerator was steady, there were no significant losses of sorbent due to attrition/entrainment, and the BsCEU was able to operate with predictable control over the sorbent inventory in each reactor.

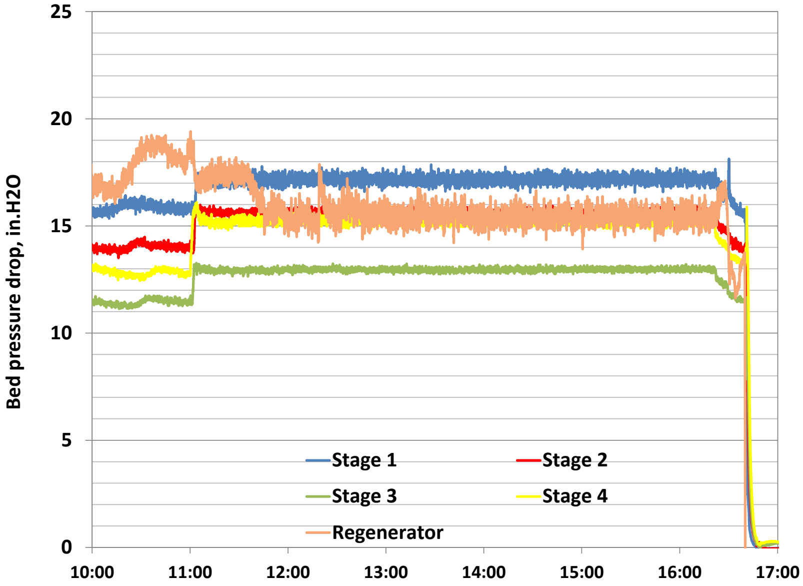


Figure 49. Sorbent bed pressure drop for the single-stage Regenerator and 4 Adsorber stages

System cooling and heating control: The temperatures within the Adsorber stages was controlled using tempered cooling water flow through heat transfer internals embedded in each stage. When the BsCEU was capturing CO_2, and thus generating heat in the Adsorber through the exothermic reaction, the cooling water inlet temperature for each stage was lowered to control sorbent bed temperatures at desired set points. Cooling water flow rate was also increased to remove additional heat in the Adsorber stages. On occasion, when capturing a higher rate of CO_2 (>4 kg/h), cooling water flow rate was increased to as high as 30 gph. **Figure 50** exhibits the tight control by which the project team controlled the temperatures in each Adsorber stage during parametric testing.

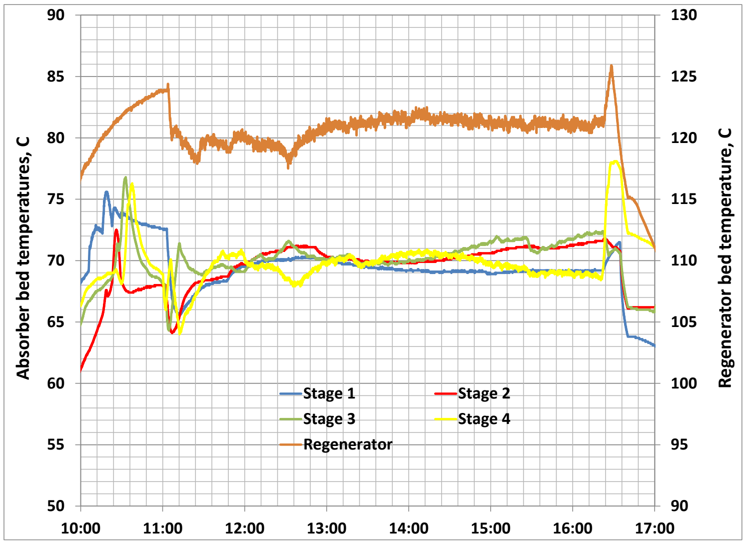


Figure 50. BsCEU temperature control in each of the 4 Adsorber stages and Regenerator

The temperature rise for the cooling water in the individual Adsorber stages was a good indication of which stages were taking part in CO_2 removal. This ΔT, coupled with the water flow rate, was used to calculate the cooling load on each Adsorber stage. The cooling load trends exhibited in **Figure 51** show how the top stage (stage 4) captured the most CO_2 while almost no CO_2 was captured in the bottom two stages. In this scenario, the cooling water was actually adding heat to the bottom two stages to make-up for heat loss. **Figure 52** shows how the experimentally-measured cooling duty was in close alignment with what was expected based on the calculated cooling duty.

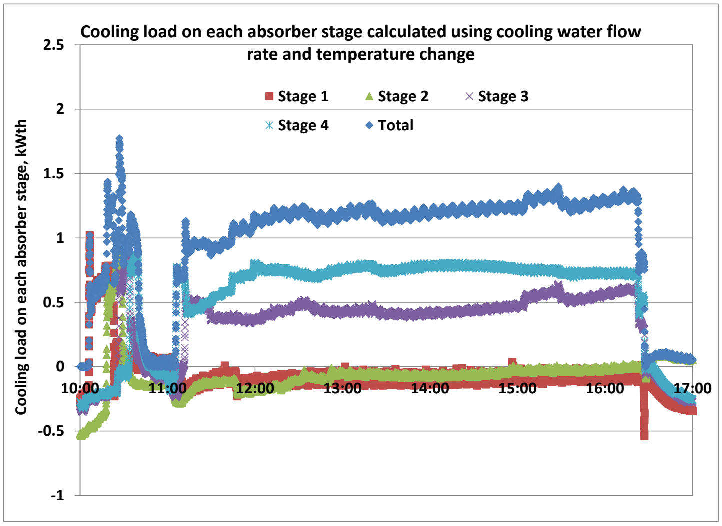


Figure 51. Measured cooling load on each BsCEU Adsorber stage during parametric testing

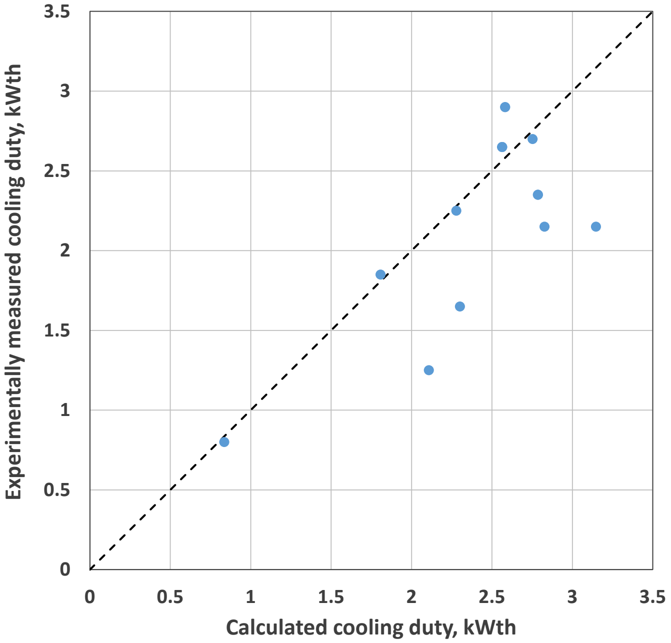


Figure 52. Experimentally measured vs. calculated total cooling duty in the BsCEU Adsorber

Within the BsCEU Regenerator, heat was required to drive the CO_2 desorption reaction – in order to match the required sorbent sensible heat and the sorbent's heat of CO_2 desorption. The Regenerator heat requirement was met by condensing steam inside the heat transfer internals within the Regenerator. Since the heat transfer capacity (UA) of the internals is fixed, a variance in Regenerator energy demand was met by regulating the steam supply pressure. As steam condensed and flows out of the Regenerator internals, it was collected in a self-draining container. The container weight was continuously recorded to calculate the instantaneous and time-averaged steam consumption rate within the Regenerator.

During start-up of the BsCEU, any residual CO_2 that may be on the sorbent in the Regenerator was desorbed by adding thermal energy to the Regenerator. This addition of heat also effectively balanced the Regenerator's heat loss to the environment. Once the Regenerator bed temperature reached a set point and the complete desorption of CO_2 was confirmed (as indicated by the absence of CO_2 in the Regenerator off gas), the additional and continuous steam condensate collection was driven by the amount of heat being lost to the environment. When the accumulated steam condensate weight was plotted over time (**Figure 53**), a distinct change in the slope of the line is observed when CO_2 capture was initiated. The change in slope is representative of the additional Regenerator heat duty that was required for CO_2 desorption and the sorbent's sensible heat. In addition to this experimentally-measured heat duty, the heat duty was also calculated using the following measurements and assumptions: 1) amount of CO_2 desorbed, 2) sorbent circulation rate, 3) Adsorber temperature, 4) Regenerator temperature, 5) heat of desorption value of 78,000 kJ/kmol, and 6) sorbent heat capacity of 1 kJ/kg˚C. The measured and calculated Regenerator heat duty were compared (**Figure 54**) and show close agreement within ±10 to 15%.

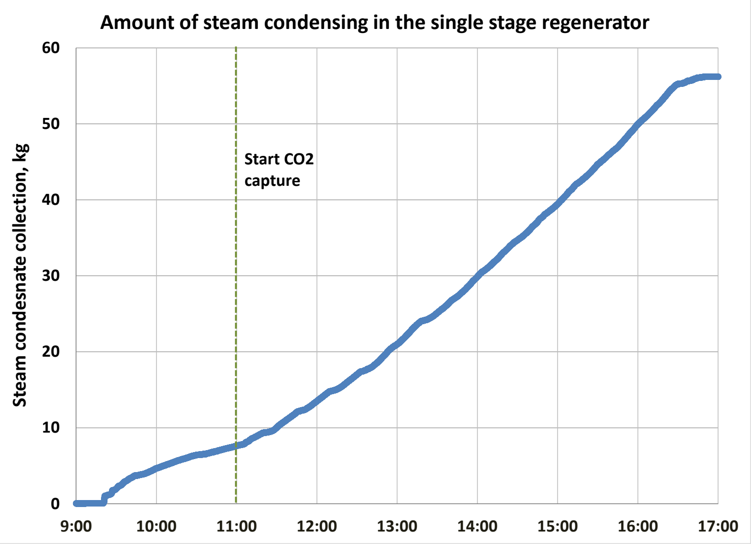


Figure 53. Condensed steam collected in the BsCEU during start-up and CO_2 capture tests

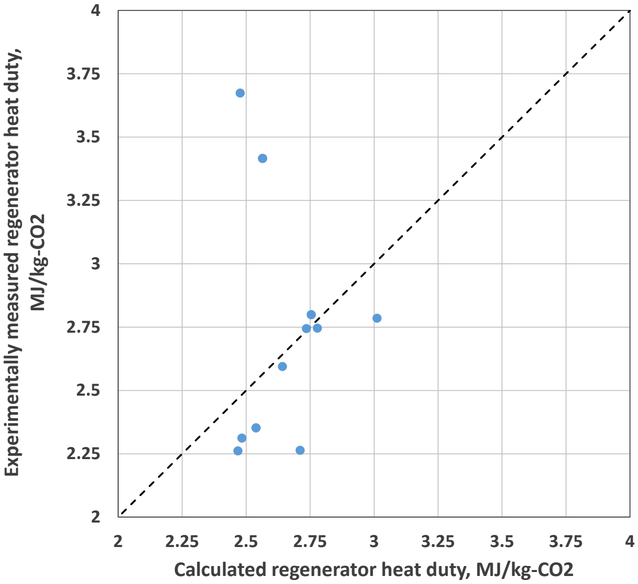


Figure 54. Experimentally measured vs. calculated total heat duty in the BsCEU Regenerator during parametric tests

CO_2 mass balance in the BsCEU: During BsCEU tests, the CO_2 balance was continuously evaluated to provide confidence that process measurements were correct. As exhibited in **Figure 55**, the project team was able to show near agreement and balance between the CO_2 entering the system (in the simulated flue gas) and the CO_2 leaving the system (from the Regenerator during CO_2 desorption). In-line, Detcon CO_2 analyzers were used to measure CO_2 concentration of the feed flue gas, effluent flue gas, and Regenerator off-gas. Additionally, a UV analyzer was used to measure CO_2 and H_2O concentrations in the gas streams mentioned above as well as the stripping gas. Each of the analyzers was routinely calibrated to enable closure of the CO_2 mass balance throughout BsCEU parametric tests.

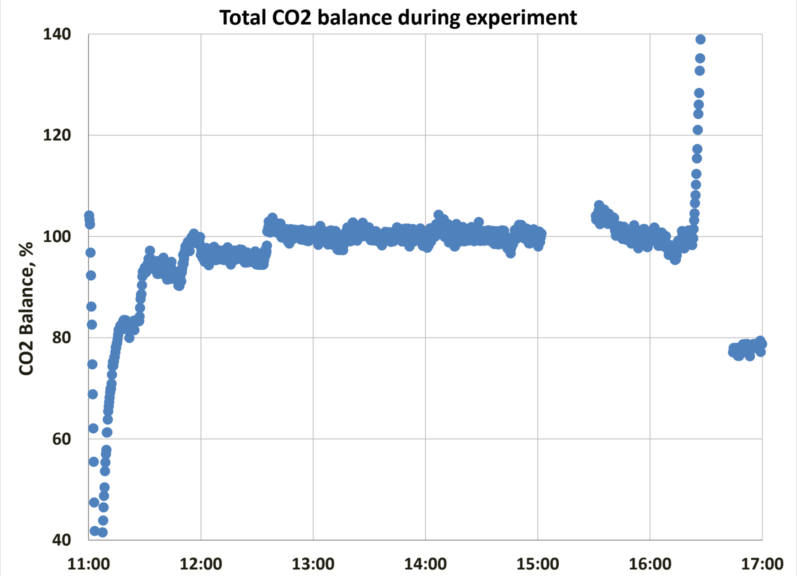


Figure 55. CO_2 mass balance measured during BsCEU parametric tests

<u>CO_2 capture tests with BsCEU (original configuration)</u>

Following many of the system improvements and process control experiments, the project team conducted CO_2 capture experiments to test the range of operation and performance of the BsCEU. CO_2 capture experiments using simulated flue gas were performed to demonstrate that the bench-scale unit was capable of continuous, stable CO_2 removal and sorbent regeneration over an extended test period, as shown in **Figure 56**. BsCEU parametric CO_2 capture testing in the original system configuration resulted in several observations including: the capture of 90% of the CO_2 in the simulated flue gas stream was achievable under a multitude of process conditions. The sorbent was capable of rapid removal of CO_2 from the flue gas as evidenced by the capture of CO_2 in only three of the four Adsorber stages. Also, as soon as simulated flue gas was fed in the Adsorber, a large exotherm was observed in the first stage and required ~1.5 kW_t heat to be removed from a single stage, as shown in **Figure 57**. As the experiment progressed the exotherm migrated up through the Adsorber stages, showing the propagation of CO_2 removal throughout the various Adsorber stages.

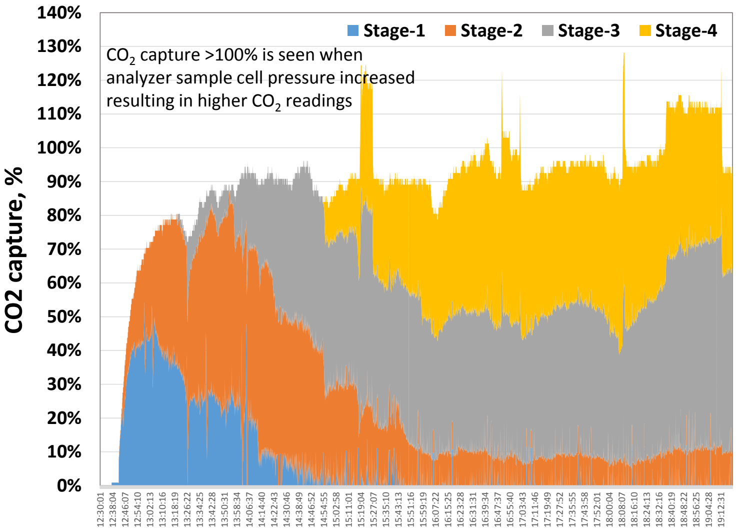


Figure 56. Test data exhibiting BsCEU capability to achieve 90% CO$_2$ capture and CO$_2$ capture propagation across stages

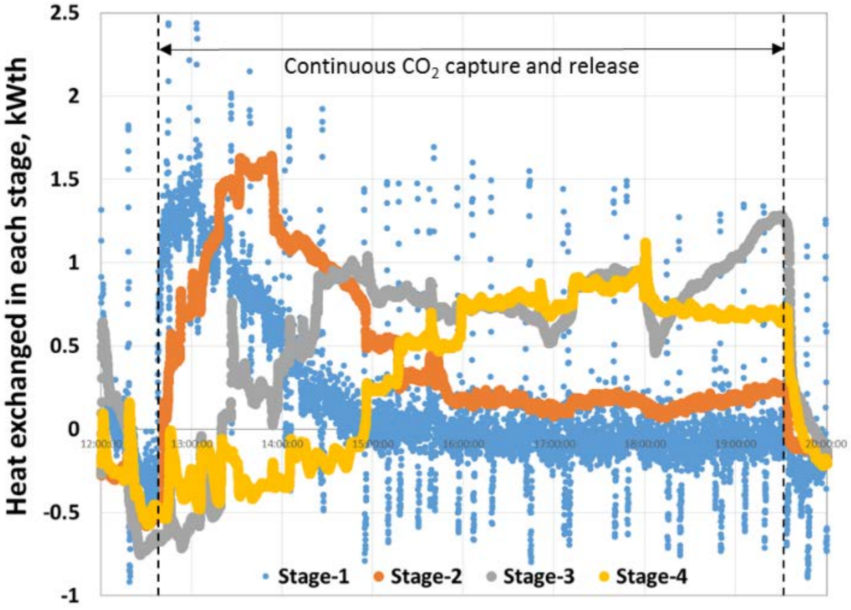


Figure 57. BsCEU test data exhibiting need to removing heat of adsorption in the CO$_2$ Adsorber

Short-term parametric testing with the BsCEU (original configuration)

Having the BsCEU allowed the project team to focus on short-term parameter testing. These short-term tests were critical in collecting sorbent performance and process design data and information. The following report sections are grouped by the various "parameters of interest" explored in each of these tests.

Solids to gas ratio: In evaluating the solids to gas ratio (S/G) within the BsCEU, it was assumed that the CO$_2$ capture performance would improve with higher sorbent circulation rates. In these parametric tests, sorbent circulation was changed while keeping all other operating conditions constant. **Figure 58** exhibits how the sorbent circulation rate was adjusted over time (from 20 to 75 kg/h stepwise) resulting in the CO$_2$ capture rate improving from 35% capture to 95% capture for a circulation rate of 75 kg/h. This experiment shows how S/G ratio can be adjusted to achieve target CO$_2$ capture rates and how this may relate back to commercial system size and energy penalty associated with solids handling equipment. Additional work in the BP (in the reconfigured BsCEU) focused on optimizing the system performance based on S/G ratio and determining if higher circulation rates impact sorbent attrition.

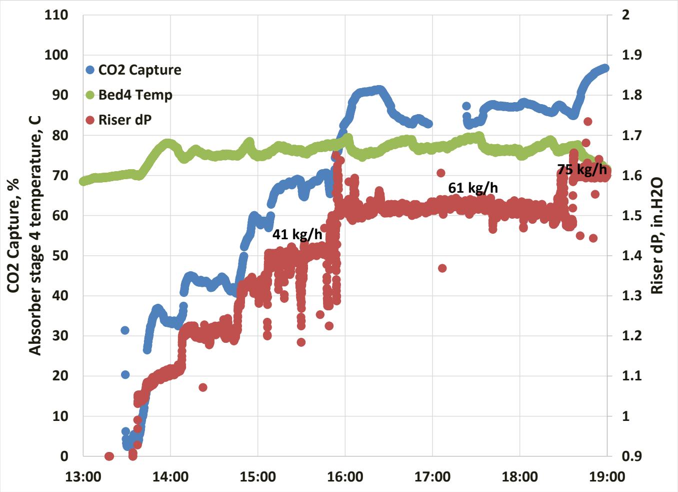


Figure 58. BsCEU parametric tests showing the impact of S/G ratio on CO_2 capture performance

Flue gas velocity: In order to minimize the Adsorber reactor footprint, flue gas superficial velocity needed to be maximized. However, as the flue gas velocity increased, the sorbent bed height needed to be increased to maintain reasonable gas residence time and approach to equilibrium. The effect of superficial gas velocity on the performance of the 4-stage Adsorber was studied at an adsorption temperature of 70 °C and CO_2 concentration of 15 vol% in the simulated flue gas. The regeneration temperature was maintained at 120 °C with the effluent CO_2 partial pressure below 2 psia; representing an equilibrium lean loading of 0.8 wt.%. Four flue gas velocities were studied. The impact on Adsorber performance was measured relative to the sorbent circulation rate which was adjusted for each flue gas velocity set point in order to maintain ~90% CO_2 capture. Results are summarized in **Table 25**.

Table 25. BsCEU parametric tests showing the impact of superficial gas velocity on Adsorber CO_2 capture performance

Flue gas velocity, ft./s	**Sorbent working capacity, wt.%**	**Distribution of CO_2 capture, wt.%**				**Regenerator heat duty, MJ/kg-CO_2**
		Stage 4 (Top)	Stage 3	Stage 2	Stage 1 (Bottom)	
0.63	6.8	57	36	0	0	2.50
0.74	7.1	52	39	0	0	2.50
0.88	6.3	46	51	<5	0	2.55
1.03	5.3	30	42	21	0	2.70

Ideally the sorbent CO_2 working capacity should be unaffected if: 1) the 4-stage Adsorber is not kinetically limited, and 2) the sorbent lean loading is the same. However, during these parametric tests, a drop in sorbent working capacity (from 7 wt.% to 5 wt.%) was observed with the increase in flue gas velocity to 1.03 ft./s. In evaluating the distribution of CO_2 between the four Adsorber stages, it was observed that during testing at 0.63 ft./s flue gas velocity, the bulk of the CO_2 (~57%) was captured in the very top Adsorber stage with the remaining CO_2 captured in the second (from the top) stage and no CO_2 capture was observed in the bottom two stages. The sorbent working capacity was ~7 wt.%. Similar CO_2 capture distribution and sorbent working capacity were observed at 0.73 ft./s. As the flue gas velocity was increased to 0.88 ft./s, a difference in capture distribution and working capacity was observed. In this test, an even CO_2 capture split was seen in the top two stages, however, there was a small amount (<5%) of CO_2 captured in the third-from-top stage, now acting as a polishing step for the stages above. The sorbent working capacity dropped slightly to 6.3 wt.%. As the parametric tests were stepped up to a flue gas velocity of 1.03 ft./s, additional changes were observed for CO_2 capture distribution and sorbent working capacity. While testing under this new parameter, the second-from-top stage captured the most CO_2 (~42%) while the top stage captured only 30% of the CO_2 present in the simulated flue gas. The remaining CO_2, a relatively high 21%, was captured in the third-from-top stage and the sorbent exhibited a relatively low working capacity of ~5.3 wt.%.

Since the bottom-most Adsorber stage did not participate in the CO_2 adsorption at any flue gas velocity setting, it was evident that the existing Adsorber is capable of processing an even larger flue gas flow rate and higher amounts of CO_2. However, a drop in sorbent working capacity was observed and since the Adsorber was not the limiting factor, it indicated that the lean loading of the sorbent leaving the Regenerator was increasing over time. Preliminary calculations indicated that the increase in lean loading was the result of insufficient heat transfer due to ineffective heat transfer internals (i.e. measured UA) and a lack of staging within the Regenerator.

Adsorber temperature: The optimal adsorption temperature requires a trade-off between having higher CO_2 loading capacity at lower temperature versus a lower sensible heat requirement at a higher adsorption temperature. This dynamic was studied at three different adsorption temperatures. During these parametric tests, other parameters were kept fixed, such as the flue gas superficial velocity maintained at ~0.88 ft./s, flue gas CO_2 concentration at 15 vol%, and the CO_2 capture rate at 90% (achievable through adjustment of the sorbent circulation rate). Results from these parametric tests are summarized in **Table 26**.

Table 26. BsCEU parametric tests showing the impact of Adsorber temperature on CO_2 capture performance

Adsorber temperature, °C	Sorbent working capacity, wt.%	Regenerator heat duty, MJ/kg-CO_2
60	6.3	2.75
70	6.1	2.55
80	5.8	2.45

Isotherm data collected for the sorbent in RTI's lab-scale PBRs had exhibited a 1 wt.% CO_2 loading drop when the adsorption temperature was increased from 60 to 70 °C. By contrast, during the parametric tests mentioned above, the sorbent working capacity only decreased by 0.4 wt.% over a larger difference in adsorption temperature (i.e. 60 to 80 °C). This minimal drop in the CO_2 working capacity of the sorbent is surprising and needs to be studied further. **Table 26** also shows that with the same increase in adsorption temperature, the Regenerator heat duty decreases from 2.75 MJ/kg-CO_2 to 2.45 MJ/kg-CO_2 suggesting that it is preferred to operate the Adsorber at higher temperatures (~80 °C).

Effect of lean loading: The working capacity of the sorbent can be maximized by increasing the rich loading and/or lowering the lean loading. Two strategies for lowering the sorbent's lean loading involve lowering the Regenerator CO_2 partial pressure and increasing the regeneration temperature. However, both of these approaches will lead to higher Regenerator heat duty. This dynamic was studied by performing parametric tests at different sorbent lean loadings which were achieved by changing the Regenerator temperature between 110 °C and 120 °C. According to laboratory isotherm data, the equilibrium lean loading nearly triples from 0.8 wt.% to 2.6wt% when the regeneration temperature drops from 120 °C to 110 °C (at Regenerator effluent CO_2 partial pressure of ~2 psia). The effect of lean loading was studied at adsorption temperatures of 60 °C and 70 °C while maintaining the flue gas superficial velocity at 0.88 ft./s. At both adsorption temperatures (60 and 70 °C) the working capacity dropped by 2 wt.% (from ~6 wt.% to ~4 wt.%). However, since the temperature difference between the Adsorber and the Regenerator was 10 °C lower, the Regenerator heat duty only increased by 0.2 MJ/kg-CO_2 at the lower regeneration temperature.

Sorbent stability: During parametric tests, the chemical stability of the sorbent was checked routinely by measuring the CO_2 capacity of sorbent samples using a standard PBR testing method. These sorbent samples were taken after extensive parametric testing and evaluated in RTI's PBRs at a CO_2 adsorption temperature of 65˚C and a flue gas composition of ~15% CO_2, 5.3% H_2O, 4.5% O_2, and a balance of N_2. **Figure 59** shows how the sorbent maintained desired CO_2 capture performance stability even after 5 months of parametric testing. The "fresh" sample represents a sorbent sample taken from the original batch of sorbent manufactured by RTI's commercial manufacturing partner. The "Jul-15" and "Oct-15" samples were sorbent samples taken during parametric testing in July 2015 and October 2015 respectively. In addition to this CO_2 capture performance stability, the solid sorbent showed no signs of significant attrition during parametric tests as evidenced by maintaining a similar particle size distribution, observing a low fines collection rate in the BsCEU, and the fact that no sorbent make-up had been required even after 5 months of testing.

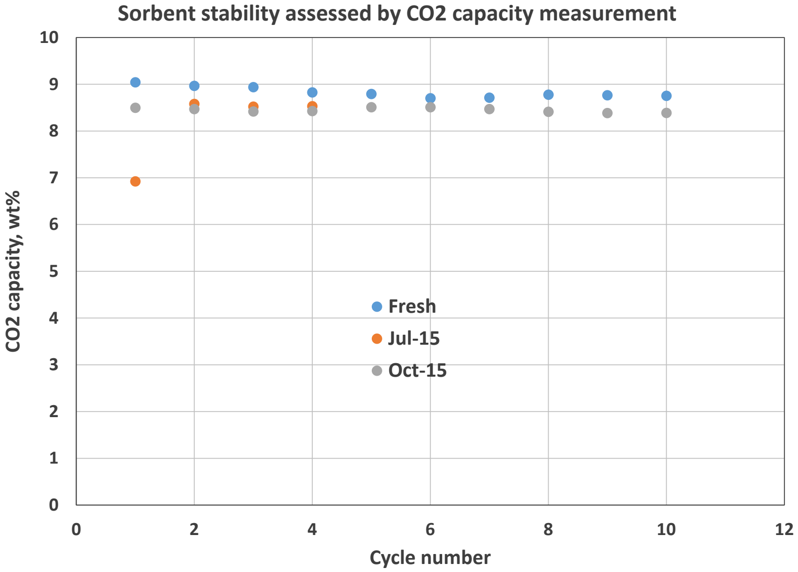


Figure 59. Sorbent stability, as measured by CO_2 loading capacity, observed over time during parametric testing

Reconfigured BsCEU parametric testing procedure

As discussed in the Subtask 7.1 report section, the BsCEU was reconfigured to be able to operate the system with a staged Regenerator which was theorized to allow for optimal operation and performance of a solid sorbent CO_2 capture system. The following is a description of how the reconfigured BsCEU was operated during parametric testing in BP3: The BsCEU start-up began by flowing N_2 through the Adsorber, Regenerator, riser, and system loopseals to aerate the solid sorbent contained within the system. Simultaneously, the dry gas electric heaters and line heaters were turned on to start heating the simulated flue gas and stripping gases. Once the sorbent beds in the 2-stage Adsorber and 2-stage Regenerator had levelled, circulation of the solids was started by opening the slide valve and setting the aeration in the bottom Regenerator standpipe to a desired flowrate. The circulating sorbent first filled the top Adsorber stage to the overflow connection point upon which the sorbent then flowed to the bottom Adsorber stage and back to the Regenerator top stage. Sorbent circulation was stopped once the bed levels in all four fluidized beds had stabilized. This was done to allow for more-controlled heating of the Adsorber/Regenerator beds during start-up (prior to restarting the sorbent circulation). In parallel, the 2-stage Adsorber and 2-stage Regenerator sorbent beds were heated. The Adsorber bed was heated through indirect contact with cooling water. In this case, electric water heaters were used to attain higher cooling water temperatures and thus the desired bed temperatures in both Adsorber stages. The two Regenerator beds were heated through indirect contact with steam by opening the steam isolation valve and attaining the required steam pressure independently through separate pressure control valves.

As the Adsorber stages approached a desired set point, the flow of CO_2 was increased in small steps in order to not let the heat of adsorption raise the temperature of the sorbent beds beyond the desired set point. This was continued until the desired CO_2 flow and Adsorber bed temperatures were reached. The temperature of the tempered cooling water was modulated continuously to assist in regulating Adsorber bed temperature. Once the stripping gas line temperature and Regenerator bed temperatures were higher than the dew point temperature, stripping gas humidification was initiated by setting the water pump to a desired flow rate and supplying steam to the water vaporizer plate heat exchanger and into the Regenerator.

After ~30 minutes at steady-state operation, the sorbent circulation was reinitiated to start capturing CO_2. During CO_2 capture tests, the cooling water and electric water heater, and steam pressure to both Regenerator stages were adjusted continuously to maintain the desired adsorption and regeneration temperatures respectively.

Commissioning of the reconfigured BsCEU

The reconfigured BsCEU was commissioned to confirm sustained operation of the new Regenerator configuration, to confirm that it worked together with the "old" BsCEU process components, and to resolve any mechanical issues that may arise.

Data from a representative CO_2 capture experiment (**Figure 60**) shows the efficiency that was achieved in the operation of the reconfigured BsCEU. The hydrodynamic performance of the sorbent in the staged Adsorber-Regenerator design was evaluated using the pressure drop measured across the sorbent in each reactor. As N_2 flow was initiated through the Adsorber and Regenerator at start-up, the sorbent had accumulated in the bottom stages as sorbent had leaked through the gas distributor plates into the bottom stages. As sorbent circulation was restarted in order to start the CO_2 capture experiment, sorbent was transferred from the bottom Regenerator stage into the rest of the BsCEU stages and eventually leveled-off in the stages as CO_2 capture was continued until shutdown. These intervals of on and off sorbent circulation were well-defined by the pressure drop across the riser as exhibited in **Figure 61**.

The ability to heat the sorbent beds during start-up and control bed temperatures during continuous CO_2 capture is shown in **Figure 62**. The plot indicates that the reconfigured system allowed for good temperature control in the entire BsCEU system, especially the two Regenerator stages. The new set of heat transfer internals that were installed in the reconfigured Regenerator were designed with an improved efficiency (UA) and allowed for the Regenerator to achieve the same bed temperatures at lower steam supply pressure (as compared to the original BsCEU configuration). Cooling load measurements in top and bottom Adsorber stages are exhibited in **Figure 63** as calculated by cooling water flow rate and temperature change.

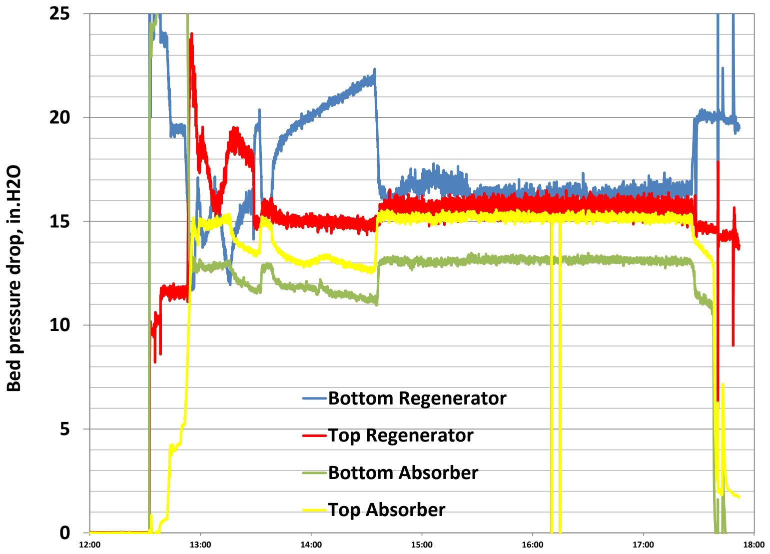


Figure 60. Adsorber and Regenerator bed pressure drop observed during CO_2 capture tests in the reconfigured BsCEU

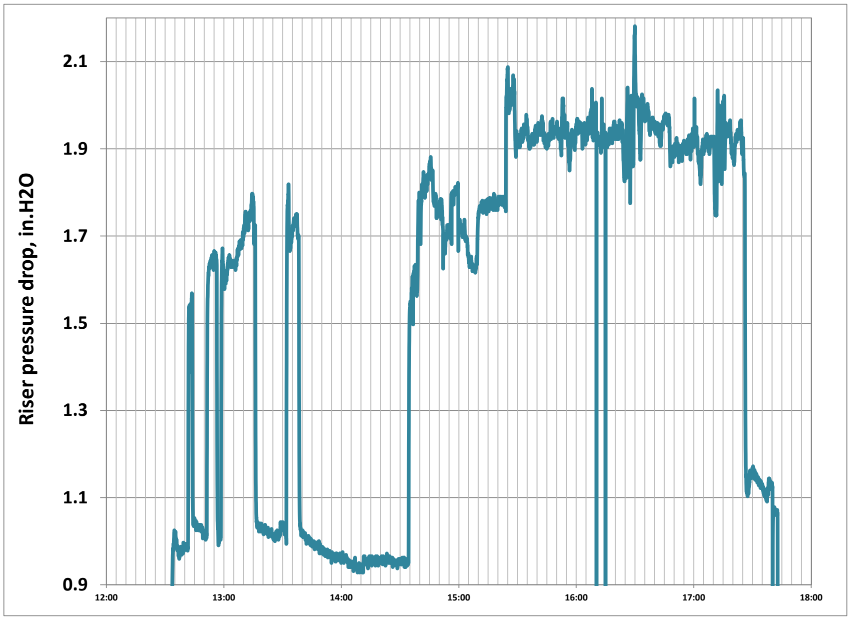


Figure 61. Riser pressure drop in the reconfigured BsCEU – quantifying the rate of sorbent circulation (e.g. a baseline reading of 0.95” w.c. indicates no sorbent circulation)

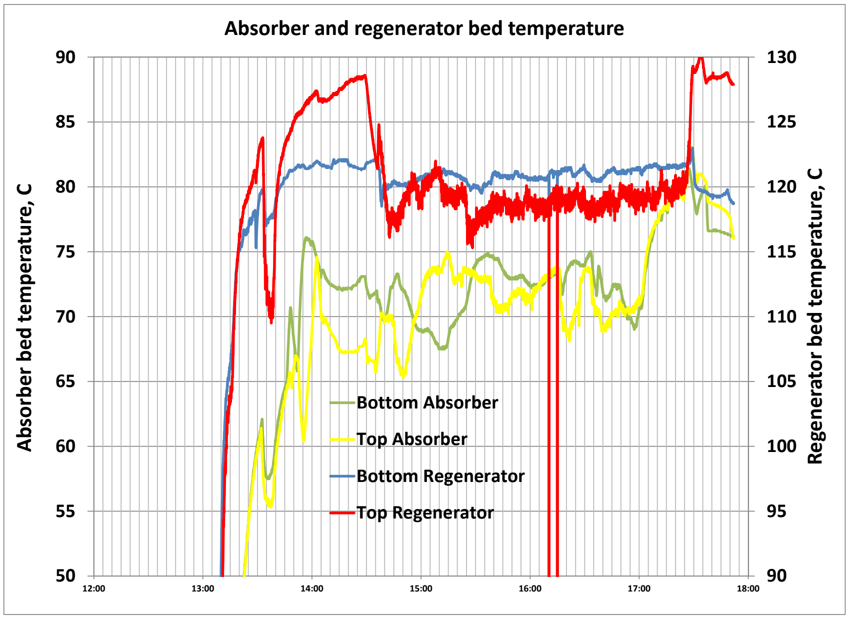


Figure 62. Sorbent bed temperature in the Adsorber and Regenerator top and bottom stages (in the reconfigured BsCEU)

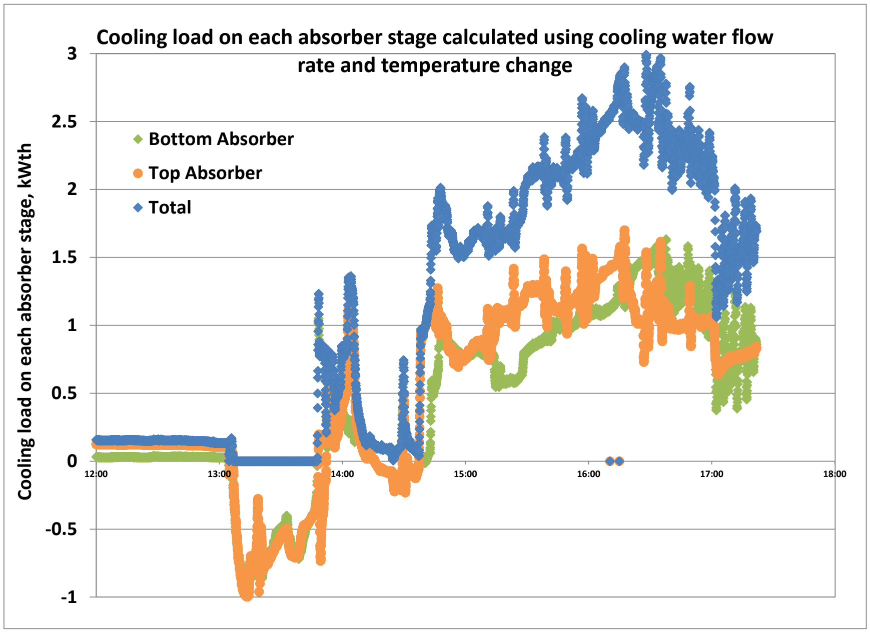


Figure 63. Cooling load in top and bottom Adsorber stages (reconfigured BsCEU) – e.g. negative numbers represent sorbent bed heating during start-up

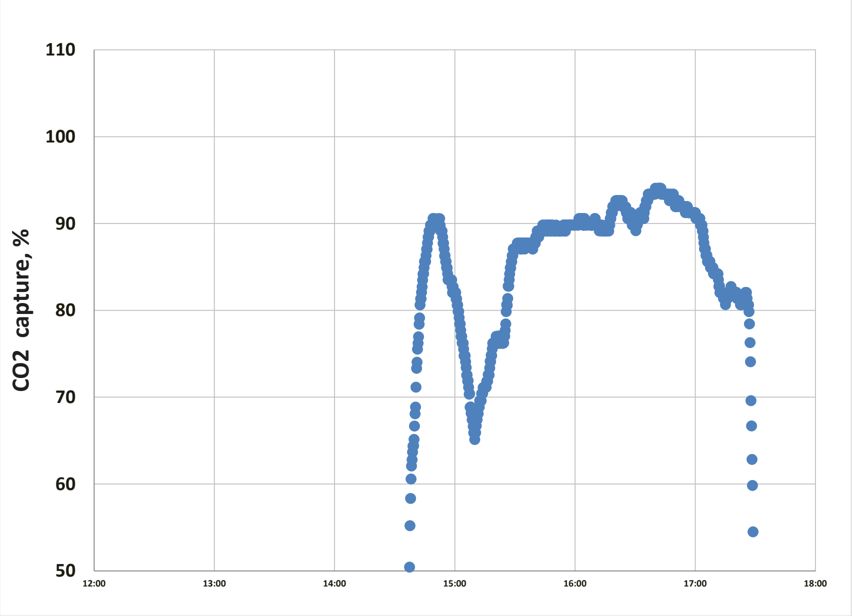


Figure 64. 90% CO_2 capture in reconfigured BsCEU

Most importantly, the ability to tightly control the rate of CO_2 capture was confirmed in the reconfigured BsCUE and is illustrated in **Figure 64**. The sorbent circulation rate was modulated to control CO_2 capture at a desired rate. The approach to tuning and controlling sorbent circulation rate was philosophically the same as the original BsCEU configuration, but with different process variable inputs.

Subtask 7.4: Long-term Performance Testing of the Bench-scale FMBR Prototype

Upon completion of shakedown, commissioning, and parametric testing of the reconfigured BsCEU in Subtasks 7.1 and 7.3, it was planned that the project team would conduct long-term performance testing of the high-fidelity BsCEU at RTI's ETDF.

The objectives of this long-term testing were to 1) demonstrate that the sorbent-based process could operate continuously without interruption for an extended period of time, 2) identify optimal operating conditions for coal-fired power plant applications, 3) identify any detrimental impacts of sorbent exposure to flue gas constituents, 4) investigate the effect of prolonged circulation and adsorption/regeneration cycling on long-term sorbent and process performance and reliability, 5) understand the effect of selected operating parameters on the efficiency of CO_2 capture, and 6) collect quality performance data to support an updated technology feasibility study. These objectives were achieved by coupling the parametric testing performed in Subtask 7.3 with extended continuous testing of the reconfigured BsCEU in Subtask 7.4.

<u>100-hr Long-Term Performance Testing</u>

In order to complete all of the objectives of long-term performance testing in one continuous run, 5 days of continuous BsCEU operation and data collection was conducted and the project team completed a 100-hr long-term testing campaign. Performing system parameter evaluations through a long-term testing campaign allowed for time-effective experimentation and data collection as the team was able to avoid delays associated with regular start-up and shutdown – as experienced in much shorter, individual experiments. This long-term testing campaign highlighted the robustness of the unit by operating at various operating conditions, continuously maintaining the performance target of 90% CO_2 capture, and generating high quality experimental data.

Table 27. Test matrix used during the 100-hour, BsCEU long-term performance testing campaign

Bed Temperature, C				Flue gas velocity, ft./s	CO_2 conc., vol%		Studied Parameter
Top Adsorber	Bottom Adsorber	Top Regenerator	Bottom Regenerator		Flue gas	ROG	
70	70	120	120	0.60	15.0%	~30%	Baseline
60	60	120	120	0.60	15.0%	~30%	Adsorption temperature
80	80	120	120	0.60	15.0%	~30%	
70	70	120	120	0.50	15.0%	~30%	Flue gas velocity
70	70	120	120	0.75	15.0%	~30%	
70	70	110	110	0.75	15.0%	~30%	Regeneration temperature
70	70	130	130	0.75	15.0%	~30%	
70	70	120	120	0.75	20.0%	~30%	Flue gas CO_2 concentration
70	70	120	120	0.75	4.5%	~30%	
70	70	130	130	0.60	15.0%	~30%	Optimal conditions

During the totality of the 100-hr test campaign, the main sets of operating conditions shown in **Table 27** were run for approximately 6 hours each to ensure steady-state performance had been reached (Note: "ROG" refers to "regeneration off gas"). In addition to measuring the set operating conditions from **Table 27**, some of the other critical experimental data collected were:

- Sorbent circulation rate
- CO_2 concentration from the Adsorber and Regenerator stages
- Adsorber cooling water flow and inlet and outlet temperature
- Regenerator heating steam supply pressure and rate of steam consumption
- Sorbent CO_2 loading (as measured through PBR testing of samples taken during the test campaign)

Throughout the 100-hour test campaign, the rate of CO_2 capture was maintained at 90% ±2% for the vast majority of the testing period (**Figure 65**), even as the operating conditions were changed multiple times during the campaign. With the operating conditions changing throughout the 100-hour campaign, the CO_2 capture rate was maintained at 90% by varying the sorbent circulation rate. The CO_2 capture rate was out of this range only once when operating with 4.5 vol% CO_2 in flue gas. This was mainly due to the limitation of the inline analyzer to reliably measure effluent flue gas CO_2 concentration <0.5 vol%. As shown in **Figure 66**, the sorbent circulation rate was varied over a wide range of 20 to 140 kg/h during the 100-hour test campaign.

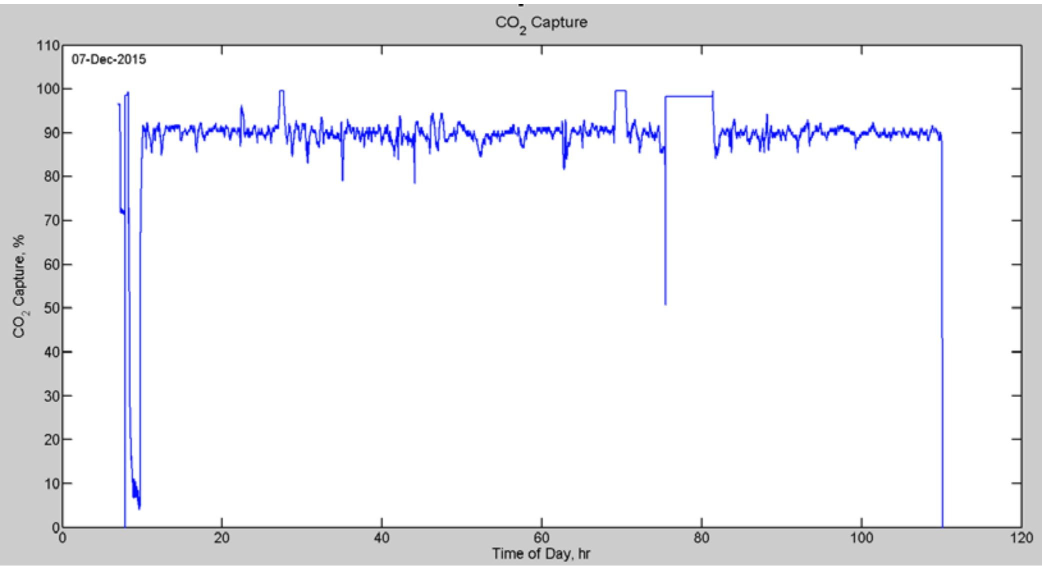


Figure 65. Measured rate of CO_2 captured during the 100-hour test campaign within RTI's BsCEU

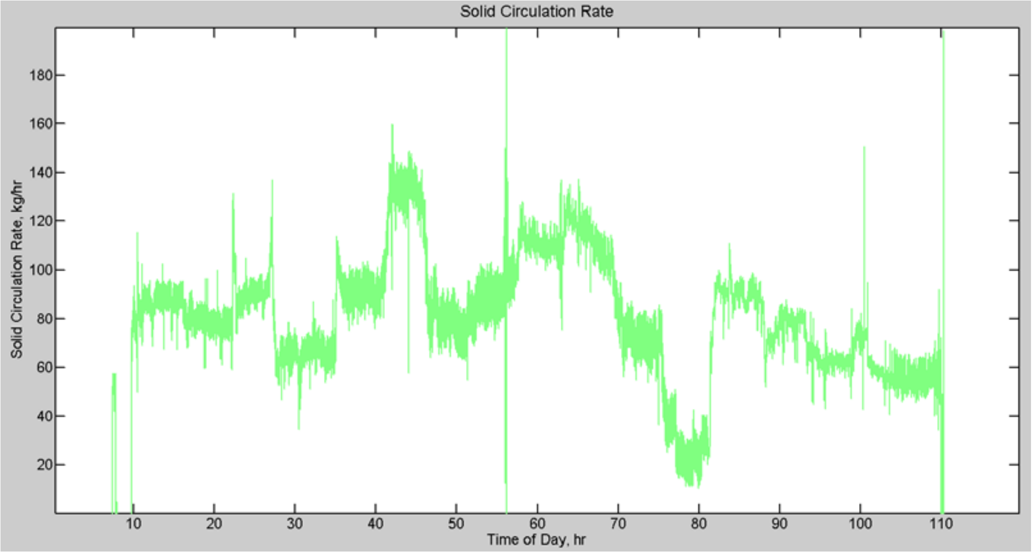


Figure 66. Measured sorbent circulation rate during the 100-hour test campaign (continuously adjusted as needed to maintain 90% CO_2 capture throughout the experiment)

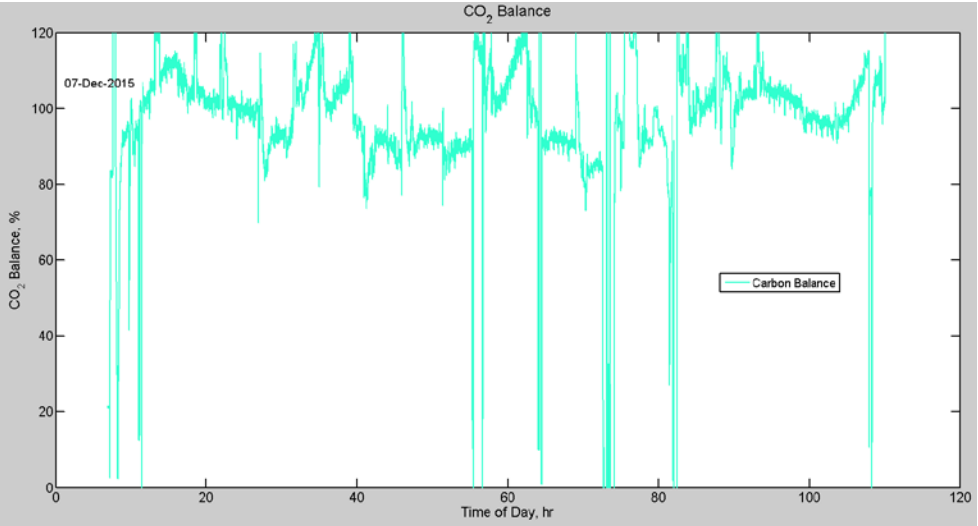


Figure 67. CO_2 mass balance data collected during the 100-hour test campaign (confirming the quality of data collected)

The quality and reliability of CO_2 composition data collected is summarized by the CO_2 mass balance plot in **Figure 67**. The CO_2 mass balance term is defined as the amount of CO_2 measured in the two effluent streams (effluent flue gas and regeneration off-gas) divided by the CO_2 present in the feed flue gas. The CO_2 analyzers were calibrated several times during the 100-hour test campaign to ensure CO_2 mass balance was accurate. Although not shown here, the fluidization behavior of the sorbent was also stable throughout the test and did not cause any downtime or system upsets. Additionally, the desired temperature set points for all four reactor stages (i.e. Adsorber and Regenerator stages) were tightly controlled throughout the experiment as exhibited in **Figure 68** and **Figure 69**. Sorbent working capacity was also monitored and the sorbent performed well, maintaining a reasonable CO_2 working capacity between 4 and 7 wt.% loading for the majority of the test campaign (**Figure 70**).

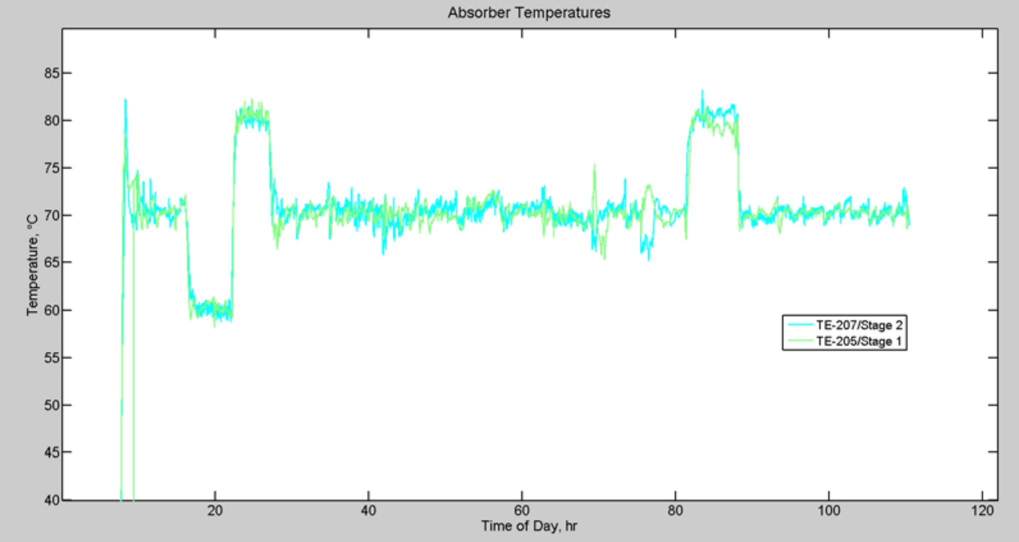


Figure 68. Measured Adsorber bed temperature during the 100-hour test campaign (confirming ability to tightly control)

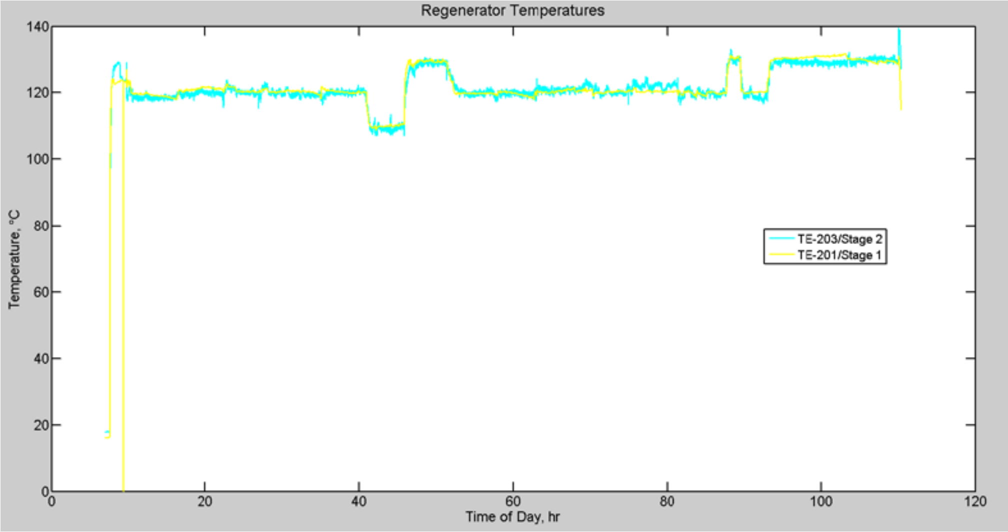


Figure 69. Measured Regenerator bed temperature during the 100-hour test campaign (confirming capability of tight control)

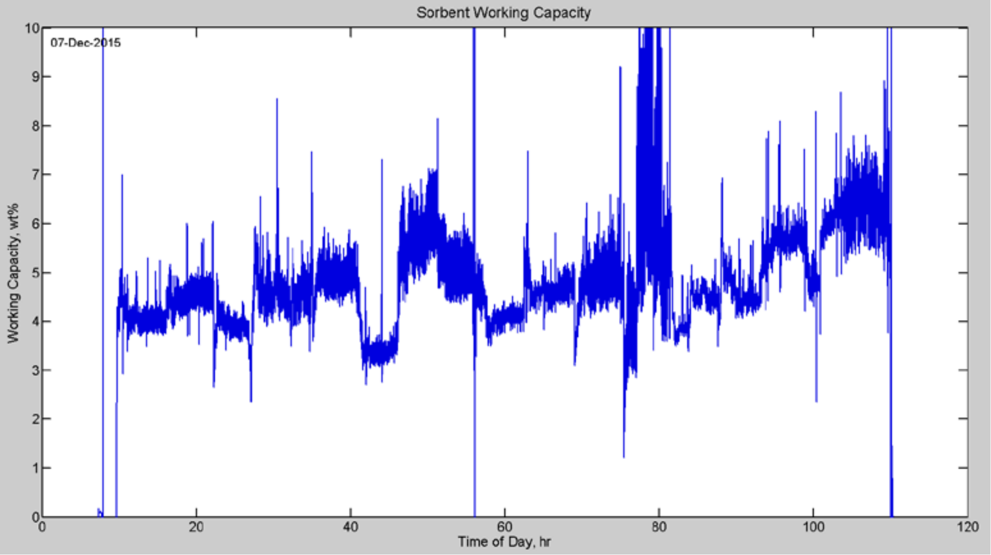


Figure 70. Calculated sorbent working capacity achieved during the 100-hour test campaign

Effect of Operating Parameters on Working Capacity

Working capacity is one of the most important performance metrics to evaluate in order to understand the effect of changing operating parameters. During the 100-hr long-term testing campaign, the project team explored how the sorbent's working capacity was impacted by four main operating parameters: adsorption temperature, regeneration temperature, flue gas velocity and flue gas CO_2 concentration. **Table 28** displays the set points used for each parameter and the associated working capacity measured at that condition.

Table 28. Operating parameter set points used for long-term testing variables

Parameter	Set point	Working Capacity, wt.%
Adsorption temperature	60 °C	4.4
	70 °C	5.0
	80 °C	3.9

Regeneration temperature	110 °C	3.4
	120 °C	5.0
	130 °C	5.7
Flue gas velocity	0.5 ft./s	4.5
	0.6 ft./s	5.0
	0.75 ft./s	5.0
Flue gas CO_2 concentration	4.5 vol%	5.0
	15.0 vol%	4.1
	17.5 vol%	4.6

Adsorption temperature: A lower adsorption temperature is thermodynamically favored for a higher equilibrium CO_2 loading, however, a higher adsorption temperature is favored to achieve better kinetics and lower the sensible heat required to heat the sorbent up to the regeneration temperature. Based on adsorption isotherm data collected during lab-scale testing, the sorbent working capacity should be the highest at 60 °C, but due to slower kinetics, the working capacity measured in BsCEU testing is actually lower than that at 70 °C. Increasing the adsorption temperature from 70 to 80 °C lowered the working capacity from 5.0 wt.% to 3.9 wt.%, a substantial drop of ~22%. In that scenario, the sorbent circulation rate would increase 22% and thus negates the benefit of the lower temperature delta between the Adsorber and Regenerator. Thus, this testing has identified 70 °C as the optimal adsorption temperature.

Regeneration temperature: Unlike the adsorption temperature, a higher regeneration temperature is thermodynamically and kinetically preferred as it will lead to a lower sorbent lean loading. However, the higher regeneration temperature will raise the sensible heat demand. In the 100-hr test campaign, the regeneration temperature was increased from 110 to 120 to 130 °C. As a result, the sorbent working capacity increased steadily from 3.4 to 5.0 to 5.8 wt.% respectively. With a ~47% increase in working capacity, increasing the regeneration temperature from 110 to 120 °C is advantageous in terms of both higher working capacity and lower heat of CO_2 regeneration. As the regeneration temperature increased from 120 to 130 °C, the sorbent CO_2 working capacity increasesd only 14%, not a large enough improvement to match the increased regeneration heat requirement. Thus, this testing has identified 120 °C as the optimal regeneration temperature.

Approach to equilibrium: The project team developed a simple simulation tool to be able to use the isotherm data and operating condition information, match the experimentally-measured CO_2 gas composition profile, and then predict the CO_2 loading on the sorbent leaving each reactor stage by varying the approach to equilibrium in each stage. A summary of how well the simulation predicted the experimental measurements and the quality of the experimental measurements can be viewed in **Figure 71**.

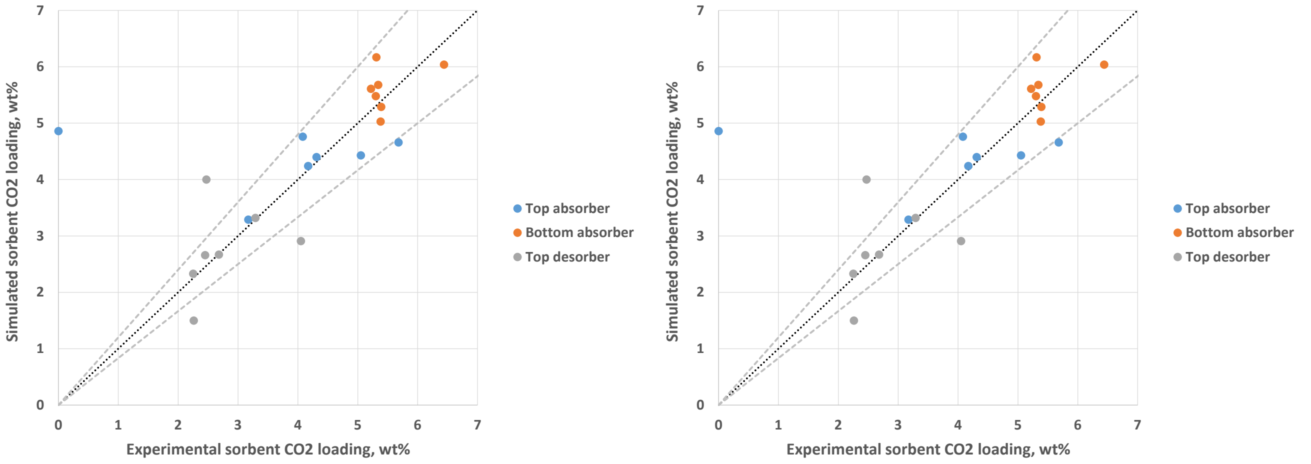


Figure 71. Parity plot comparing experimental vs. simulated gas CO_2 composition and sorbent CO_2 loading during the 100-hr long-term performance test

The parity plots in **Figure 71** exhibit a strong agreement between simulated and experimental values of gas CO_2 composition and sorbent CO_2 loading. The approach-to-equilibrium values and the approach to their analysis is described in the following report section.

Analyzing Approach-to-Equilibrium Factors

The "approach-to-equilibrium" is defined as a ratio of the experimentally-observed amount of CO_2 exchanged by the sorbent (adsorbed or released) to the calculated equilibrium amount of CO_2 exchanged by the sorbent when using the sorbent adsorption isotherm, operating conditions, and composition of CO_2 in effluent gas. The driving assumption in this analysis was that each fluidized bed (in both the Adsorber and Regenerator) will at maximum be in equilibrium with the partial pressure of CO_2 in the effluent gas.

Flue gas velocity: The effect of changing the feed gas velocity on the approach-to-equilibrium in both Adsorber stages is shown in **Figure 72**.

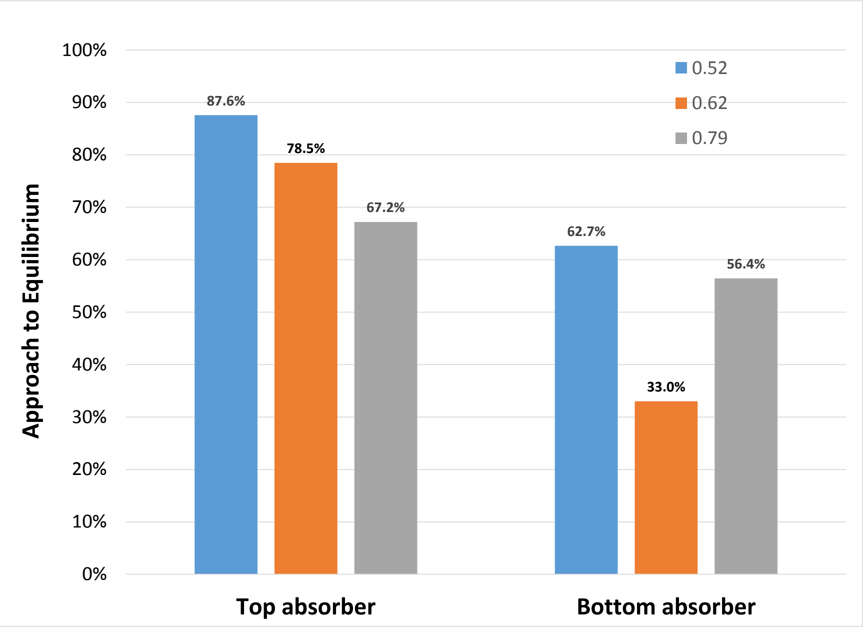


Figure 72. Effect of the Adsorber feed gas velocity on the approach-to-equilibrium in both Adsorber stages

The approach-to-equilibrium in the top Adsorber stage decreased from 87.6% to 67.2% as Adsorber feed gas velocity increased from 0.52 ft/s to 0.79 ft/s. This decrease was attributed to the drop in gas-solid contact residence time as the feed gas velocity increased. However, this trend was not observed in the bottom stage of the Adsorber. The approach-to-equilibrium dropped as the feed gas velocity increased from 0.52 ft/s to 0.62 ft/s, however, a further increase to 0.79 ft/s, resulted in the approach-to-equilibrium increasing from 33% to 56.4%. The uptick was attributed to two main factors:

1. As the approach-to-equilibrium in the top stage decreased, CO_2 loading in the bottom stage became "easier" as CO_2 was more accessible to leaner sorbent. This is the reason why the top stage always showed higher approach-to-equilibrium (compared to the bottom stage) as it was loading CO_2 on the leanest sorbent
2. Higher flue gas velocity led to higher turbulence and better mixing and mass transfer in the fluidized bed. Note that this is a hypothesis derived from reviewing the collected data, but further work would be necessary to substantially confirm its accuracy.

Adsorption temperature: The effect of changing the Adsorber temperature on the approach-to-equilibrium in each Adsorber stage is shown in **Figure 73**. The approach-to-equilibrium in the top Adsorber stage decreased with an increase in adsorption temperature. By definition, the approach-to-equilibrium calculation takes into account the decreasing equilibrium CO_2 loading with the increasing adsorption temperature. This increase in temperature should also improve the kinetics of CO_2 capture. Both of these reasons suggest that the approach-to-equilibrium should increase with increasing adsorption temperature, however, the observed trend is in contrast to this assumption. Currently, the project team has not identified a plausible theory for this observation and it is suggested that this be studied further. In the bottom Adsorber, the approach-to-equilibrium increased with an increase in temperature, as expected based on the two reasons previously noted. Additionally, as discussed in the previous section, with a lower approach-to-equilibrium in the top stage, the tendency to see higher approach-to-equilibrium in the bottom stage is more likely due to the opportunity for "easier" CO_2 capture based on a higher CO_2 capture driving force.

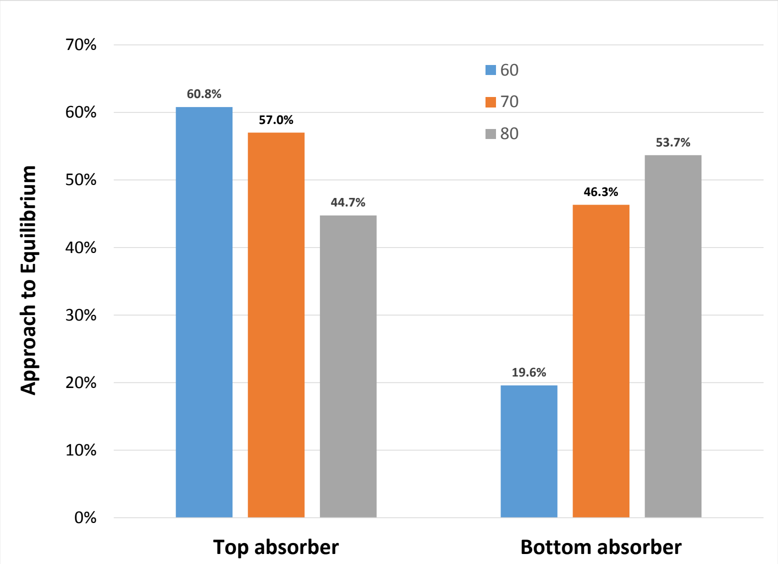


Figure 73. Effect of the Adsorber operating temperature on the approach-to-equilibrium in both Adsorber stages

Regeneration Temperature: The impact of Regenerator temperature on the approach-to-equilibrium in both Regenerator stages is shown in **Figure 74**. In this case, the improvement in the approach-to-equilibrium in both Regenerator stages is attributed to improved kinetics at higher operating temperature.

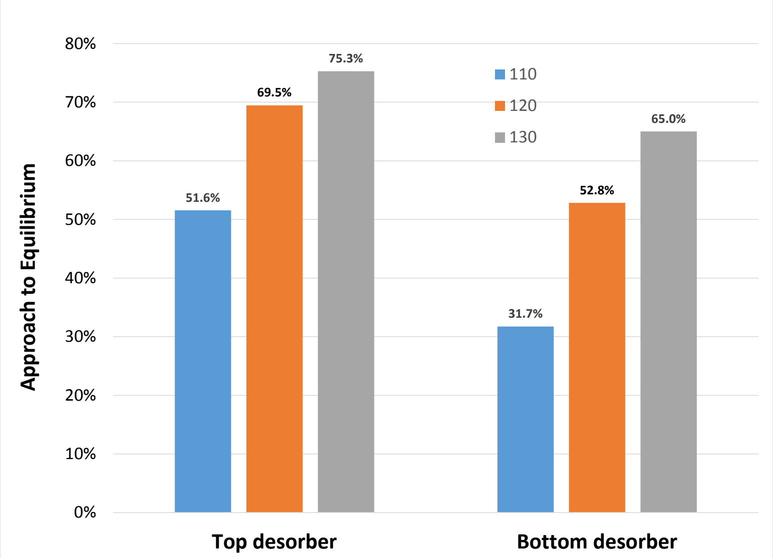


Figure 74. Effect of the Regenerator operating temperature on approach-to-equilibrium in both Regenerator stages

4.4 Techno-Economic Analyses (Tasks 2 and 8)

The overall goal of the project's techno-economic analyses was to develop a commercial design as well as cost and performance targets for a PEI sorbent-based process technology. As part of this project a comprehensive technology feasibility analysis of RTI's CO_2 capture process was completed. The results of this analysis allowed the project team to better understand the technical and cost advantages of the technology and guide the process and sorbent improvement efforts throughout the project. The project team's analysis was based on DOE/NETL's requirements for a Technical and Economic Feasibility study with particular attention paid to DOE/NETL's report "Cost and Performance Baseline for Fossil Energy Plants, Volume 1: Bituminous Coal and Natural Gas to Electricity" (Updated, November 2010). As required under the project's funding opportunity guidelines, the project team evaluated the technical and economic feasibility of this technology and has developed: 1) a general process flow diagram for a combined CO_2 capture and compression system, 2) a process equipment list, 3) material and energy balances exhibiting heating, cooling, and electric power requirements, 4) complete stream tables, and 5) cost estimates for all major process equipment and consumables.

4.4.1 Preliminary Techno-Economic Analysis (Task 2)

A preliminary feasibility study of RTI's CO_2 capture technology was completed in BP1 using the DOE/NETL guidelines. In this study, the CO_2 capture plant was sized to capture >90% CO_2 from flue gas derived from a net 550 MWe pulverized coal power plant. The process concept was simulated using Aspen Plus to generate material and energy balances and stream tables. The information from Aspen Plus was transferred to Aspen Process Economic Analyzer to size and cost individual equipment used in the simulation while vendor quotes were also used for some major equipment that could not be evaluated by Aspen PEA. Simulation results and total cost values were used to estimate the performance parameters of RTI's technology.

The results from the preliminary feasibility study demonstrated that RTI's advanced sorbent-based CO_2 capture process consumes significantly lower amounts of low pressure steam and electricity compared to the state-of-the-art (SOTA) Econamine FG Plus process (hereafter referred as "SOTA amine process") reported in Case 10 of the DOE/NETL report (Ref. 4). RTI's process was found to consume 0.86 lb.-steam/lb-CO_2 captured in comparison to the SOTA amine process which consumes 1.45 lb.-steam/lb-CO_2 (69% higher than RTI's process). RTI's process was found to consume 84 kWh/ton-CO_2 compared to 109 kWh/ton-CO_2 for the SOTA amine process, which is 30% higher. The annual cost of electricity consumption is $18,584,717/yr. The rate of consumption of low pressure steam and electric power is equivalent to a total parasitic power loss rate of 112 MWe. This results in a decrease in PC plant efficiency by 7.5 percentage points (versus 11.9 percentage points for the SOTA amine process). The total parasitic power loss results in an increase in cost of electric power from 64.0 to 98.3 mills/kWh while the cost of steam increases from $5.83 to $8.95 per 1,000 lbs of steam.

The total bare-erected cost of RTI's capture and compression plant is $189,886,865. Using factored estimates for engineering, process and project contingencies, as prescribed in the DOE/NETL's "Cost and Performance Baseline Report", the total installed cost was estimated to be $294,324,640. The total cost of capturing 3,476,848 ton-CO_2/yr (equivalent to 90% CO_2 from a net 550 MW power plant) was calculated as $138,0030,888/yr resulting in a capture cost per tonne of CO_2 as 39.7 $/T-$CO_2$. The impact on COE is equivalent to ~ 58% increase in cost of electricity (ICOE), which is a promising step forward compared to the SOTA amine process, which carries about an 86% ICOE penalty. It should be noted that a major contributor to the CO_2 capture cost is the cost of transportation, storage and monitoring of CO_2 at 10.3%.

Implementing the SOTA amine process for CO_2 capture results in a CO_2 avoided cost of 68 $/T-$CO_2$, 70% higher than RTI's advanced sorbent process. The utilities consumed by RTI's process represent 43.8% of the total CO_2 capture cost while the capital charge accounts for 37.3%. **Figure 75** provides a breakdown of the relative contributions that capital, variable, fixed, as well as transportation, storage, and monitoring (TS&M) costs have on the overall CO_2 capture cost. **Figure 76** provides a breakdown of the components that make up the variable cost including steam, electricity, cooling water, sorbent, maintenance, waste disposal, and other consumables. Taken together, these variable costs contribute 52.3% to the total CO_2 capture cost (as shown in **Figure 75**). **Figure 77** provides a breakdown of the components that make up the capital cost, which taken together have a 37.3% cost contribution to the total CO_2 capture cost (**Figure 75**). **Figure 78** exhibits the relative contributions of reactors, compressor, blowers, coolers, and other capital costs on the overall capital cost of RTI's technology.

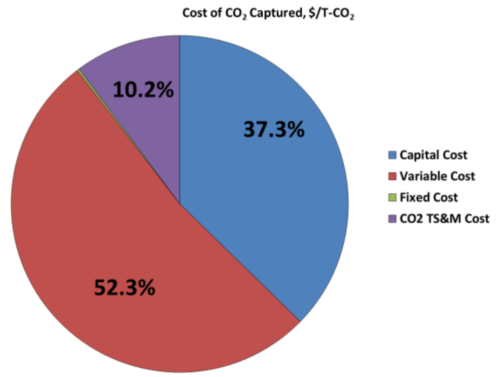


Figure 75. Contributions of capital, variable, fixed, as well as TS&M costs on the overall CO_2 capture cost of RTI's advanced solid sorbent CO_2 capture technology

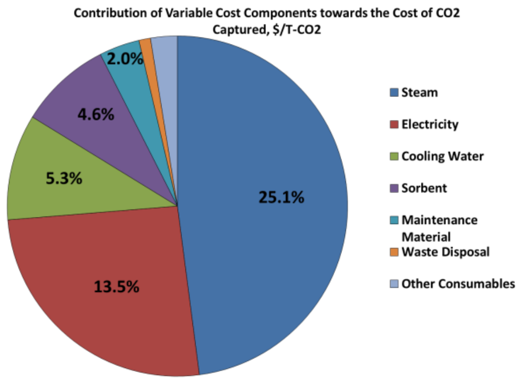


Figure 76. Contributions of steam, electricity, cooling water, sorbent, maintenance, waste, and other consumables costs on the overall variable cost of RTI's technology

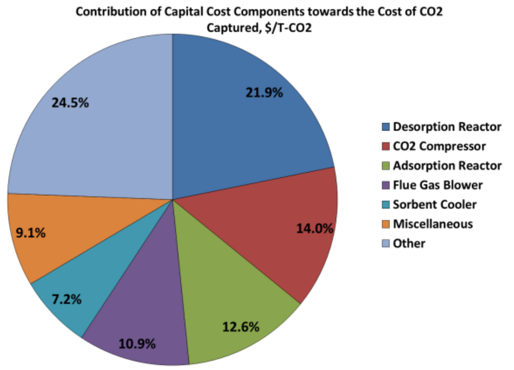


Figure 77. Contributions of reactors, compressor, blowers, coolers, and other capital costs on the overall capital cost of RTI's technology

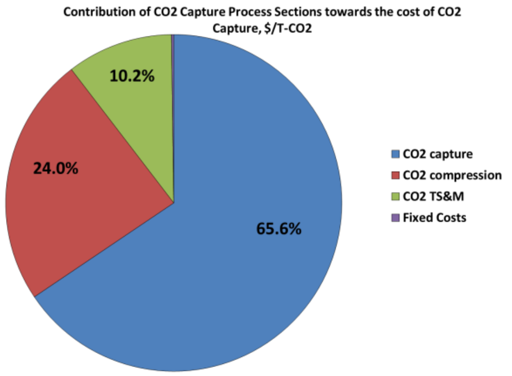


Figure 78. Contributions of individual systems (capture, compression, and TS&M) to the overall CO_2 capture cost of RTI's technology.

Sensitivity analysis: The cost of CO_2 capture included the cost of materials, utilities, waste disposal, maintenance material, fixed costs and the capital charges. The contribution of the individual components towards the total cost of CO_2 capture is shown in **Figure 75**. Various assumptions were made during the feasibility study based on what the research team thought was feasible for the proposed technology. A detailed sensitivity analysis was conducted to gauge how critical certain assumptions were to precisely predicting the cost of the advanced sorbent CO_2 capture process. A short list of the parameters evaluated is provided below.\

- Sorbent loss rate and sorbent price
- Sorbent capacity
- Impact of sulfur and nitrogen on sorbent performance
- Alternative SO_x and NO_x removal processes
- Heat of absorption and regeneration reactions
- Stripping steam demand
- Reactor design based on equilibrium-limited kinetic model

The sensitivity analysis greatly helped the project team to develop pathways to achieve the DOE/NETL's targets for CO_2 capture economics. **Figure 79** is a tornado diagram depicting the impact of various process parameters on the overall cost of CO_2 capture in RTI's technology. Also included in this diagram is the value for the SOTA amine process. This analysis shows that RTI's technology can achieve CO_2 capture at about 43% ICOE. To reach the DOE/NETL target of <35% ICOE, an additional 8% reduction is required. We believe that this cost reduction can be achieved by further optimization of the process technology. Some of these optimization elements include heat recovery from the CO_2 Adsorber, heat recovery in CO_2 compression, further reduction in system pressure drop by optimizing hydrodynamics, different materials of construction, and reduction of process and project contingencies through technology advancement (additional details provided in the following report section which reports the details of Task 8/BP3 efforts).

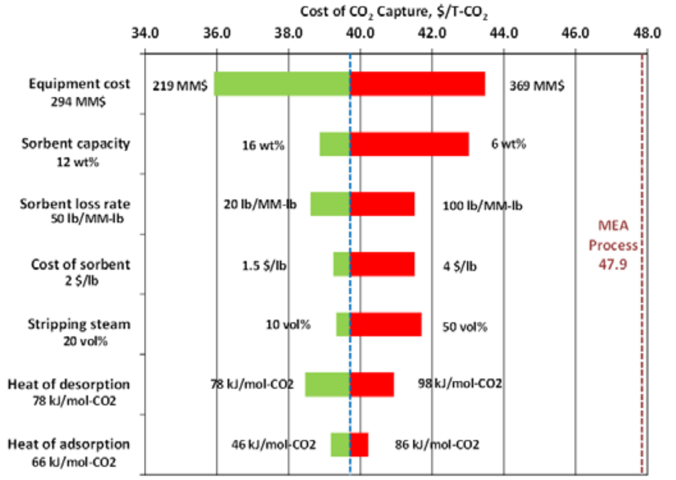


Figure 79. Sensitivity analysis associated with RTI's PEI sorbent-based CO_2 capture technology

4.4.2 Final Project Techno-Economic Analysis (Subtask 8.1)

The overall goal of Subtask 8.1 was to update the technology feasibility study from Task 2 (BP1) with data and information collected during continuous bench-scale testing. Subtask 8.1 represented a second technology feasibility "checkpoint" – essentially a detailed update of the work conducted in the first technology feasibility study. This second study benefited from all data collected during the entire project. These data included, but are not limited to: optimal process conditions, actual CO_2 capture and sorbent regeneration performance, actual sorbent and process stability measurements, heat recovery potential, sorbent manufacturing costs, etc. In addition to updates of the Task 2 economic outputs, Subtask 8.1 focused on technology integration within a commercial power plant and produced quantitative estimates of parasitic power losses, net plant efficiency loss, levelized cost of electricity, and the cost of CO_2 capture for a coal-fired power plant.

Updated Process Assumptions for the Updated TEA

In the BP1 technical feasibility study, the project team made various process assumptions based on what research has been accomplished at that time and what the research team thought was feasible for a commercial version of the proposed technology. Over the course of the project several assumptions were investigated at various scales and different phases of operation. Through this research and development progress, the project team identified several assumptions that required updating (or redefinition) in the concluding stage of the project. **Table 27** provides a summary of the critical assumptions that were either verified or needed to be updated based on the project team's lab-scale and bench-scale investigations. The following sections provides details on why the assumptions were changed and/or how they were verified.

Table 29: A list of TEA assumptions (taken from the BP1 analysis) that were either updated or verified at project conclusion

	BP1 Assumption	Revised Assumption
Regeneration temperature, ˚C	110	120
Working capacity, wt.%	12	10
Sorbent cost, $/kg	4.4	11
Regenerator effluent CO_2 concentration, vol%	80	60
Adsorber pressure drop, psi	2.7	2.7
Attrition losses, ppm	50	50

Reactor heat transfer coefficient, kJ/h.m^2.K	2044	2044

Regeneration temperature: During this project, sorbent capacities were often measured by conducting regeneration tests in humidified nitrogen (i.e. non-CO_2) gas flow. However, in a staged regenerator reactor (as designed and implemented in BP3), it is known that the CO_2 partial pressure is going to be ≥15 kPa (even in the bottom-most Regenerator stage) due to a combination of operating pressure and CO_2 concentration. As is exhibited in **Figure 80**, the PEI-based sorbent's equilibrium lean loading at ~15 kPa and 110 °C is ~2.7 wt.%. In comparison, the equilibrium lean loading at ~15 kPa and 120 °C is ~0.8 wt.%. Given this significant difference in lean loading and working capacity (i.e. ~1.9 wt.% improvement), it was determined that RTI's Regenerator should be operated at 120 °C. Similar results were observed during BsCEU operation where the lean loading was improved by ≥1.2 wt.% when the regeneration temperature increased from 110 to 120 °C. This assumption was changed accordingly in the project team's updated economic analysis.

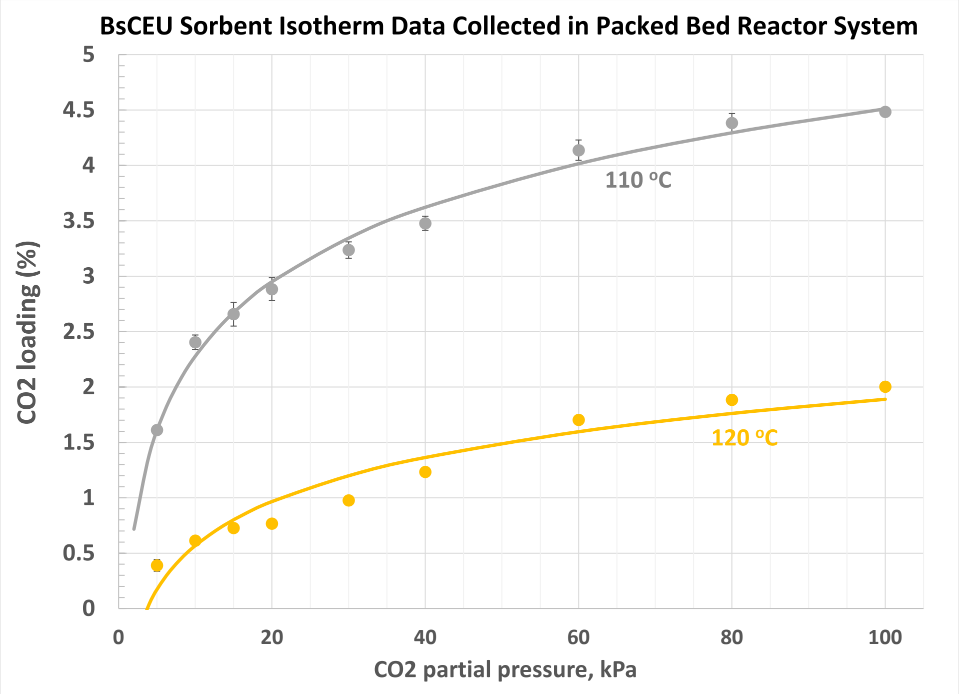


Figure 80. PEI-based sorbent CO_2 lean loadings at 110 to 120 °C in various CO_2 partial pressures

Working capacity: Three primary factors affect a PEI-based sorbent's working capacity:

1. equilibrium CO_2 loading of the sorbent
2. operating conditions within the process
3. reactor design

The PEI-impregnated sorbent that was scaled-up for BsCEU testing had a CO_2 capacity of 8.9 wt.% when tested using the "standard capacity measurement conditions" (described earlier in this report). The CO_2 capacity of the same sorbent at conditions mimicking the Adsorber inlet (temperature of 70 °C and CO_2 partial pressure) is 8 wt.%. In addition, with a staged Regenerator operating at 120 °C and low CO_2 partial pressure, the lowest lean loading possible was calculated as 0.5 wt.%. Therefore, it was determined that the maximum achievable working capacity for this "Generation 1" sorbent was 7.5 wt.%. Even though the reconfigured BsCEU may not be ideally configured with two-stages in each the Adsorber and Regenerator, based on sorbent isotherm data and assuming complete approach-to-equilibrium, the BsCEU should be able to achieve the 7.5 wt.% working capacity. However, the highest working capacity observed in the BsCEU was ~5 wt.%. This lower working capacity was a result of inefficient operation of both reactors. Given this result, the project team decided to revisit the working capacity assumption used in the TEA and revised it down to 10 wt.% (from 12 wt.% in the original TEA).

Justification for having a higher-than-observed working capacity assumption is two-fold: 1) as mentioned previously, in a more optimal process, the "Generation 1" sorbent is capable of at least 7.5 wt% loading, and 2) it had been shown through the project team's research that the scaled-up PEI-impregnated sorbent was not the highest performing sorbent in terms of CO_2 loading. Other sorbent formulations synthesized in this project have exhibited CO_2 loadings up to 12 wt.%. The project team theorized that such a sorbent in an optimized reactor design, and in a "Nth" commercial plant, could realize a sorbent working capacity of ~10 wt.%.

Sorbent cost: In RTI's preliminary technical feasibility study (BP1), it was assumed that the sorbent would have a commercial-scale cost of $4.4/kg. This assumption was made on an "Nth" plant scenario where the sorbent (and process technology) would be well-advanced and established in the commercial marketplace. Through sorbent development efforts in this project, the project team has driven down the initial cost of the PEI-based sorbents from $1000/kg to $100/kg. This cost reduction has been achieved through PEI substitution, refinements in the manufacturing procedure, and primarily by substituting expensive mesoporous silicas with equivalent or better-performing, commercial silica supports. The project team worked closely with silica manufacturers to identify the silica support best suited for the project's development efforts and continuous bench-scale testing. RTI continues to collaborate and strategize with these commercial manufacturers on ways to make further cost reductions while also maintaining desirable properties. The most promising "Generation 1" sorbent, although not optimized, was scaled up to 150 kg and met the project's targets for physical and chemical properties and performance. The sorbent production costs at this scale totaled ~$100 $/kg. Based on discussion with various PEI and silica suppliers, and our sorbent manufacturing partner, the next scale-up (i.e. sorbent production for pilot-scale) can easily achieve a ~$50/kg cost target. For larger scale manufacture (i.e. large demonstrations) the silica provider has already identified ways to cut the silica production cost by 2/3. This pathway of sorbent cost reduction needs to continue and to do so, additional cost-reduction methods may need to be employed, for example:

- Use of water for solvation of PEI prior to deposition on silica. (Note: the project team has successfully demonstrated this method at lab-scale)
- Replace the pure PEI precursor with a less-expensive ethylenediamine end-capped version
- Recover / re-use any alcohol solvent after evaporation from the deposition vessel.

Although the sorbent costs have been dramatically reduced, and there are pathways for further reduction, they have not declined enough to validate the project team's sorbent cost assumption of $4.4/kg used in the initial TEA. Based on the work done to date, and the additional cost reduction pathways available, the project team believed that a more realistic sorbent cost estimate for the updated TEA would be $11/kg.

Regenerator effluent CO_2 concentration: The use of stripping steam in the Regenerator helps to lower the partial pressure of CO_2 which enables improved CO_2 desorption and lower lean loading on the sorbent. In the BP1 technical feasibility study, it was assumed that the Regenerator could operate with a CO_2 concentration in the Regenerator effluent stream of 80 vol% (balance steam). By operating at a high CO_2 concentration in the Regenerator the consumption of stripping steam was cut by 2/3 compared to conventional, solvent-based CO_2 capture technologies. This is exhibited in **Figure 81** where the molar ratio of steam to CO_2 released in the Regenerator drops to ~0.25. However, for the sorbent used in RTI's BsCEU testing, the equilibrium lean loading from a two-stage regenerator is ~1.2 wt.% when operating at a 80 vol% CO_2 concentration. A lean loading of 1.2 wt.% may be too high for commercial operation, unless the total CO_2 loading capacity of the sorbent can be further improved. Utilizing a three or four-stage Regenerator will further reduce the equilibrium lean loading, but the capital cost of the Regenerator will escalate (e.g. possibly by 2.5 to 3.5x).

Upon updating the technical feasibility study in BP3, the Regenerator effluent CO_2 concentration assumption was revised down to 60 vol% in order to achieve improved sorbent lean loadings in the Regenerator. This revision increases the molar stripping steam demand to a ~0.65 steam/CO_2 ratio, but lowers the equilibrium sorbent lean loading to 0.7 wt.%.

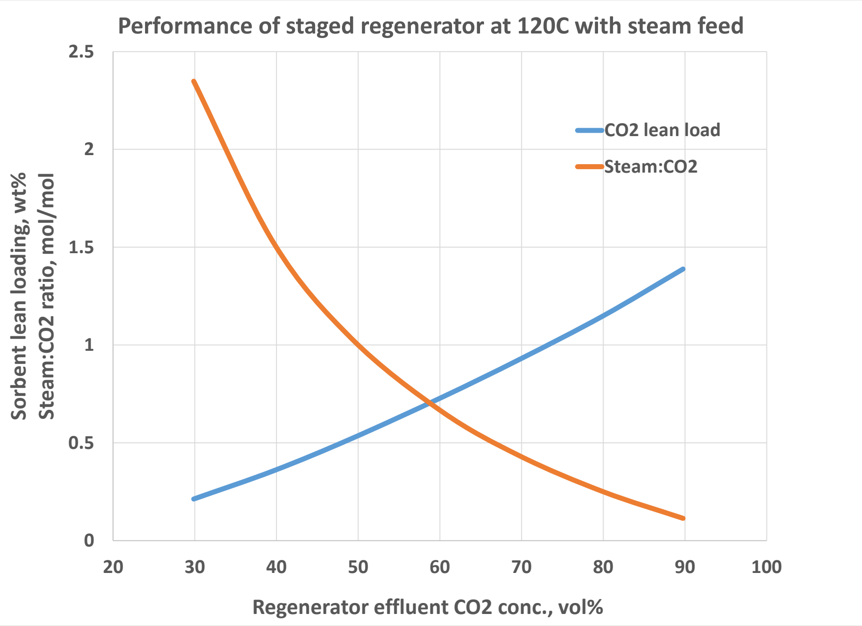


Figure 81. Performance of staged Regenerator at 120˚C under different assumptions for Regenerator effluent composition

Adsorber pressure drop: Adsorber pressure drop has a relatively significant impact on the economics of a CO_2 capture system due to it relationship with the size of the blower/compressor required to move flue gas through the process. In RTI's initial technical feasibility study an Adsorber pressure drop of 1.9 psi was assumed. The observed pressure drop across the two-stage Adsorber during BsCEU testing was 1.7 psi. At commercial scale, the Adsorber reactor is envisioned to be a two or three stage Adsorber with a total sorbent bed height of 7.5 ft. The sorbent bulk density in the Adsorber's fluidized beds is expected to be on the lighter side at 25 lb./ft^3, thus the total pressure drop across the Adsorber reactor (sorbent bed and gas distributor plates) was calculated to be similar to that observed in bench-scale testing (~1.7 psi). Since this calculated result is not significantly different than the assumption made in BP1, the Adsorber pressure drop assumption was maintained at 1.9 psi in the revised TEA. The total pressure boost provided by the flue gas blower (which includes the Adsorber beds and other peripheral equipment/piping) was also maintained at 2.7 psi.

Sorbent losses to attrition: The sorbent's physical strength (and resistance to attrition) is an important factor in confirming both the technology's technical and economic viability. The project team was able to make some general observations about attrition over the total BsCEU testing period, but also set-up a system for measuring fines generation rate during the 100-hour long-term performance tests. Fines collection was done for both the staged Adsorber and Regenerator. At the start of the 100-hour test, the project team observed an average sorbent attrition loss of ~120 kg/MM-kg circulated during the first 24 hrs of testing. During the last 48 hours of the long-term testing campaign, the average sorbent attrition loss actually decreased to ~85 kg/MM-kg circulated (**Table 30**). Even though the BsCEU does not represent an optimized design and is not at a representative scale (compared to commercial scale), demonstrating attrition losses of <100 ppm is encouraging. This result is very encouraging and suggests that the original TEA assumption of a 50 ppm sorbent attrition loss rate is achievable. Further development and optimization of the sorbent and the process design will bring the attrition loss rate down to that 50 ppm range.

Table 30. Sorbent losses due to attrition in long-term, BsCEU testing

	Fines collected, g	Average circulation rate, kg/h	Sorbent attrition rate, ppm
First 24 hours	240	85	120
Last 48 hours	260	65	85

Heat transfer coefficient of reactor internals: Heat management and temperature control are critical considerations for RTI's technology and have significantly impacted how the reactors have been designed and sized for both bench-scale implementation and at the conceptual commercial-scale. Fluidized-bed design was preferred in part due to their ability to achieve high heat transfer coefficients compared to fixed-bed reactors. Higher heat transfer coefficients offer better heat and temperature control. Design and sizing of fluidized-bed reactors are primarily dictated by the sorbent hydrodynamics and the heat released by the sorbent-CO_2 reaction. Although reaction kinetics play a role in the design and sizing, the heat transfer internals are not a limitation only when heat transfer coefficients are high (>1500 $kJ/h.m^2.K$). Based on RTI's extensive experience in fluidized-bed design and operation, it was expected that the Adsorber and Regenerator reactors can achieve even higher heat transfer coefficients. The heat transfer internals in both reactors were designed and sized based on a heat transfer coefficient assumption of 2044 $kJ/h.m^2.K$.

During BsCEU operation of the staged Adsorber and Regenerator, experimental data (i.e. temperatures, gas and solids flow rates, pressure drops, etc.) were collected and allowed for an estimation of the system's heat transfer coefficients. Based on these data, the project team estimated that the system could achieve a heat transfer coefficient of ~1900 $kJ/h.m^2.K$. Even though the BsCEU reactors were not optimized for a specific heat load, the observed heat transfer coefficient was quite encouraging being only <10% lower than the assumed TEA value. It is believed that in commercial operation, the heat transfer coefficients may even exceed, by >20%, the assumed values, but for the time being, the original assumption was retained in the updated TEA.

Capital cost: In RTI's original technical feasibility study, capital cost contributes 37.3% towards the cost of CO_2 capture, as shown in **Figure 75**. For a first-of-a-kind technology, as presented here, there can be significant uncertainty around a capital cost estimation and there may be several ways to cut capital cost as the technology develops over time. For RTI's technology, some of the major capital cost contributors are:

- Adsorption reactor
- Regeneration reactor
- Flue gas blower
- CO_2 compression and drying
- Flue gas cooling and acid gas removal.

Given the scale of development to date, it was not possible to extensively verify the estimated capital costs within the scope of the project. The adsorption and regeneration reactors were originally assumed to be single-stage, rectangular, concrete reactors with horizontal heat transfer internals. Concrete was chosen as the reactor's material of construction and enable fabricating rectangular cross-section reactors which would be able to support horizontal heat transfer tubes banks. Horizontal heat transfer tubes are preferred as they allow for staging of the cooling water flow outside of the reactor and also help to prevent gas channeling in the fluidized beds. However, since such a reactor type is not of standard design, estimation of its capital cost bears a higher level of uncertainty.

Several other cost-reduction strategies were introduced in RTI's BP1 technical feasibility study. Although most of them exhibit significant promise, the executed project scope did not allow for a detailed analysis and quantification of the proposed cost reduction strategies. The following are some strategies introduced in the BP1 analysis and carried through with the updated TEA:

1. Adsorber flue gas velocity maximized to lower the reactor cross-section area while maintaining high mass transfer rates and heat transfer coefficients
2. Optimized the cost of flue gas conditioning by using spent-sorbent guard beds for acid gas removal
3. Modified proposed sorbent transport strategy of using belt conveyors. Reactor columns are planned to be stacked on top of each other which can eliminate one sorbent transport leg
4. Utilization of heat released during CO_2 adsorption through a low-temperature heat recovery system.

In general, there were few compelling reasons to modify the technology capital cost up or down based on results generated from BsCEU testing. The one main area observed for cost reduction came through the replacement of the Caustic Gas Scrubbing system. The Caustic Gas Scrubbing system was used to remove acid gas contaminants in the flue gas, especially SO_2, down to 10 ppmv. The cost of CO_2 capture associated with this system (as well as the Direct Contactor Cooler, which was required for efficient srubbing performance) was \$3.4/T-CO_2. This value included the cost from capital, utilities, waste disposal, and materials usage. RTI has proposed the use of spent sorbent, from the CO_2 capture unit, to remove similar acid gases – essentially a replacement for the Caustic Gas Scrubbing system. Using this approach would eliminate two large systems and replace it with a smaller system with a lower capital cost contribution and no make-up material requirement. Waste disposal costs for the spent sorbent were already taken into account in the original TEA, so no additional waste disposal cost was assumed for this new arrangement. The overall savings in cost of CO_2 capture was calculated to be \$1.7/T-CO_2.

Updated Cost of CO_2 Captured

As described in the sections above, several assumptions from the original technical feasibility study had to be revised for an updated analysis carried out in BP3. Most revisions were made in making the parameter assumption less aggressive, thus most revisions negatively impacted the cost of CO_2 capture. A summary of the main revisions, and their individual impact on the ICOE, is provided in **Table 31.** The biggest cost impact was due to the increase in sorbent cost (from \$4.4 to \$11/kg-sorbent), which caused a \$2.7/T-CO_2 increase in the cost of CO_2 capture. The second highest impact resulted from revising the assumption for CO_2 concentration in the Regenerator effluent. The increased stripping steam demand increases the cost of CO_2 capture by \$1.0/T-CO_2. Lowering the sorbent's working capacity and raising the target Regenerator temperature had relatively small impacts on the cost of CO_2 capture. The combined effect of changing all the assumptions simultaneously, allowing for the interdependencies of all parameters, is \$3.4/T-CO_2 which increases the cost of CO_2 capture to \$43.3/T-CO_2. An example of how the parameters are connected and have differing impacts on total cost is exhibited when the working capacity and sorbent costs are changed simultaneously. The lower working capacity demands higher sorbent circulation rates and hence higher sorbent make-up rates (as dictated by the attrition loss rate assumption). Since the sorbent cost has also increased, the impact on the cost of sorbent make-up is two-fold. Therefore, in RTI's revised technical feasibility study, the baseline, Nth plant cost, is reported to be higher than that reported in the original TEA conducted in BP1. At a CO_2 capture cost of \$43.3/T-CO_2, RTI's technology is close, but ultimately falls short of the DOE/NETL's cost target of \$40/T-CO_2. Given how close this value is to the DOE/NETL's targets, it would not be prudent to say RTI's technology will never meet that target. It will certainly be challenging, but there is a pathway to further cost reductions (as described in the next section).

Table 31. Revised assumptions used in RTI's updated TEA and their individual impact on cost of CO_2 capture

	Revised Assumption	Increase in cost of CO_2 capture, \$/T-CO_2
Sorbent cost, \$/kg	11	+ 2.7
Capture stream CO_2 concentration, vol%	60	+ 1.0
Working capacity, wt.%	10	+ 0.6
Regeneration temperature, C	120	+ 0.4
Acid Gas Scrubbing strategy	Use spent sorbent	- 1.7

Pathway to Cost Reductions

Various strategies have been identified that have significant potential to further reduce the capital and operating costs and energy penalty of RTI's solid sorbent-based CO_2 capture process. If any (or all) of these cost reductions materialize, RTI's technology will have a good chance of meeting DOE/NETL's 2025 goal of \$40/T-CO_2 capture costs. Some of the strategies on this cost reduction pathway are summarized in **Table 32**.

Table 32. Pathway to meet DOE/NETL's \$40/T-CO_2 capture target (i.e. strategies to reduce capital and operating costs and energy demand)

Adsorber and Regenerator Design	Sorbent Stability and Cost
• Reduce capital cost using low-cost MOC (concrete or fiber-reinforced plastic). • Reduce reactor volume by using high efficiency heat transfer internals. • Effectively design Regenerator staging to minimize stripping steam demand. • Design fluidized-bed reactors and sorbent properties to minimize entrainment and attrition	• Estimate heats of reaction more reliably. • Further improve long-term stability and CO_2 capacity. • Improve tolerance towards contaminants. • Select sorbent precursors and synthesis routes that minimize sorbent preparation costs. • Recycle sorbent particles for reformulation and reuse. • Recycle attrited sorbent particles for removal of acid gases – this eliminates a NaOH wash and reduces waste.
Heat Recovery and Integration	
• Effectively recover heat from the CO_2 Adsorber and compression train and integrate into the process. • Utilize novel heat recovery approaches such as an Organic Rankine Cycle to recover heat in the Adsorber	

4.4.3 Environmental, Health, and Safety Analysis (Subtask 8.2)

The project team conducted an environmental, health, and safety (EH&S) review of RTI's PEI-based sorbent process. This review helped to identify any EH&S technology risks and mitigation strategies for those risks. The information gained from this study helped to give the project team better clarity on how the PEI-based sorbent process technology compared on an EH&S basis to other developing technologies. Information gained included: composition and quantity of waste streams (e.g. fugitive emissions, wastewater, and solids waste), waste disposal strategies, sorbent manufacturing concerns, exposure hazards, operational hazards, etc. This analysis was based to the greatest extent on existing environmental and safety information available to the project team, either through literature research or through testing conducted throughout the project. This analysis did not include actual toxicology testing.

Emissions to Air

It is expected that RTI's solid sorbent CO_2 capture technology would produce a small amount of particulate matter (PM) emissions to the air. A commercial system will include effective gas-solid separation devices which are expected to remove particulate matter from the treated flue gas such that it meets prescribed PM regulation standards. In terms of contaminant emissions, it is actually expected that the PEI-based sorbent will polish and remove acid gases (SO_2, NO_x) from a coal-fired power plant's flue gas prior to emitting the flue gas to the atmosphere.

Emissions to Water

It is expected that RTI's solid sorbent CO_2 capture technology will not produce any significant increase in emissions to water at a coal-fired power plant. Water present in the power plant flue gas will be condensed and drained from the commercial system. This water may be slightly acidic due to dissolved acid gases, but it is expected that it will not require any treatment prior to discharge, depending on the amount of water condensed and discharged. Cooling water used in the process will be handled within a closed loop and any blowdown from the cooling water system is expected to be discharged by similar means already undertaken at the power plant.

Emissions to Land – waste generation and handling

It is expected that RTI's solid sorbent CO_2 capture technology will produce PEI-containing waste sorbent from the fine particulate matter collected by a commercial system's solids filtration devices. This waste sorbent will require disposal. Sorbent waste containing PEI (and adsorbed SO_2, NO_x, and CO_2) may be classified as hazardous waste, similar to conventional amines such as MEA, but PEI has a lower HMIS rating (2) compared to MEA (3). No extraordinary measures are required to safely handle the spent PEI-based sorbent. Standard personal protective equipment including safety glasses and gloves are recommended during operation of the commercial process.

Operational Risk

In considering the operational risk, the project team put together a table to summarize the findings **(Table 33)**. This table discusses the operational risk, resulting, potential impact on process and performance, and strategy for risk mitigation associated with all aspects of operating RTI's solid sorbent CO_2 capture process at commercial scale.

Table 33. Operational risk, potential impact, and strategy for risk mitigation of RTI's solid sorbent CO_2 capture process

Operational Risk	Effect on Process and Performance	Mitigation
Liquid gets into fluidized bed via: • water condensing in the CO_2 Adsorber, • heat transfer tube rupture	Liquid water in the fluidized bed of dry sorbent particles could lead to: • agglomeration of the particles, high pressure drop, and possible mechanical failure of system • fouling of heat transfer internals → ineffective heat removal → reduction in CO_2 capture efficiency.	• Use tempered cooling water with an entrance temperature of at least 40°C. • Modify cooling water flow path to flow downward such that the coldest cooling water contacts the warmest flue gas.
Loss or significant interruption of gas flow • Blower failure • Shutdown • Obstruction of flue gas	Although unlikely, gas flow interruption would cause the fluidized bed to rapidly de-fluidize causing the bed to rapidly "drop". This may lead to the bottom of the vessel experiencing a large applied force in a very short timeframe and possible rupture.	• Process design will include devices to prevent backflow. • Vessel design and structural analysis will account for potential weight of bed "drop".
Loss of heating or cooling services	Loss of heating service would result in failure of the process to remove CO_2 from FG. Loss of cooling would result in reduced CO_2 capture performance.	• No major safety concerns. Process would remain stable until services are returned. Therefore, no mitigation strategy required.
Failure of gas-solid separation devices • Filter bag rupture in Baghouse	Without effective gas-solid separation, fine attrited particles may be released.	• Release of fines from Regenerator may be mitigated by a product gas cooler that condenses water prior to compression. Particles would be collected in condensate.
Regenerator over-temperature	PEI-impregnated sorbents can thermally degrade. Localized hotspots due to poor mixing in the fluidized bed or increased steam pressure could result in a reduction in sorbent performance, additional sorbent waste/make-up, and possibly PEI degradation products appearing in the CO_2 product gas.	• Careful control of steam delivery to sorbent regenerator. • Operate process optimally to achieve the highest attainable heat transfer coefficient in the sorbent regenerator.

Ultimately, the EH&S analysis has determined that RTI's technology has no major hurdles for commercial implementation (from the perspective of environmental, health, safety, and operational risks).

5. Technology Development Roadmap

Having proven the technical and economic viability of RTI's technology, and reducing technical risks (both for the sorbent and process) through bench-scale testing, the next logical development step and progression for this technology is to design, construct, and demonstrate a pilot-scale system for testing at a coal-fired power plant (or another industrial source of CO_2). Current techno-economic analysis results warrant further exploration and show the promise of RTI's technology and potential to meet DOE's 2025 targets of <40 \$/ton-CO_2. However, there are many improvements still needed to move the technology towards DOE's long-term goal of <30% ICOE. Various strategies have been identified that can further reduce the capital and operating costs and energy penalty of this process. Further development and refinement through systematic scale-up and demonstration is the best strategy towards realizing DOE's goals.

A comprehensive approach to advancing RTI's technology to the next development stage is exhibited in **Table 34** (along with a side-by-side comparison of what information has already been collected in previous R&D efforts). The key to RTI's continued success in advancing step-out technologies is the employment of an integrated technology development approach which requires integration of process and materials innovation along with a detailed understanding of economic feasibility and key cost drivers. The next stage development approach highlighted in **Table 34** identifies the process evaluations and performance data needed to bridge the gap between bench-scale (completed) and commercial readiness (future target).

Table 34. RTI's technology development roadmap showing a vision of the next stage, pilot-scale step as it builds upon current bench-scale testing and focuses on what is needed for pre-commercial scale-up.

	Lab-scale (2011-2013)	Bench-scale (2013-2015)	Pilot-scale (2015-2019)	Pre-commercial (2020-2025)
Sorbent				
Form	Powder	Fluidizable	Fluidizable	Fluidizable
CO_2 Capacity	14 wt%	9 wt%	12 wt%	12 wt%
Production Scale	100 g	135 kg	20,000 kg	800,000 kg
Cost [a]	\$500/kg	\$100/kg	\$30/kg	< \$8/kg
Stability	PEI leaching	100s of cycles	1000 cycles	10,000 cycles
Process				
Flue-gas	Simulated	Simulated	Coal-derived	Coal-derived
Reactors	Packed-bed	Fluidized-bed	Fluidized-bed	Fluidized-bed
Operation	Cyclic	Continuous	Continuous	Continuous
Heat management [b]	None	Bed internals	Bed internals	Bed internals
Process Intensification [c]	None	None	None	Yes
Techno-economic Analysis				
	Preliminary, vision-based	Preliminary, vision-based	Detailed, with pilot data	Commercial

(a) – Cost at the end of each phase assuming multi-batch production (b) – Refers to management of heat within fluidized bed reactors
(c) – Refers to process modifications such as waste sorbent for acid gas scrubbing, heat integration between sorbent streams, etc.

The next development step for RTI's technology (pilot-scale testing) would focus on the technical issues and economic factors that were not feasible to study under bench-scale testing. Specific objectives of this stage of development would include:

- Performing detailed design and engineering of RTI's pilot system utilizing design data collected to date
- Refining the sorbent scale-up production process utilizing optimized sorbent preparation variables and significant input from commercial suppliers and manufacturers
- Constructing, fabricating, installing, and commissioning a pilot system with unfailing adherence to safety, quality, cost, and schedule
- Demonstrating the technical and economic attractiveness of RTI's technology through parametric and long-term pilot testing at an actual coal-fired power plant
- Continuously refining the detailed technical and economic analyses of RTI's technology using pilot test data.

It is expected that this pilot demonstration would confirm that RTI's technology substantially improves upon conventional and emerging CO_2 capture technologies in terms of energy penalty, capital/operating costs, and environmental performance.

6. Conclusions

Under a cooperative agreement with the US Department of Energy, and part of NETL's CO_2 Capture Program, RTI has led an effort to address and mitigate the challenges associated with solid sorbent CO_2 capture. The overall objective of this project, which has been met by the project team, was to mitigate the technical and economic risks associated with the scale-up of solid sorbent-based CO_2 capture processes, enabling subsequent larger pilot demonstrations and ultimately commercial deployment. An integrated development approach has been a key focus of this project in which process development, sorbent development, and economic analyses have guided each of the other development processes. This approach has resulted in significant improvements in sorbent preparation, process design, operational approaches, and a deeper understanding of the economic factors impacting RTI's technology's bottom-line cost of CO_2 capture target. Through this integrated technology development approach, the project team has advanced RTI's CO_2 capture technology to TRL-4 (nearly TRL-5, with the missing variable being testing on actual, coal-fired flue gas).Having proven the technical and economic viability of RTI's technology, and reducing technical risks (both for the sorbent and process technologies) through bench-scale testing, the next step in the development of this promising technology is to design and construct a pilot-scale system for testing at a coal-fired power plant.

The project team has completed all project objectives and has met nearly all project milestones (the one exception being that the TEA assessment narrowly misses the DOE/NETL CO_2 capture cost target of \$40/T-CO_2. Completion of these objectives has resulted in a fully operational bench-scale CO_2 capture system, collection of important CO_2 capture and heat management performance data, significant improvement to the performance and stability of RTI's PEI-based sorbent, and scale-up of this sorbent to a total of ~200 kg by a commercial manufacturer while retaining all of the performance and physical property metrics of the lab-scale sorbent. Continuous development efforts throughout the project were always focused on improving the performance stability of sorbent candidates, refining process engineering and design, and evaluating the viability of the technology through detailed economic analyses.

<u>Sorbent Development</u>

Sorbent development efforts focused on improving the base PEI CO_2 capture and regeneration performance and the chemical and thermal stability. The team focused on producing a promising first generation fluidized-bed sorbent by leveraging PSU's previous work in developing a promising fixed-bed sorbent. Later efforts were focused on optimizing this "Generation 1" sorbent. The project team focused on developing improved sorbents, needed for bench-scale testing, having improved CO_2 loading capacity, thermal and chemical stability, CO_2 capture rates, and other key properties and identifying the optimal starting materials of PEI, silica, and solvent (based on performance and cost). Scale-up efforts were also conducted. The scaled-up sorbent properties and performance have been compared to lab-prepared samples and the sorbent is nearly identical in all performance metrics. The sorbent is able to achieve a very promising CO_2 loading performance of 9 wt.%. Additional scale-up runs were performed and confirmed the consistency and reliability of the sorbent manufacturing procedure.

During bench-scale testing, the project team initially observed a steady decline in the sorbent's CO_2 capacity over several hundred hours of testing. The project team found the two most important factors affecting sorbent stability: oxygen concentration (i.e. exposure to oxygen) and the temperature at which oxygen exposure occurs. It became clear that PEI-based sorbents should avoid exposure to O_2 at temperatures above 70°C and the appropriate mitigations were performed for bench-scale testing. Over several hundred hours of additional testing there was no noticeable drop in CO_2 capacity in the scaled-up sorbent, thus confirming that oxidative degradation at higher temperatures (i.e. >70°C) was the source of capacity loss. The knowledge gained through sorbent improvement was utilized in process design improvements made to the bench-scale prototype and is absolutely critical knowledge to have when considering the next technology step – design of a pilot demonstration system.

<u>Process Development</u>

In process development, fluidized-bed modeling was first employed to help guide the sorbent improvement efforts, to establish an understanding of how process elements influence CO_2 capture performance, and to provide information for RTI's technology feasibility study. Later efforts were focused on process intensification. A bench-scale contactor evaluation unit (BsCEU) was designed, engineered, fabricated, built, and tested. This system used an inventory of sorbent manufactured by a commercial sorbent manufacturing partner. Experiments were conducted in the BsCEU evaluating key process variables to identify optimal process operating conditions and designs for the FMBR and heat transfer internals. The project team continued with bench-scale testing of the process system towards the end of the project collecting quality performance data to support a more detailed technology feasibility study. Enlisting a third-party fabrication company, the project team made several improvements to the BsCEU (including upgrades to the gas flow control, the tempered cooling water delivery, the particulate filtering mechanism, the heating capability of the current regenerator, and some process measurements) to optimize system performance. In addition, the attainment of a "high-fidelity" system was achieved through a more efficient, multiple-stage contactor design and subsequent execution of the construction and reconfiguration activities. Parametric and long-term performance testing of the bench-scale prototype were carried out at RTI's Energy Technology Development Facility (ETDF).

Through parametric testing, the project team was able to gain significant understanding of how to optimally operate the BsCEU while also being able to gain more consistent control around the variables that impact system performance.The objectives of this long-term testing were to 1) demonstrate that the sorbent-based process could operate continuously without interruption for an extended period of time, 2) identify optimal operating conditions for coal-fired plant applications, 3) identify any detrimental impacts of sorbent exposure to flue gas contaminants, and 4) collect quality performance data to support an updated technology feasibility study. The project team was able to achieve all of these objectives. Throughout a continuous 100-hour test campaign, the rate of CO_2 capture was maintained at 90% ±2% for the vast majority of the testing period, even as the operating conditions were changed multiple times during the campaign. With the operating conditions changing throughout the 100-hour campaign, the CO_2 capture rate was maintained at 90% by varying the sorbent circulation rate. The following conclusions were made from this extended testing: 1) the quality and reliability of CO_2 composition data could be confirmed based on the system's CO_2 mass balance, 2) the fluidization behavior of the sorbent was stable throughout and did not cause any downtime or system upsets, 3) the sorbent can perform well in this environment, maintaining a reasonable CO_2 working capacity between 4 and 7 wt.% loading for the majority of the test campaign, 4) 70 °C is the optimal adsorption temperature, and 5) 120 °C is the optimal regeneration temperature. In general, the BsCEU testing was critical in collecting data that can be used in the design of a larger pilot system.

Economics

Using operating data collected from parametric and long-term testing, a detailed update to the technology feasibility study was performed. An updated cost of CO_2 captured was determined to be 43.3 \$/T-CO_2. Various strategies have been identified that have significant potential to further reduce the capital and operating costs and energy penalty of RTI's solid sorbent-based CO_2 capture process. If any (or all) of these cost reductions materialize, RTI's technology will stand a good chance of meeting DOE/NETL's 2025 goal of \$40/T-CO_2 capture costs. The project team also evaluated the various risks associated with RTI's technology. An EH&S analysis has determined that RTI's technology has no major hurdles for commercial implementation (from the perspective of environmental, health, safety, and operational risks).

Impact

At a broader level, this project has advanced the whole of the solid sorbent CO_2 capture field, with advancements in process engineering and design, technical risk mitigation, sorbent scale-up optimization, and an understanding of the commercial viability and applicability of solid sorbent CO_2 capture technologies for the U.S. existing fleet of coal-fired power plants.

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Acronymns and Abbreviations

c	centi
°	degree/degrees
Δ	delta
$	Dollars (US)
‘	foot/feet
>	greater than
“	inch/inches
k	kilo
µ	micro
m	mili
%	percent
+	plus
+/-	plus or minus
~	approximately
NH_4OH	ammonium hydroxide
ATR	Attenuated Total Reflectance
atm	atmospheric
BET	Brunauer, Emmett, and Teller
BP	Budget Period
BPEI	branched Polyethyleneimine
BsCEU	Bench-scale contactor evaluation unit
BFD	Block Flow Diagram
CO_2	carbon dioxide
Ca	calcium
C	Celsius
cm	centimeter
Cm^3	cubic centimeter
CeO_2	cerium oxide
CFD	computational fluid dynamics
Cu	Copper
COE	cost of electricity
DI	Davidson Index
DOE	Department of Energy
DoE	Design of Experiments
DRIFTS	Diffuse Reflectance Infrared Fourier Transform Spectroscopy
EHS	Environmental, Health, and Safety
ETDF	Energy Technology Development Facility
etc.	et cetera (so forth)
EDEC	ethylenediamine end-capped
F	Fahrenheit
FE	Fossil Energy
FMBR	fluidized, moving-bed reactor
FS	fumed silica

ft.	feet
ft^2	square feet
Ft^3	cubic feet
FG	flue gas
FGD	flue gas desulfurization
FBR	fluidized-bed reactor
FTIR	Fourier Transform Infrared Spectroscopy
gph	gallons per hour
GHSV	gas hourly space velocity
GUI	graphical user interface
g	gram
HMIS	Hazardous Materials Identification System
h	hour
HCl	hydrogen chloride
HDI	hexamethylene diisocyanate
ICOE	increase in cost of electricity
i.e.	id est (that is)
in.	inches
Inc.	Incorporated
IR	infrared
kg	kilogram
kJ	kilojoule
kPa	kilopascal
kmol	kilomole
kW_e	kilowatt electric
kW_t	kilowatt thermal
LOI	loss on ignition
LPEI	linear Polyethyleneimine
MBS	Molecular Basket Sorbent
MCM	Mobil Crystalline Materials
Me	metal
MFC	mass flow controller
MW_e	megawatt electric
MW_t	megawatt thermal
m	meter
m^2	square meters
m^3	cubic meters
min	minute
mol	mole
mmol	mili mole
MEA	monoethanolamine
MSU	Michigan State University
MW	molecular weight
NETL	National Energy Technology Laboratory
NG	natural gas
N	nitrogen

NO_x	nitrogen oxides
OD	outer diameter
ODE	ordinary differential equation
OSBL	outside battery limits
O_2	oxygen
PBR	packed-bed reactor
ppm	parts per million
ppmv	parts per million by volume
p	per
PEI	Polyethyleneimine
PSD	particle size distribution
PSRI	Particulate Solid Research Incorporated
PSU	Pennsylvania State University
P&ID	Piping and Instrumentation Diagram
lb	pound
psia	pounds per square inch (atmospheric)
PFD	process flow diagram
PHA	process hazard analysis
R&D	research and development
RTI	Research Triangle Institute
r.t.	room temperature
ROG	regeneration off gas
s	second
SBA	Santa Barbara Amorphous
SEM	Scanning Electron Microscopy
SCFM	standard cubic per minute
S/G	solids to gas ratio
Si	Silicon
SLPM	standard liters per minute
Na	sodium
$NaHCO_3$	sodium bicarbonate
NaOH	sodium hydroxide
sorb	sorbent
SOTA	state of the art
SG	stripping gas
SO_2	sulfur dioxide
TEA	Techno-economic Analysis
Temp.	temperature
TEOS	tetraethyl orthosilicate
TiO_2	titanium dioxide
$TiOSO_4$	titanium (IV) oxysulfate
TGA	thermogravimetric analysis
TRL	technology readiness level
U.S.	United States
UV	ultraviolet
vFBR	visual Fluidized-bed Reactor

vol	volume
H_2O	water
w.c.	water column
WSS	Water-stable Sorbent
wt.%	weight percentage
yr	year
Zn	Zinc
ZnO	zinc oxide
