DE-FE0031522: Advance Syngas Cleanup for Radically Engineered Modular Systems (REMS)

Atish Kataria, Pradeep Sharma, Jian-Ping Shen, Kelly Amato, Gary Howe, Vijay Gupta, and Lindsey Chatterton

April 9th, 2019

RTI INTERNATIONAL | Center of Technology for Energy, Environment & Engineering

Small-Scale Modularization of Gasification Technology Components for REMS – Objectives of the FOA

- DOE's Clean Coal Program is focused on developing advanced technologies that increase the performance, efficiency and availability of existing and new coal-fueled power generation
- Develop emerging gasification technologies that can be scaled down to modular small-scale (1-5 MW) via the Radically Engineered Modular Systems (REMS) concept
- Develop REMS process technologies that are cost effective relative to SOTA commercial technology, due to low cost fabrication via advanced manufacturing
- REMS-based combined heat and power or polygeneration system implemented in remote areas subjected to traditionally high energy costs

Project Objective: Develop modular sorbent-based warm syngas cleanup designs that will enable 1- to 5-MW REMS-based plants utilizing all of our abundant domestic coal reserves to be cost-competitive with large state-of-the-art commercial plants.

Project Objectives

Objective: Develop modular sorbent-based warm syngas cleanup designs that will enable 1- to 5-MW REMS-based plants utilizing all of our abundant domestic coal reserves to be cost-competitive with large state-of-the-art commercial plants.

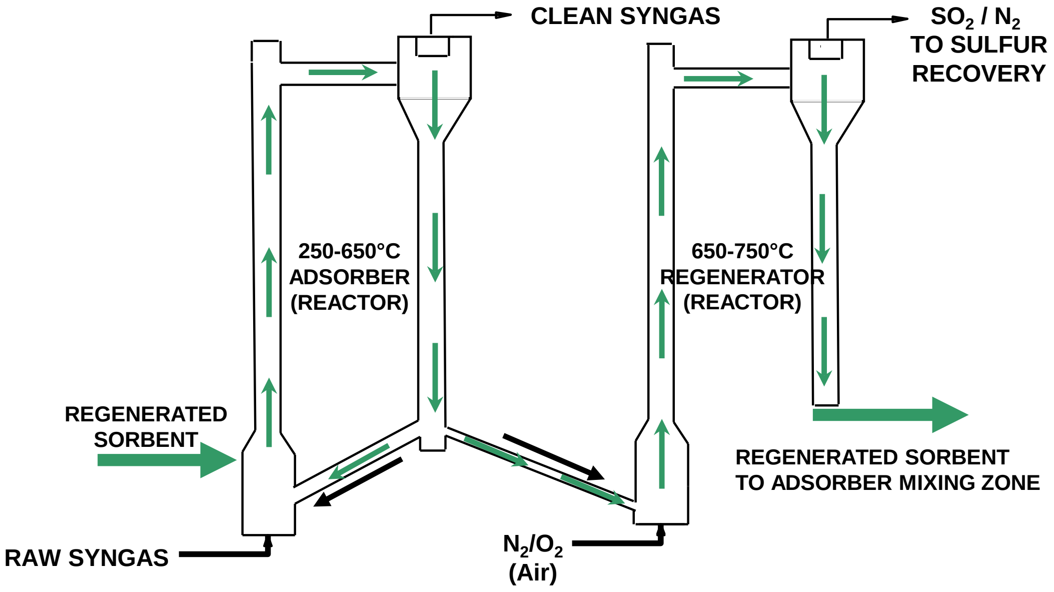
- Build on the extensive development work of RTI’s Warm-gas Desulfurization Process (WDP)
- Study desulfurization performance of WDP sorbent for low-sulfur syngas streams
- Develop a fluid-bed regenerator for REMS application, especially with low-sulfur syngas
- Develop a fixed-bed sorbent and process for its inherent suitability for small-scale modularized systems
- Develop and optimize conceptual designs for desulfurization processes based on fluidized-bed and fixed-bed reactors

RTI Warm Gas Desulfurization Process (WDP) - Overview

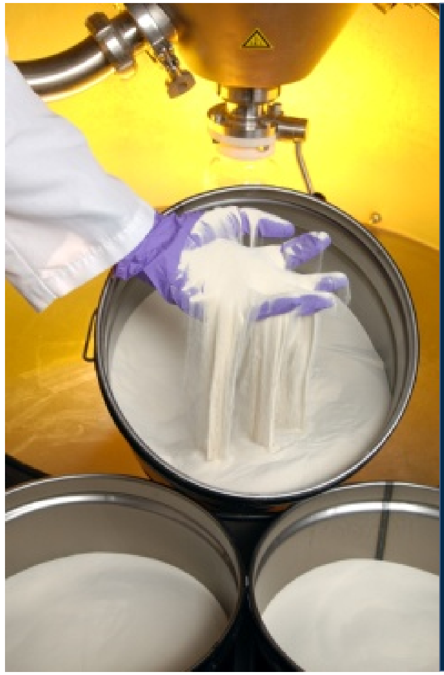
Enables high removal of total sulfur (≥99.9%) from syngas at temperatures as high as 650° C.

A unique process technology based on dual transport reactor loops (similar to FCC reactor designs)…

… and on a regenerable, high-capacity, rapid acting, attrition-resistant sorbent.



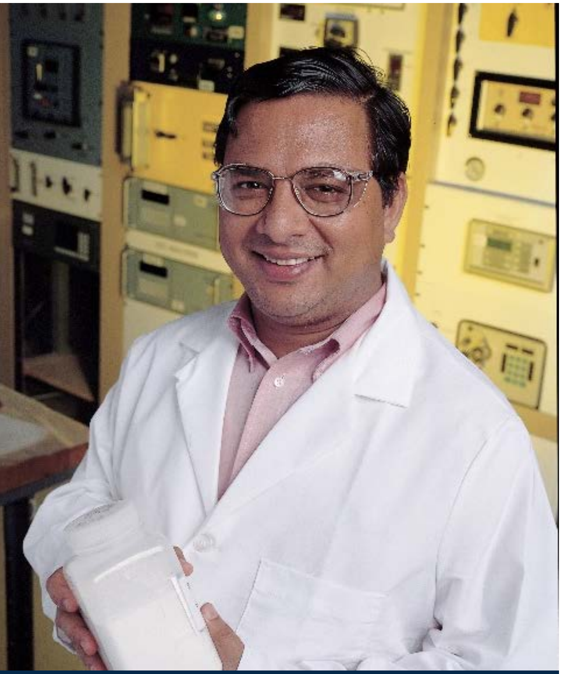
RTI Warm Gas Desulfurization Process (WDP)



RTI Proprietary Desulfurization Sorbent

- R&D 100 Award
- Unique highly-dispersed nanostructures
- Developed in long-term cooperation with Clariant (~100 tons to date)
- Covered by extensive US & International patents, including several recent improvements

Technology Development Timeline



Invention
(2001)

Lab/Bench Testing
(2001-2003)

Pilot Testing
(2006-2008)

Demonstration at TECO, Tampa, FL
(2010-2016)

WDP Potential to Address REMS FOA Objectives

Invention (2001)

Proprietary RTI sorbent

R&D 100 Award (2004)

Lab/Bench Testing (2001-2003)

RTI, NC

Concept proven & modeled

Pilot Testing (2006-2008)

Eastman Chemical Co., TN

3000 hr, coal-derived syngas

Demonstration at TECO, Tampa, FL (2010-2016)

50 MWe equivalent scale, coal/petcoke-derived syngas

$168.8MM DOE funding to design, construct, operate

NEAR REMS-scale

How does this technology development apply to REMS & low-sulfur coals?

Key Strengths of WDP still apply

- Rapid reaction rates of desulfurization and regeneration
- Proven material chemistry and scale-up
- Fundamentally applicable to any sulfur concentration and pressure
- Modular design expected to reduce capital costs over other technologies
- Anticipate similar energy savings and GHG reductions as large-scale

Knowledge gaps for application

- Expanded experimental data for low-sulfur syngas
- Identify modifications to the current process configurations to enable deployment of modular, cost-competitive cleanup systems
- Hydrodynamic data for fluid bed regenerator
- Processing steps to yield fixed-bed extrudate
- Performance of extrudates for fixed-bed
- Techno-economic assessment for REMS

Framework for Project

Extend WDP sorbent testing towards low-sulfur syngas (Tasks 2)

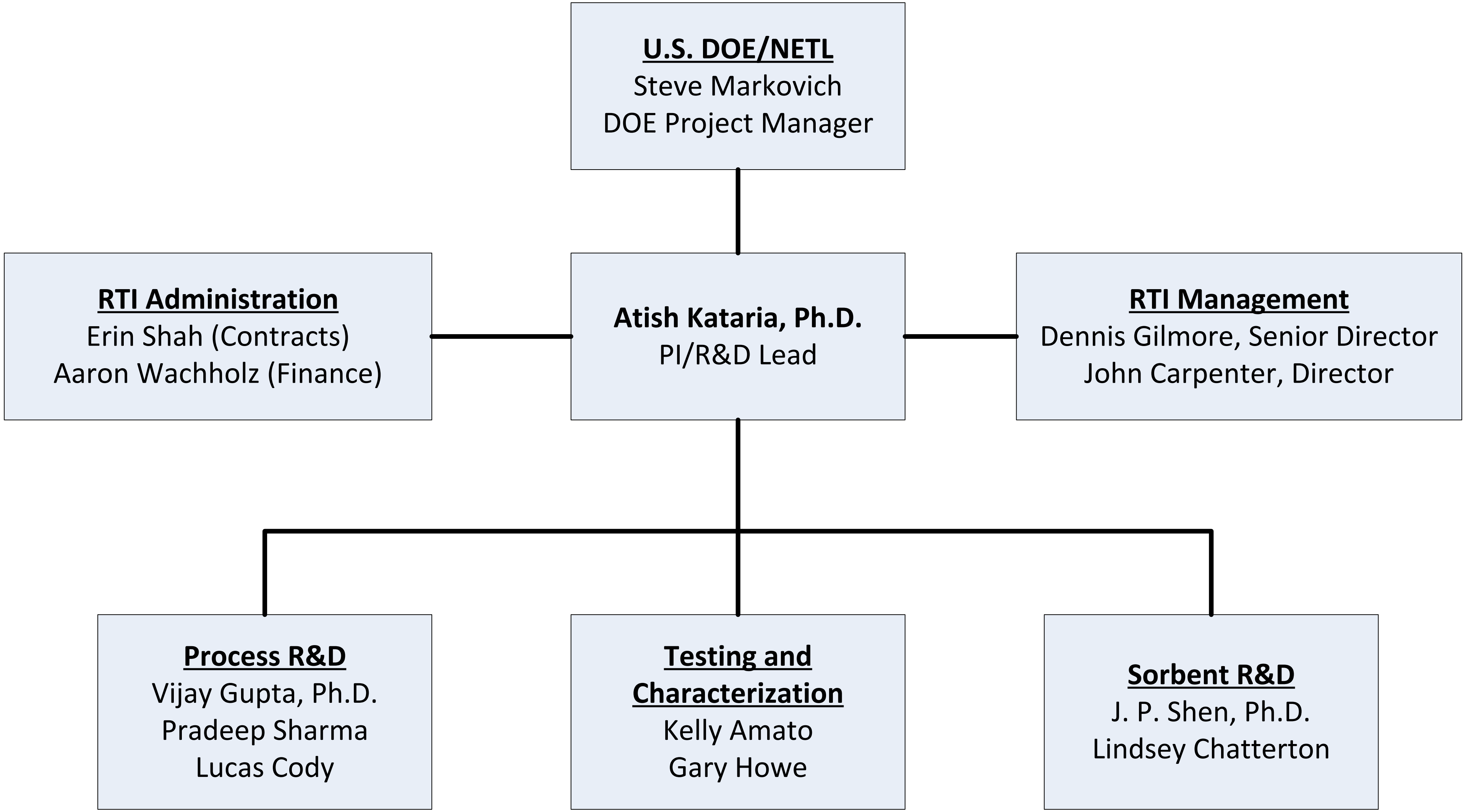
Fixed-bed process for low-sulfur syngas (Task 4)

Key Focus Areas

Modified fluidized-bed process for low-sulfur syngas (Task 3)

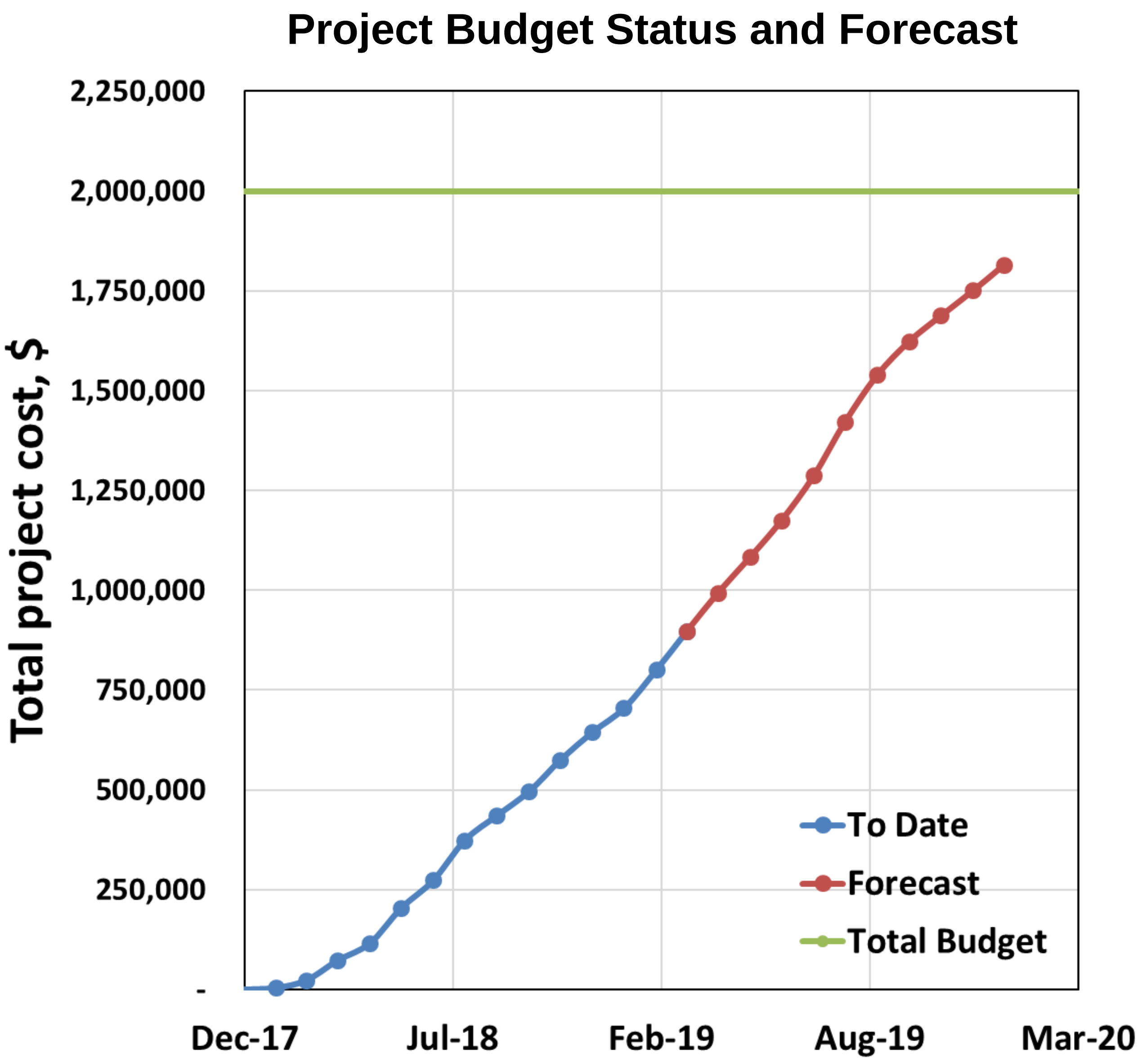
Process Modeling and Techno-Economic Assessments (Task 5)

Task 1 – Project Management

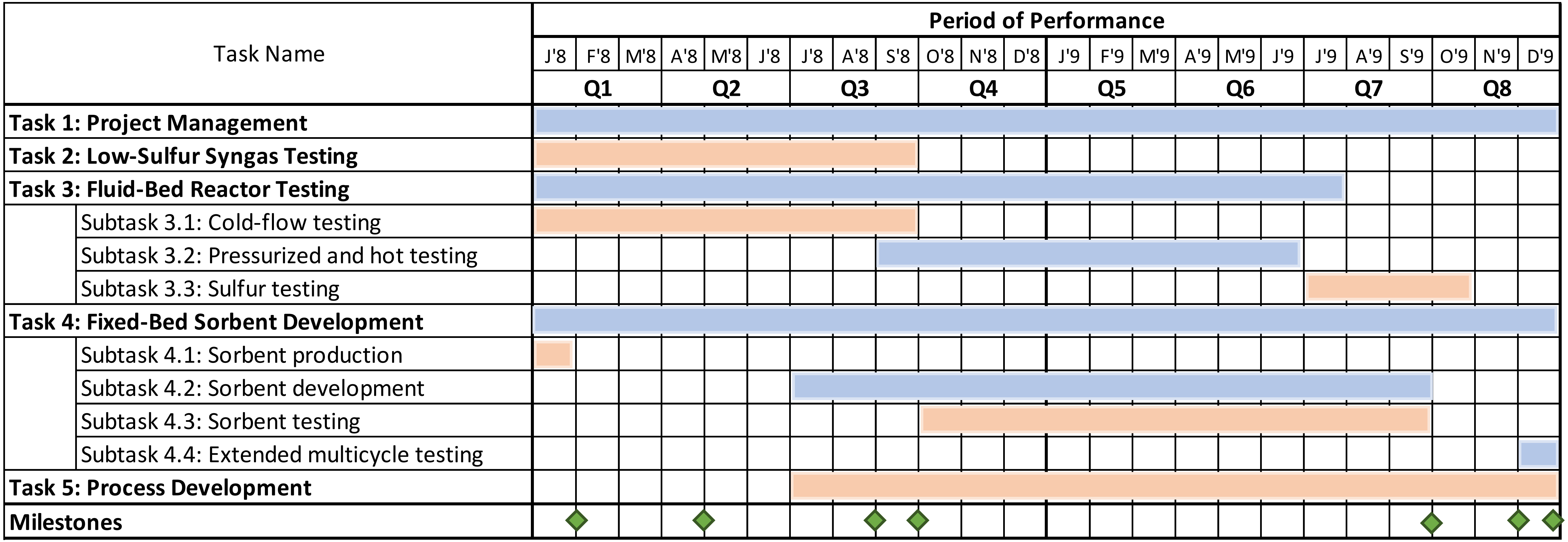


Project Management Overview

- Project making good technical progress with all milestones on track
- All necessary resources available
  - Project providing training opportunity to young engineers and chemists
- On track with all the technical and financial reporting requirements
- Made a presentation at the NETL Peer Review meeting in November 2018
  - Responded to Review Panel recommendations
  - Incorporated all four recommendations
- Investigating commercial interest in the fixed-bed process with varying sources for low sulfur



Project Timeline



Project Milestone Log

ID	Budget Period	Title	Completion Date	Actual Date
1	1	Submission of revised PMP to DOE	2/1/2018	2/16/2018
2	1	Pilot-scale sorbent wet cake delivered to RTI	4/30/2018	8/29/2018
3	1	Testing to generate a database for fluidized-bed sorbent desulfurization performance for low-sulfur syngas completed.	9/30/2018	9/30/2018
4	1	Hydrodynamic cold-flow testing supporting design of fluid-bed regenerator completed.	8/31/2018	9/5/2018
5	2	Demonstration testing of fluid-bed regenerator design at simulated operating conditions validating design for techno-economic analysis completed.	9/30/2019	-
6	2	Demonstration testing of fixed-bed sorbent and process at simulated operating conditions validating design for techno-economic analysis completed.	11/30/2019	-
7	2	Completion of techno-economic analyses for a full REMS plant incorporating fluid- and fixed-bed modular desulfurization systems, with goal of achieving a cost target of < $90/MWh[1].	12/31/2019	-

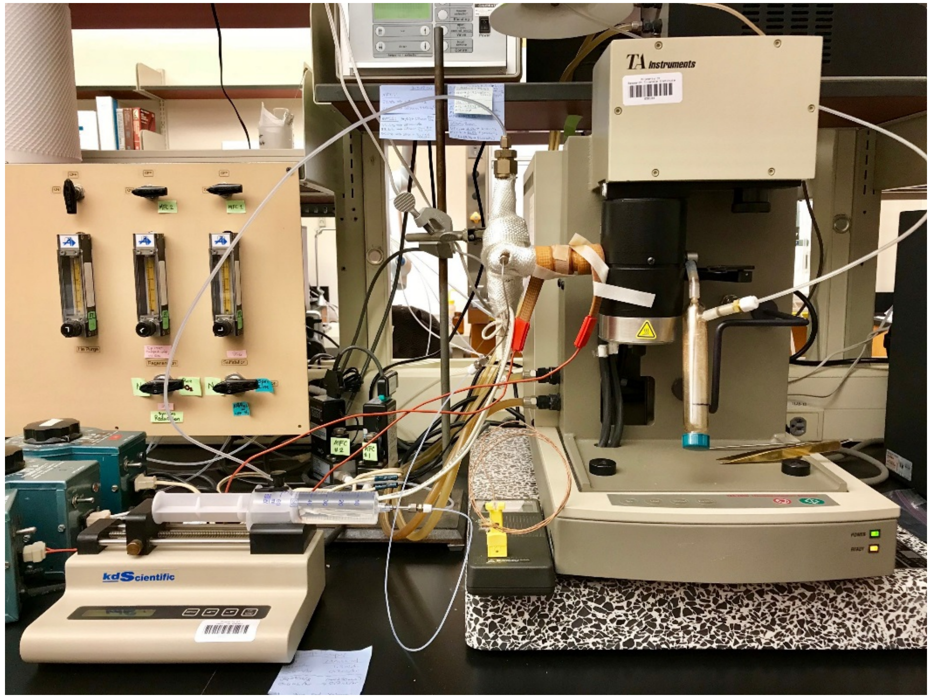
[1] This value is based on values provided in DOE/NETLs' "Cost and Performance Baseline for Fossil Energy Plant Volume 3a: Low Rank Coal to Electricity IGCC Cases (DOE/NETL2010/13990) which have been updated for 2016 costs.

Task 2.0: Low-Sulfur Testing

- Objective: Study desulfurization performance of WDP sorbent for low-sulfur syngas streams
- Commercially available fluidizable WDP sorbent was used for testing
- Testing performed in our existing Bench-Scale Fluidized-Bed Sorbent Testing System and atmospheric pressure TGA
- Parametric testing covered the typical operating conditions of temperature, pressure, syngas composition, and residence time
- Results validated the excellent performance of sorbent even under low-sulfur syngas conditions
- Task 2 and Milestone 3 completed

% Complete	100

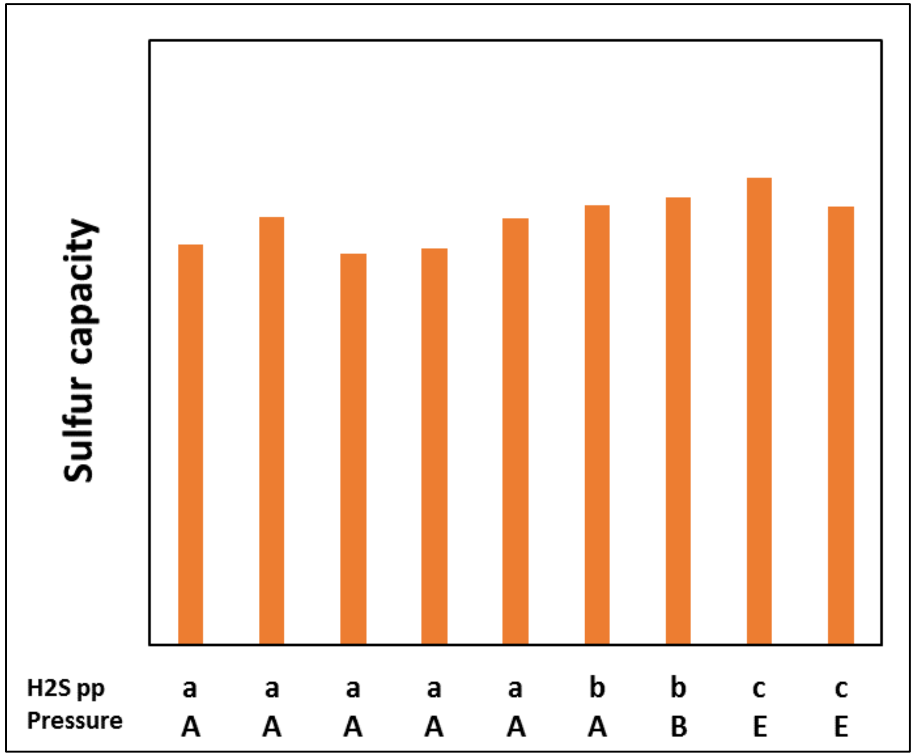
Atm-TGA and Bench-Scale Sorbent Testing System

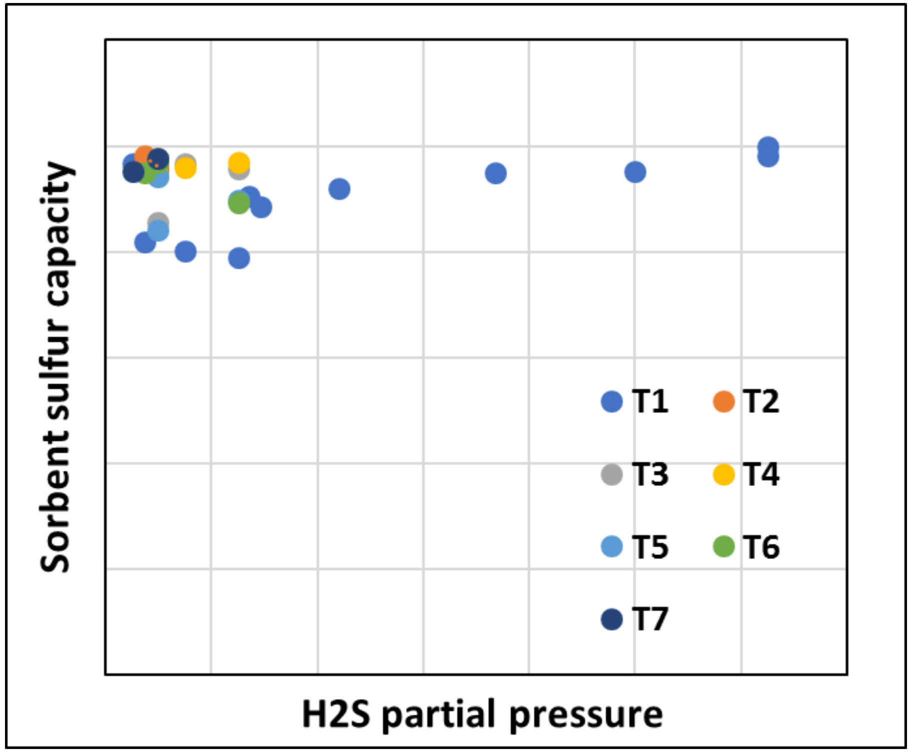


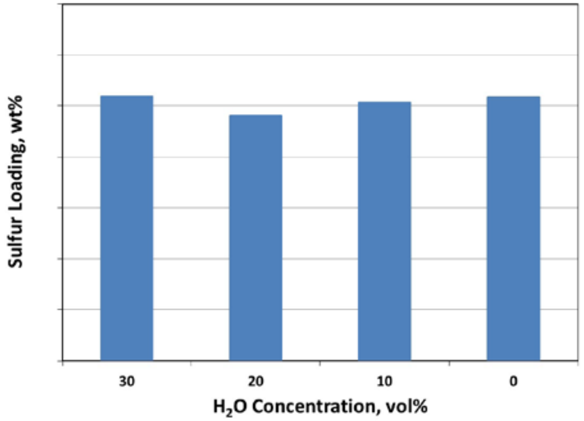
- Sorbent testing in simulated syngas and oxidation gases
- Operates at atmospheric pressure and up to 700°C
- Utilizes 5 to 20 mg of sorbent material
- Cross flow operation allows for kinetic measurements

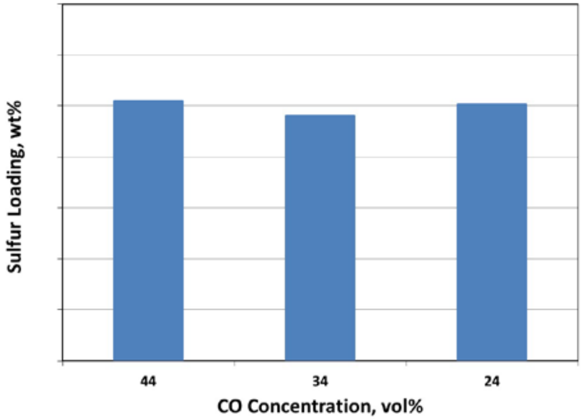
- Sorbent testing in simulated syngas and oxidation gases
- Operate up to 40 barg and 700°C
- Utilizes 100-300 g material
- Suspended quartz reactor inside stainless steel pressure vessel

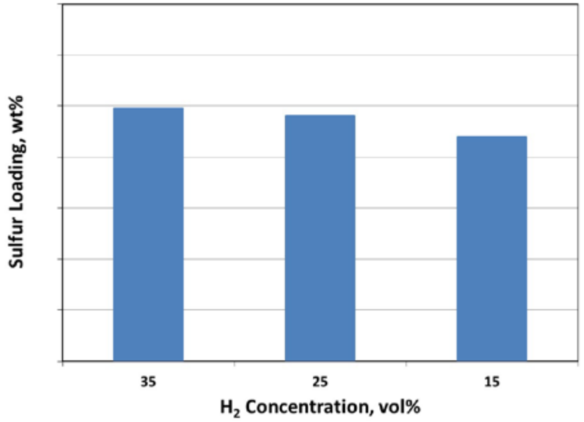
Equilibrium Sorbent Sulfur Loading





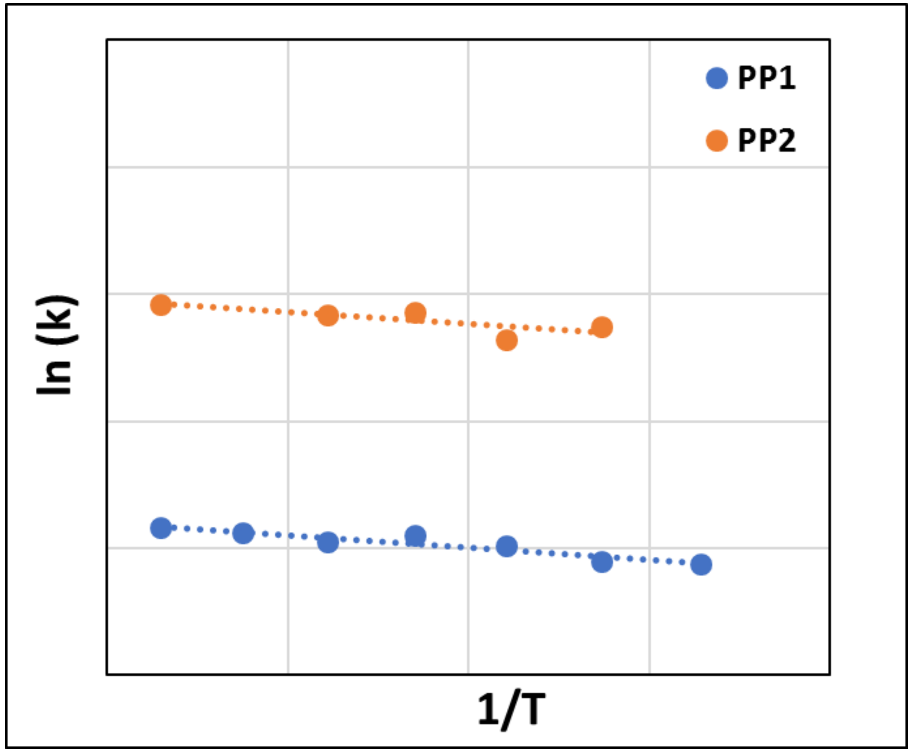


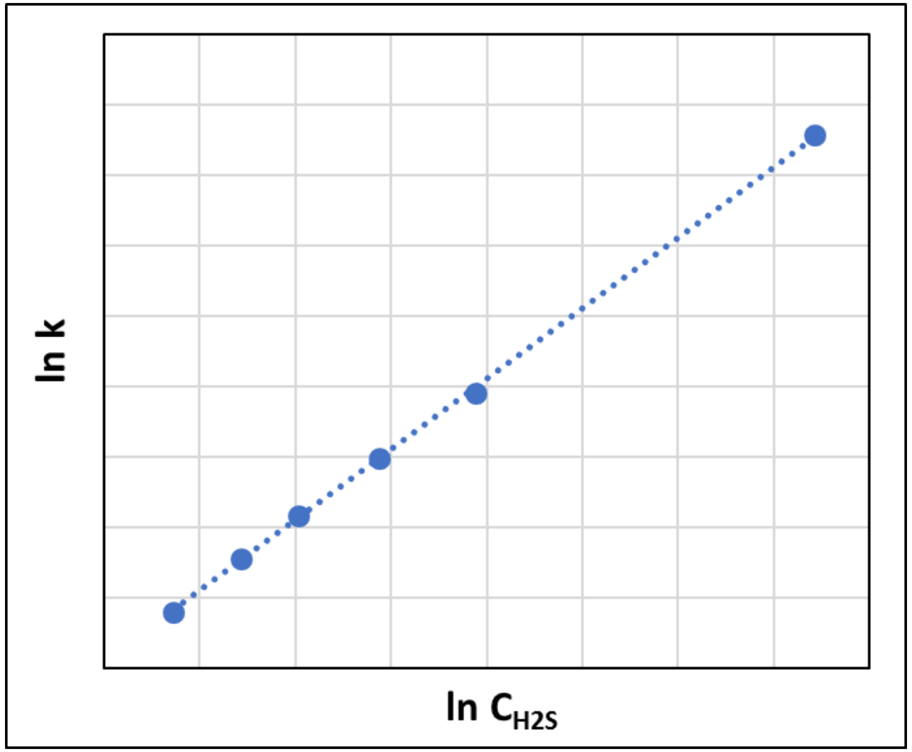




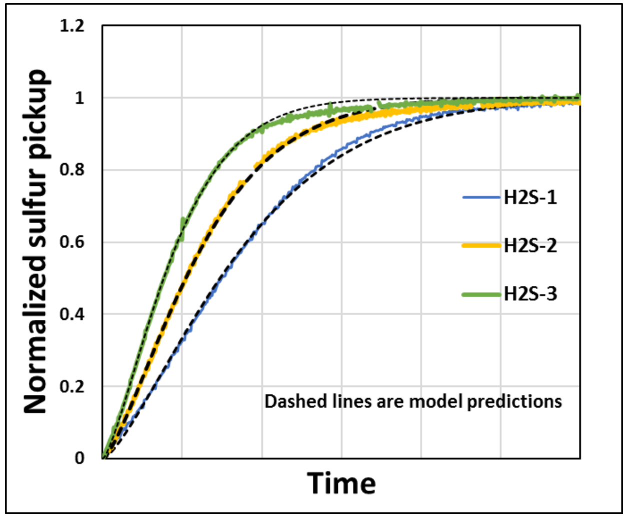
- Tested performance of fluidizable RTI-3 sorbent under varying operating conditions – temperature, pressure, H_2S concentration and syngas composition
- Generated the desired low-sulfur syngas sorbent performance database and quantified the variation in equilibrium sorbent capacity as a function of changing test conditions
- Sorbent remained stable over multiple cycles and varying test conditions

Adsorption Kinetics

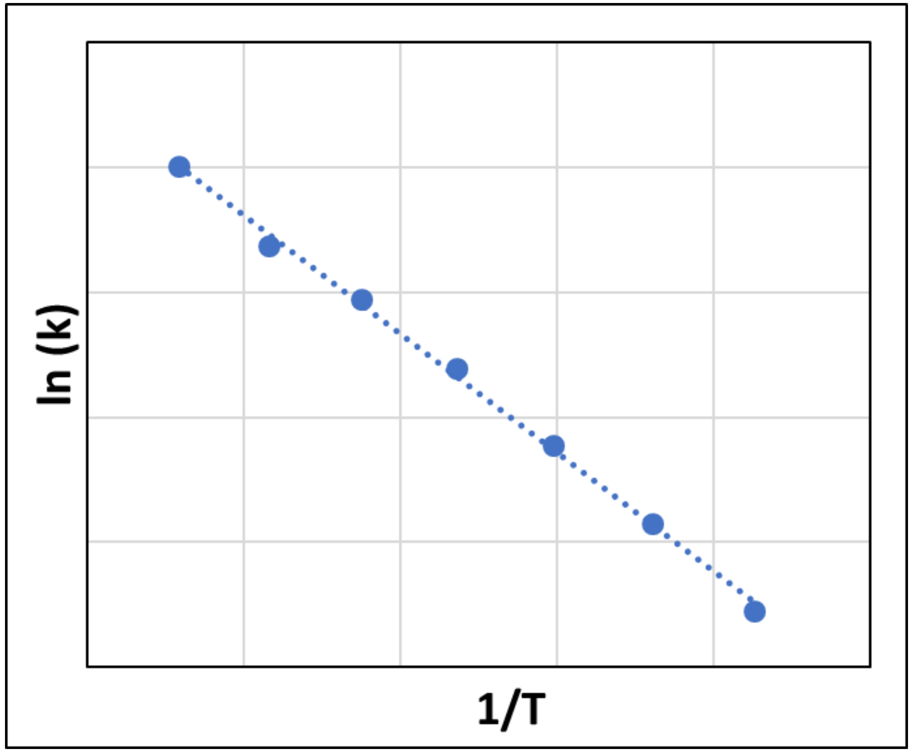


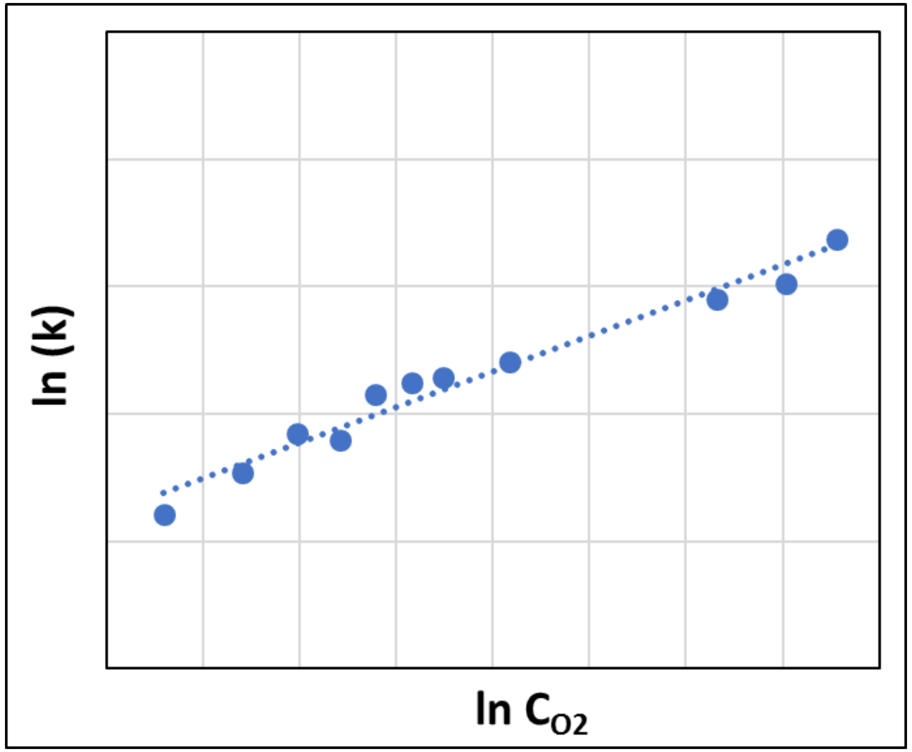


- A simplified kinetic expression was generated to incorporate the effect of adsorption operating parameters (temperature, H_2S partial pressure, etc.)
- Excellent agreement was observed between the experimental and model-predicted data

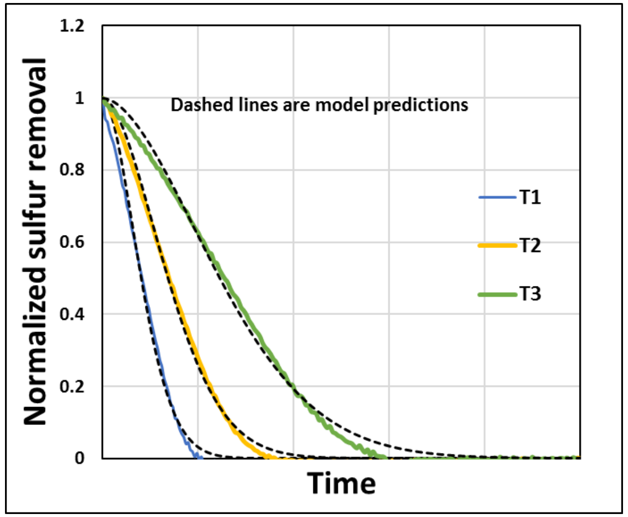


Desorption Kinetics





- A simplified kinetic expression was generated to incorporate the effect of regeneration operating parameters (temperature, O_2 partial pressure, etc.)
- Excellent agreement was observed between the experimental and model-predicted data

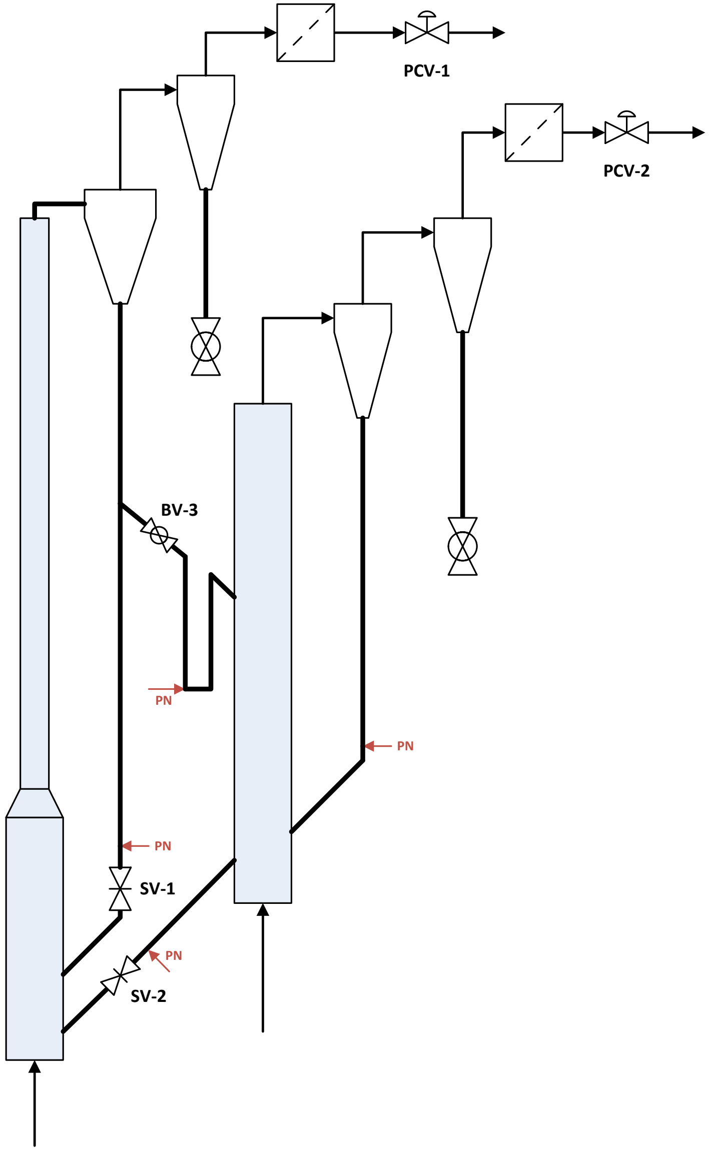


Task 3.0: Fluid-Bed Regenerator Development

- Objective: Development of a fluid-bed regenerator for REMS application, especially with low-sulfur syngas
- Completed acquiring hydrodynamic data for the sorbent at key regions within the fluid-bed reactor system using the existing cold-flow unit (Milestone 4)
- Additional hydrodynamic data will be collected in the hot-flow testing system at a combination of pressure and/or temperature to enable extending the application of the data to commercially relevant operating conditions
- Perform cyclic sorbent sulfur testing in the hot-flow unit under simulated operating conditions
- Hydrodynamic data generated at cold and hot/pressurized conditions will be used to develop sorbent hydrodynamic model

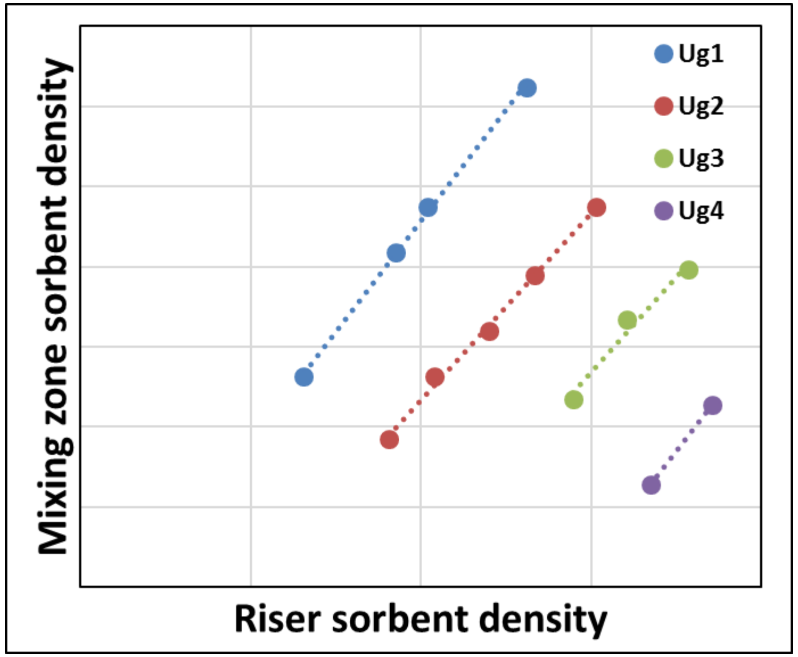
% Complete	50
Sub-task 3.1	100
Sub-task 3.2	50
Sub-task 3.3	NA

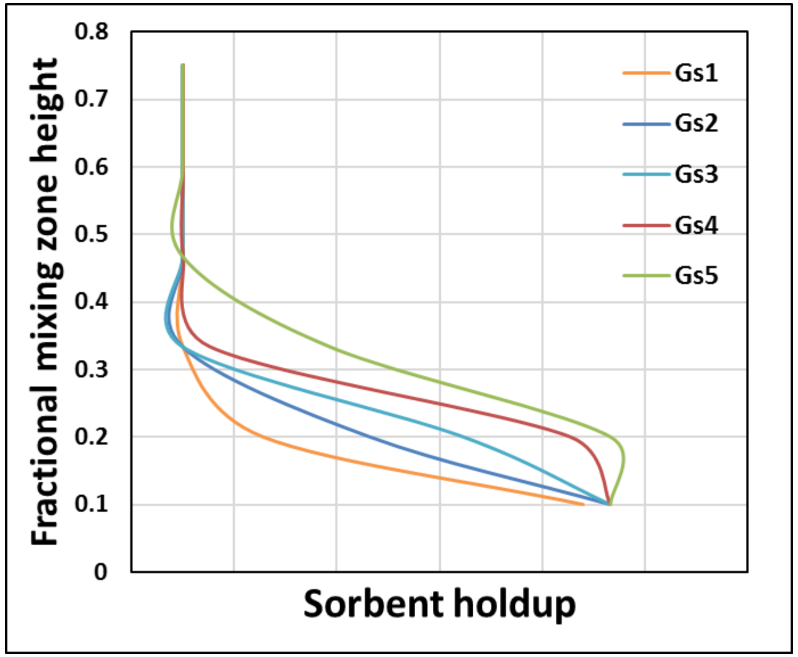
Subtask 3.1: Cold-Flow Testing

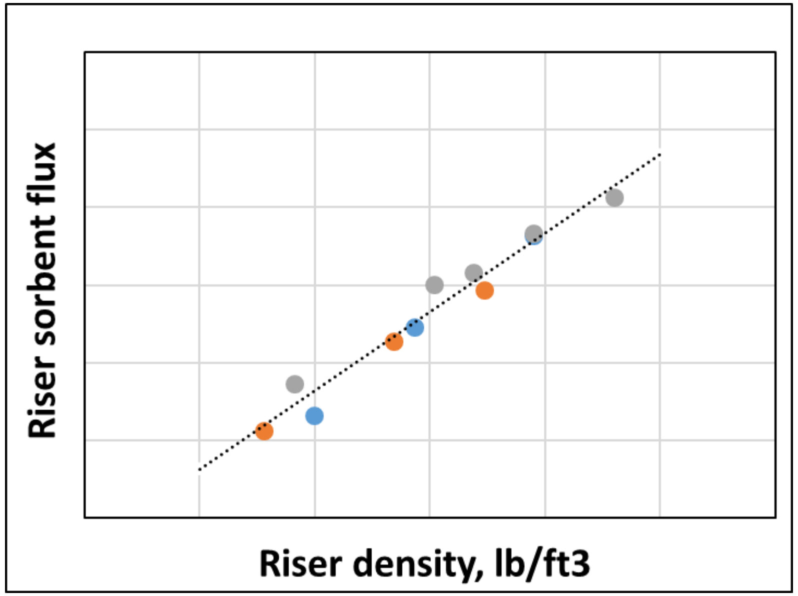


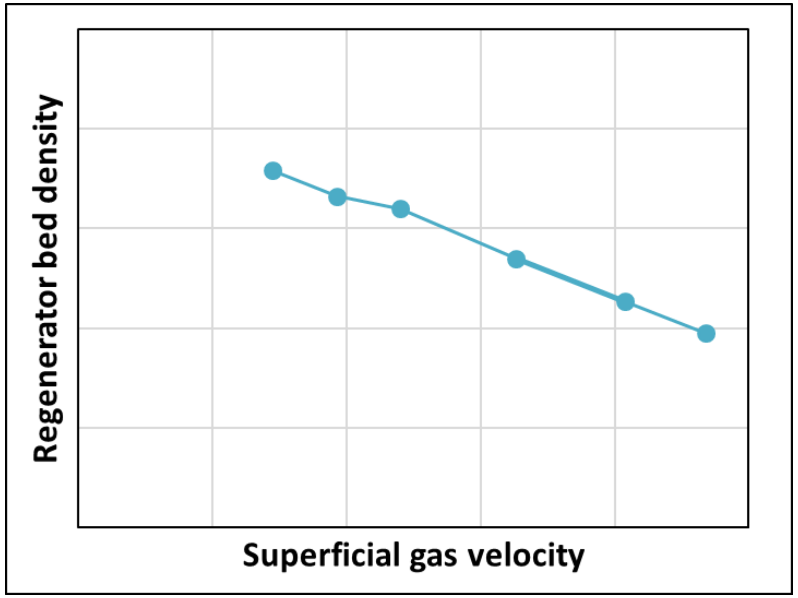
- Transport reactor absorber
  - Mixing zone-Riser Design
    - 8” mixing zone and 4” riser
- 6” fluidized bed regenerator
- 2” transfer lines
- Line size slide valves
  - Recirculation and transfer
- Two cyclones in series
- Extensively instrumented with dP transmitters

Milestone 4 Complete – Acquisition of Cold-Flow Hydrodynamic Data

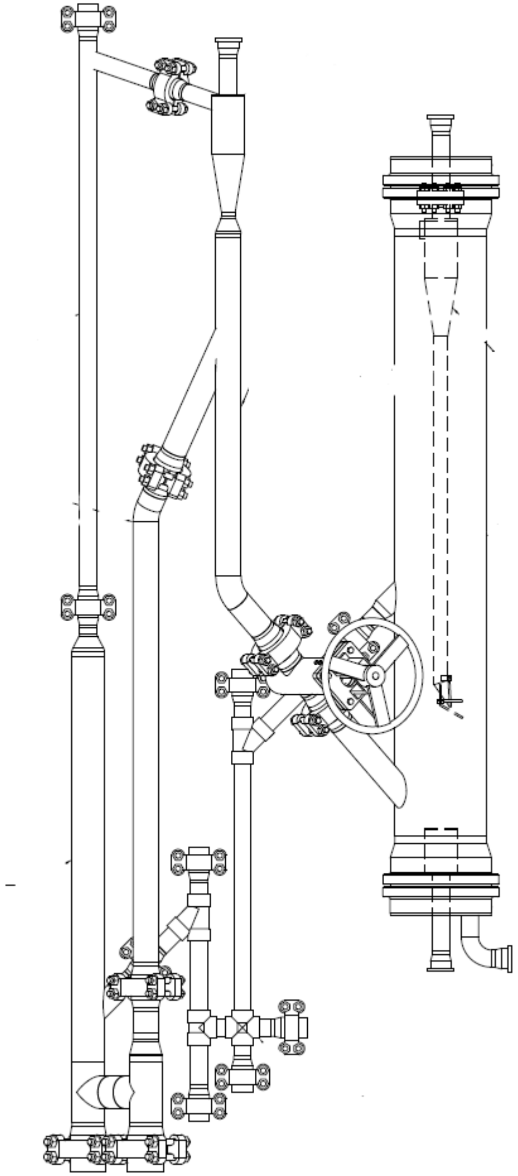




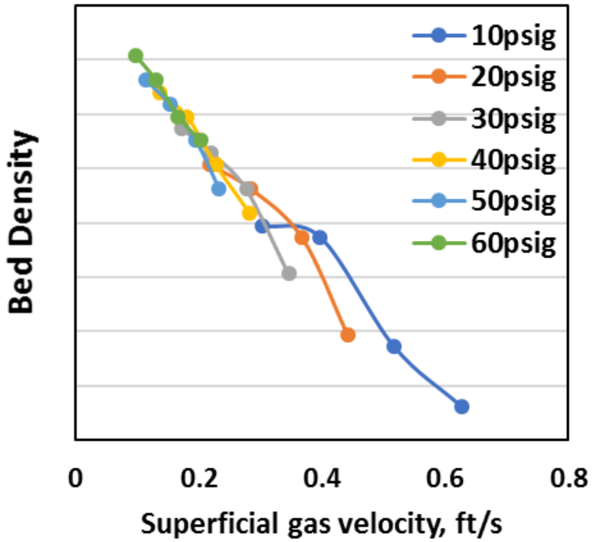


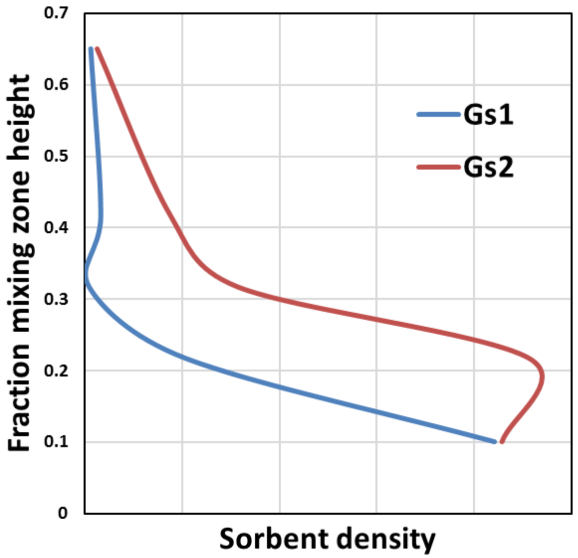


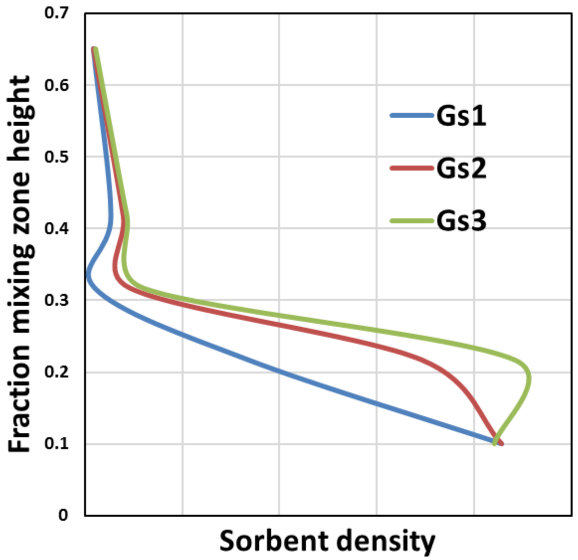
Subtask 3.2 and 3.3: Hot-Flow Testing

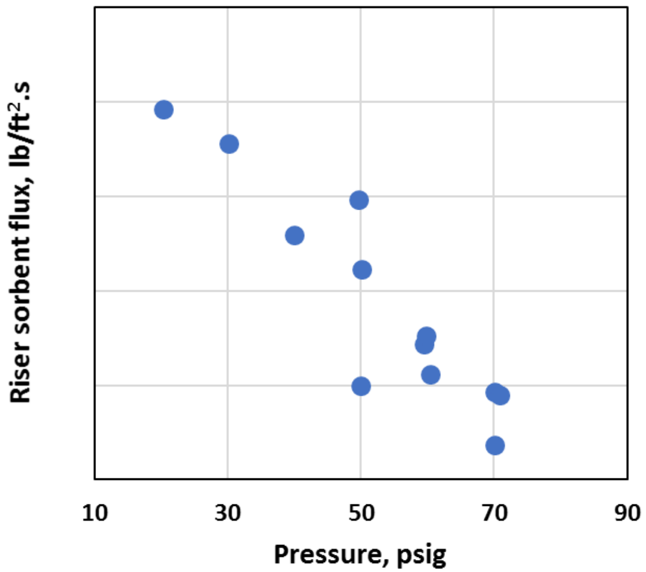


- Design similar to the cold-flow unit
- Design limits of 150 psig and 650°C
- Completed commissioning and shake down
- Generated hydrodynamic data at ambient conditions and varying pressure
- Will study the effect of temperature in the next quarter
- Cyclic adsorption-regeneration testing in Q6-Q7









Task 4.0: Fixed-Bed Sorbent Development

- Objective: Develop a fixed-bed sorbent and process for its inherent suitability for small-scale modularized systems
- Proven chemistry of the fluidizable form will be leveraged by using co-precipitation wet cake to optimize the process of making extrudates
  - Received pilot-scale wet cake from Clariant (WDP sorbent licensed supplier) – Milestone 2 complete
  - Optimization parameters of interest are binder material and composition, and calcination temperature
- Physical properties of fresh and used sorbents will be tested for surface area, compositional analysis, XRD, and crush strength
- Parametric testing being used to optimize fixed bed process parameters (time sequences, regeneration conditions, purge, etc.)
- Optimized fixed-bed sorbent will be tested for extended stability for >50 cycles

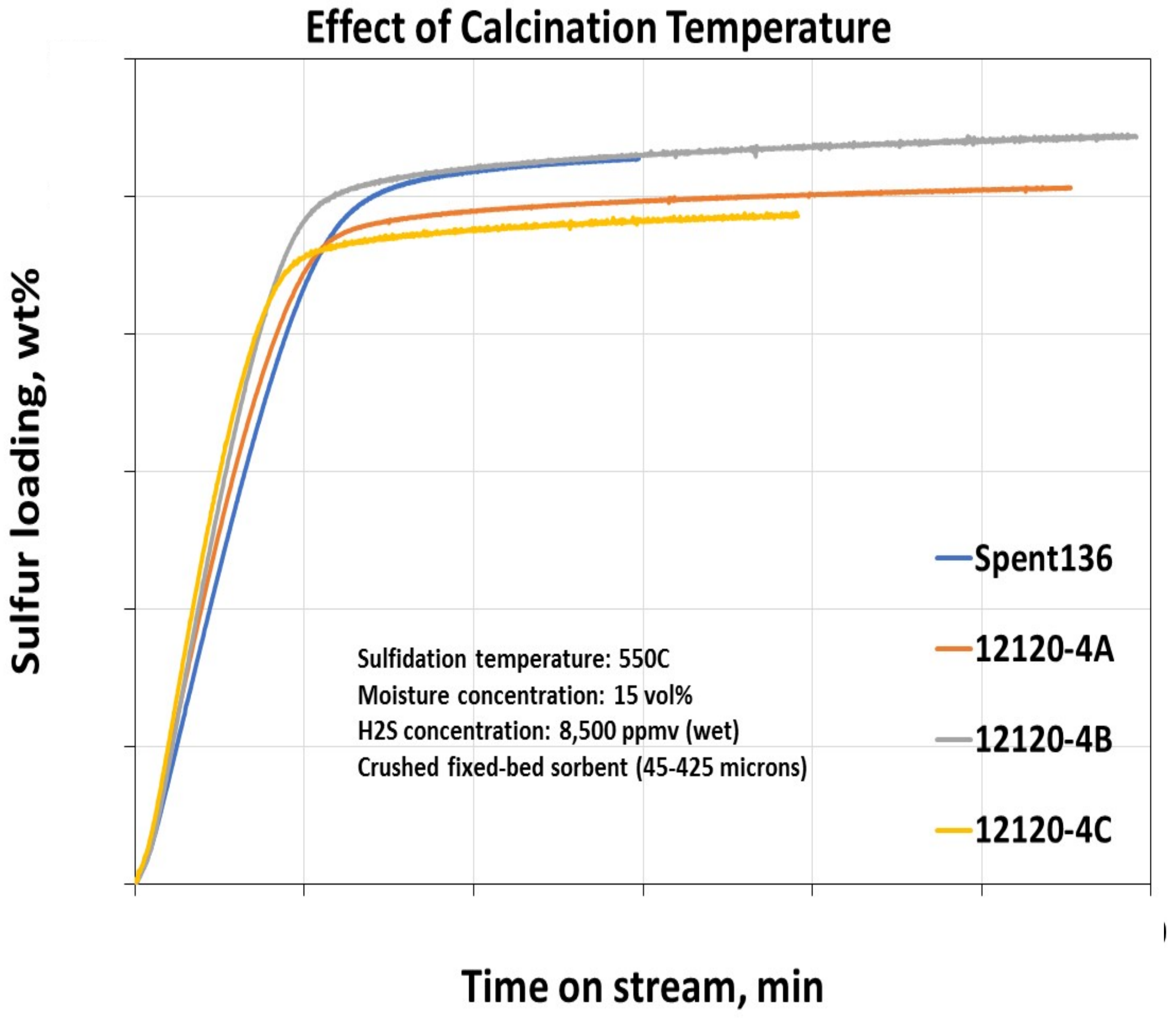
% Complete	**30**
Sub-task 4.1	100
Sub-task 4.2	40
Sub-task 4.3	NA

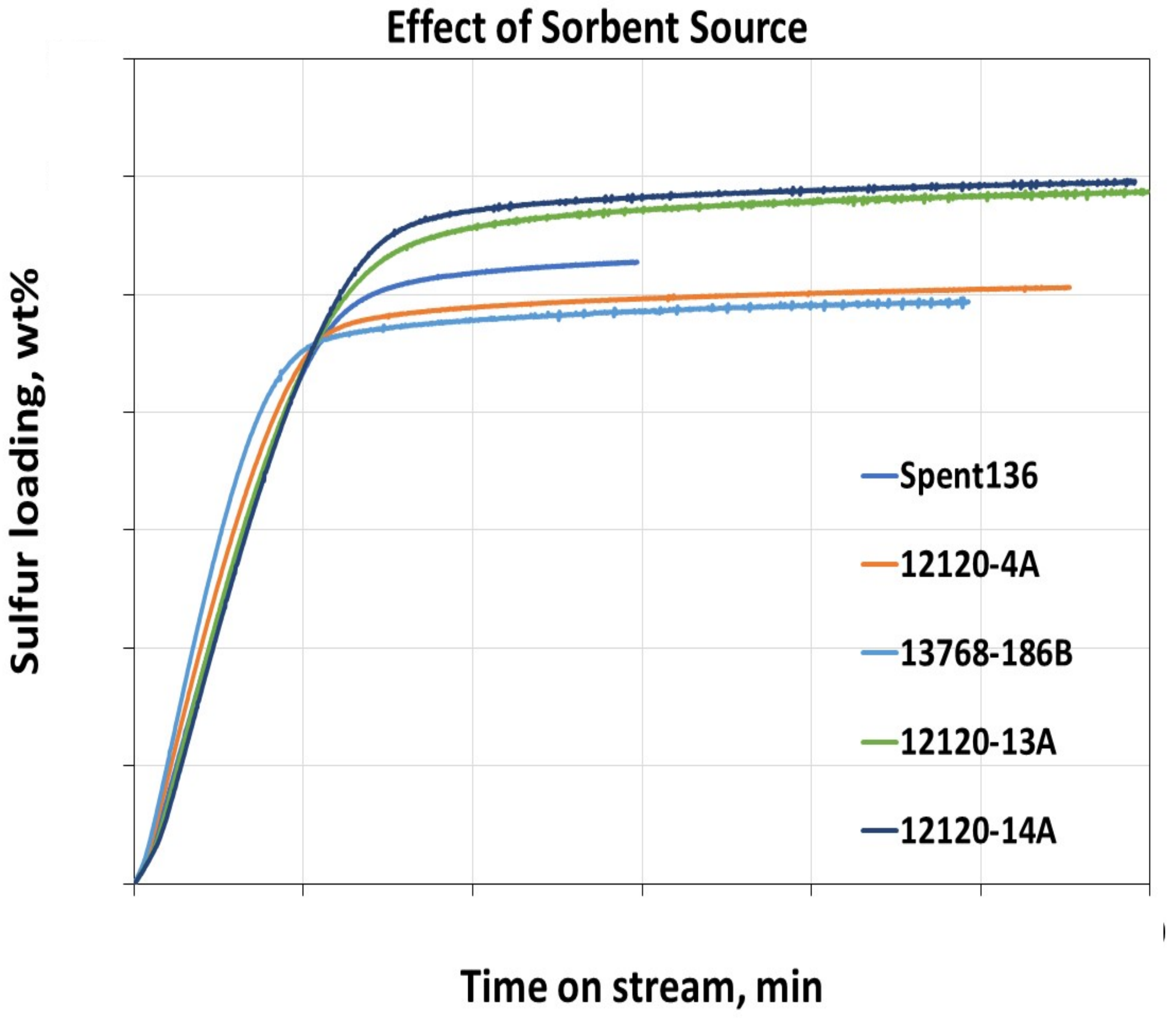
Promising Extrudates Synthesized

Sample ID	Synthesis of Extrudates		Characterization			
	Powder Source	Calcination Temp	Crush Strength, N/mm	Surface area, m2/g	Pore size, A	Pore volume, cc/g
12120-4A	A	E	80.5	27.7	126	0.087
12120-4B	A	F	84.0	35.5	102	0.091
12120-4C	A	G	59.0	25.4	130	0.082
13768-186B	A	E	-	28.9	127	0.092
12120-13A	B	E	38.8	22.4	168	0.094
12120-14A	B	E	68.7	24.9	165	0.103

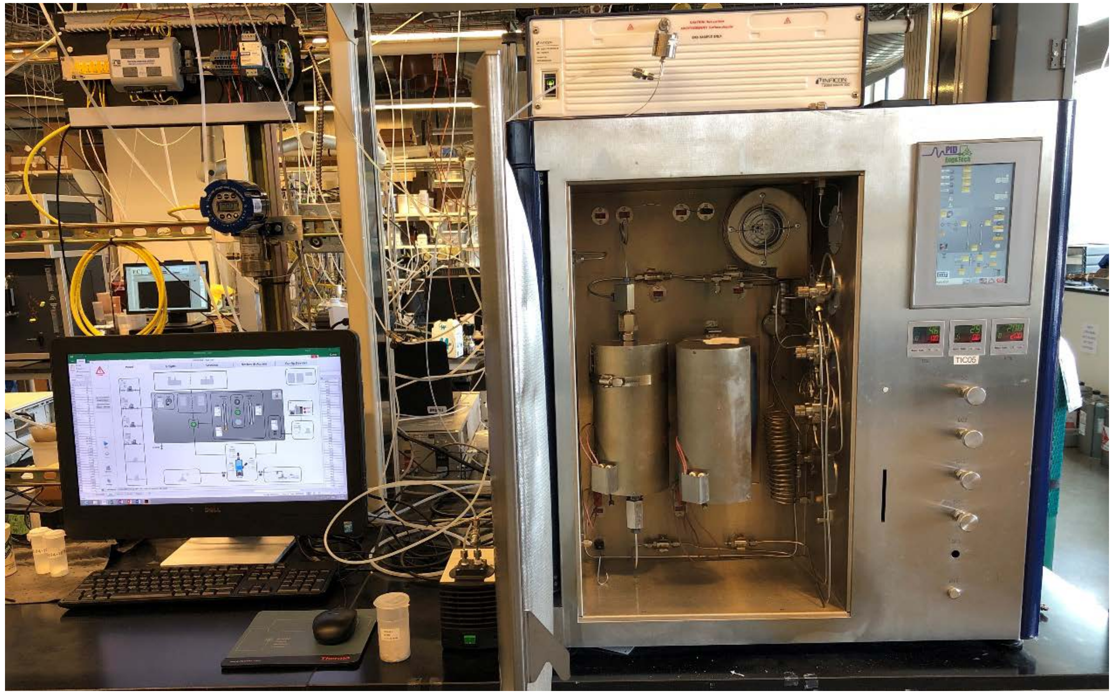
Steam reforming catalysts crush strengths in the range of 25 to 50 N/mm

Fixed-Bed Sorbent Performance – Effect of Synthesis Parameters



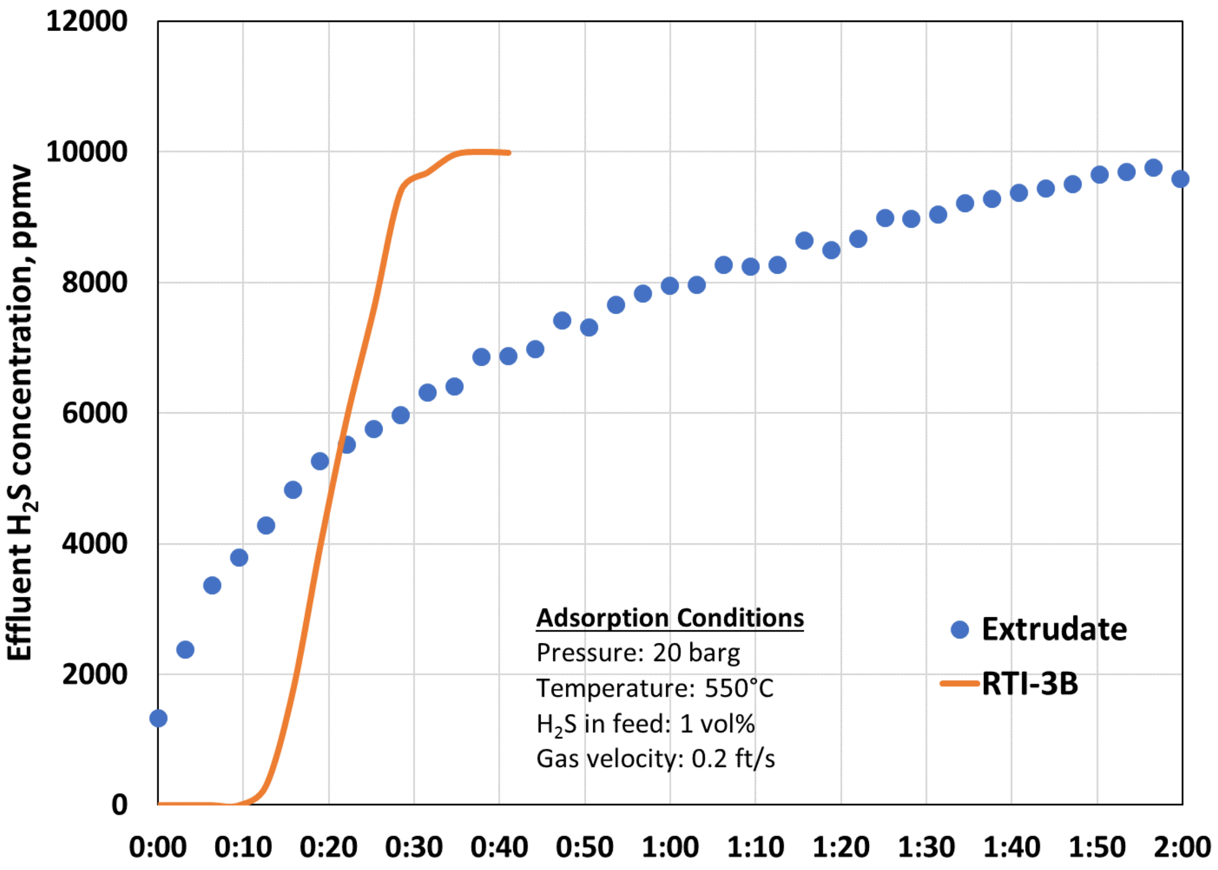


Fixed-Bed Sorbent Performance – Data for Optimization

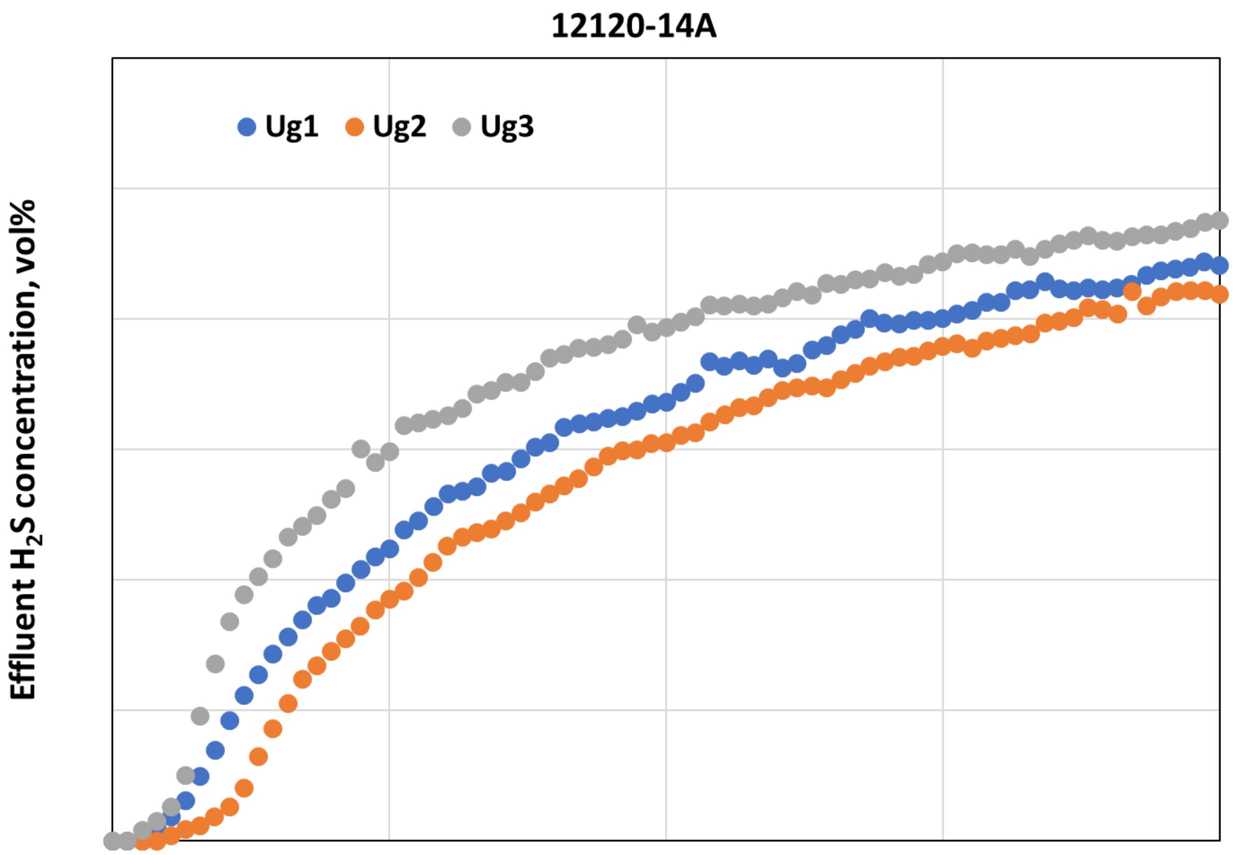


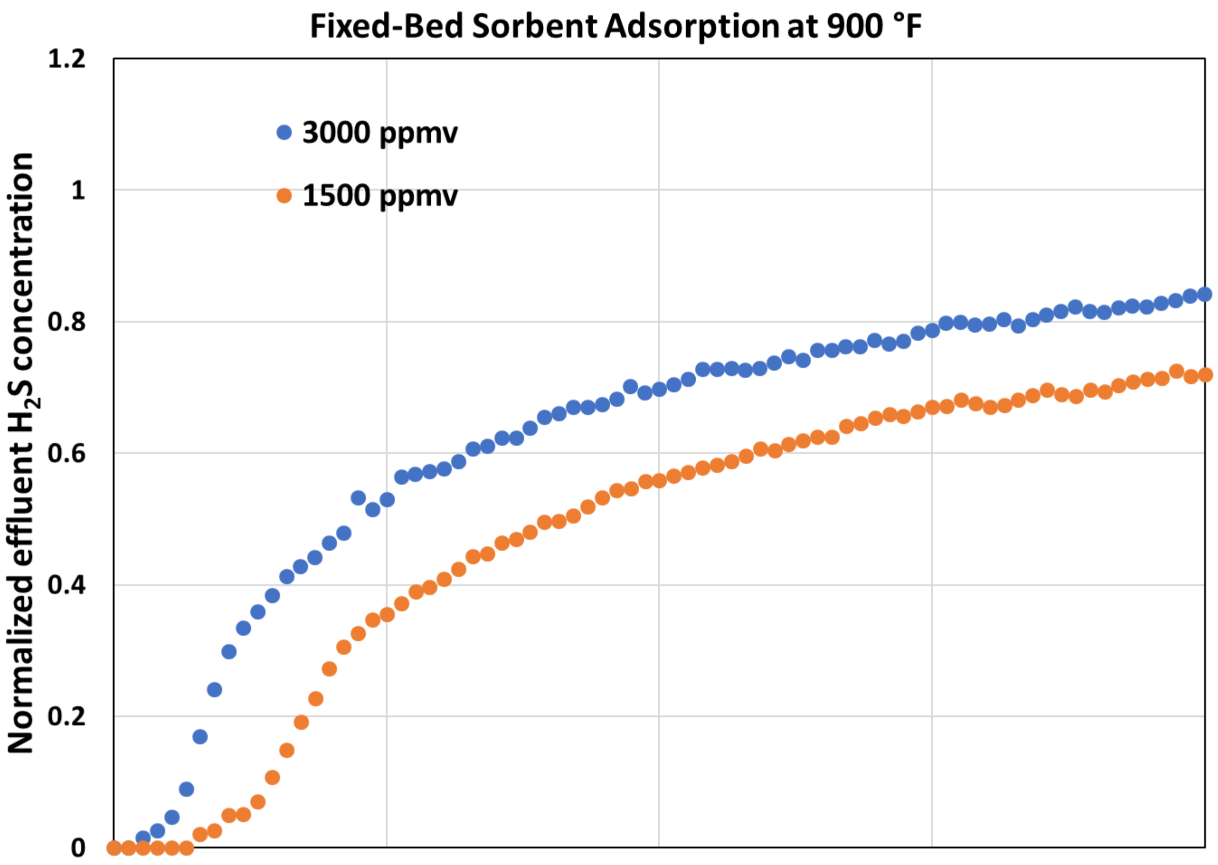
- Automated, computer controlled microreactor
- Operating limit – 100 bar and 790 C
- Standard 316 stainless steel reactor holds up to 3 mL of sorbent
- Four MFC gas feed channels
- On-line analysis of gas composition using Inficon Micro GC every 2.5 minutes
- Data logging for all instrument parameters

- Commissioned the automated system to collect data for sorbent and process optimization
- Experimental plan to study extrudate size and shape, and adsorption and desorption operating conditions



Fixed-Bed Sorbent – Parametric Testing Data



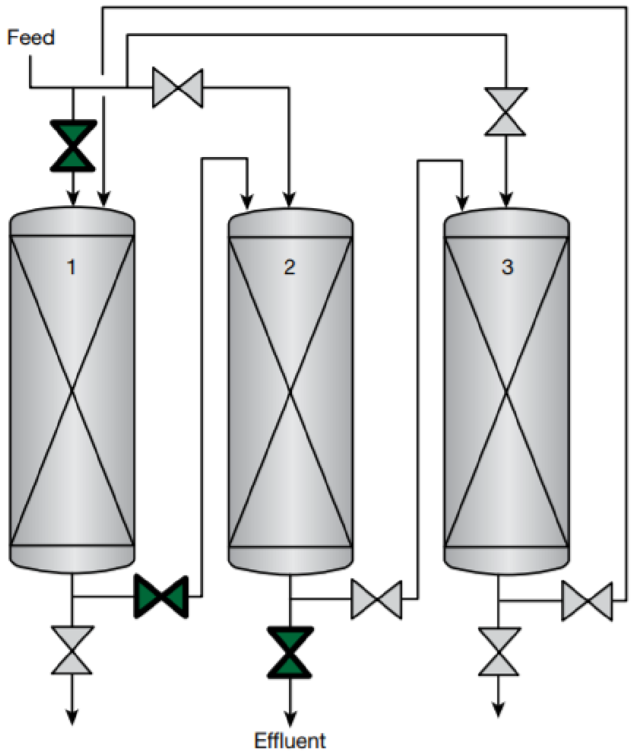


Task 5.0 Techno-Economic Analysis

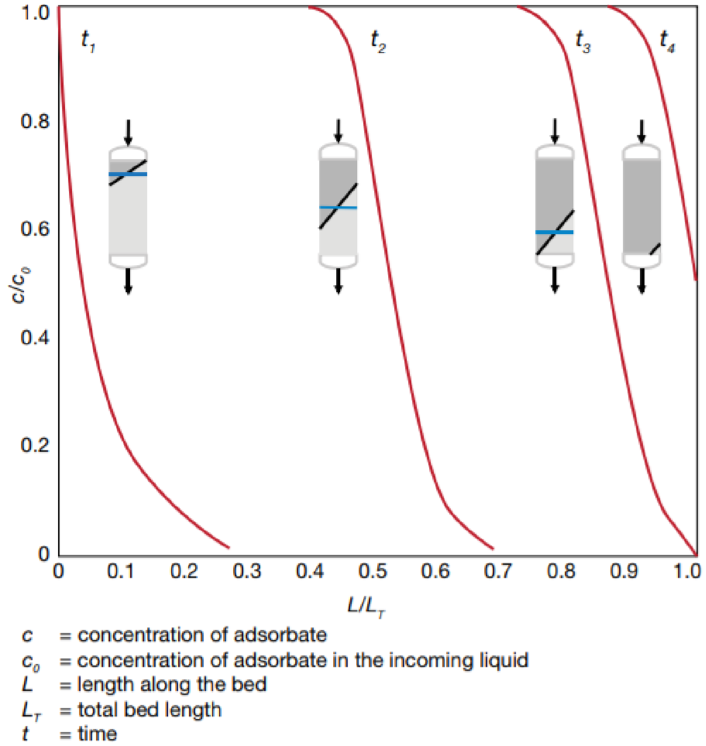
- Objective: Develop and optimize conceptual designs for desulfurization processes based on fluidized-bed and fixed-bed reactors
- Data generated from Tasks 2, 3, and 4 will be used to develop and optimize fluidized-bed and fixed-bed processes
- Potential to reduce system cost through standardization, modular production and other advanced manufacturing techniques will be investigated
- The TEAs developed in this task will be developed for the overall plant from upstream gasification to syngas conversion
- Sensitivity analyses will be utilized to help optimize the overall system integration and to assess relative benefits of RTI’s WDP
- Results from this task will be captured in a TEA report as a deliverable

% Complete	25

Fixed Bed Process Development Parameters



An example three column arrangement where column 1 serves as the lead and column 3 serves as the guard with column 2 in regeneration mode

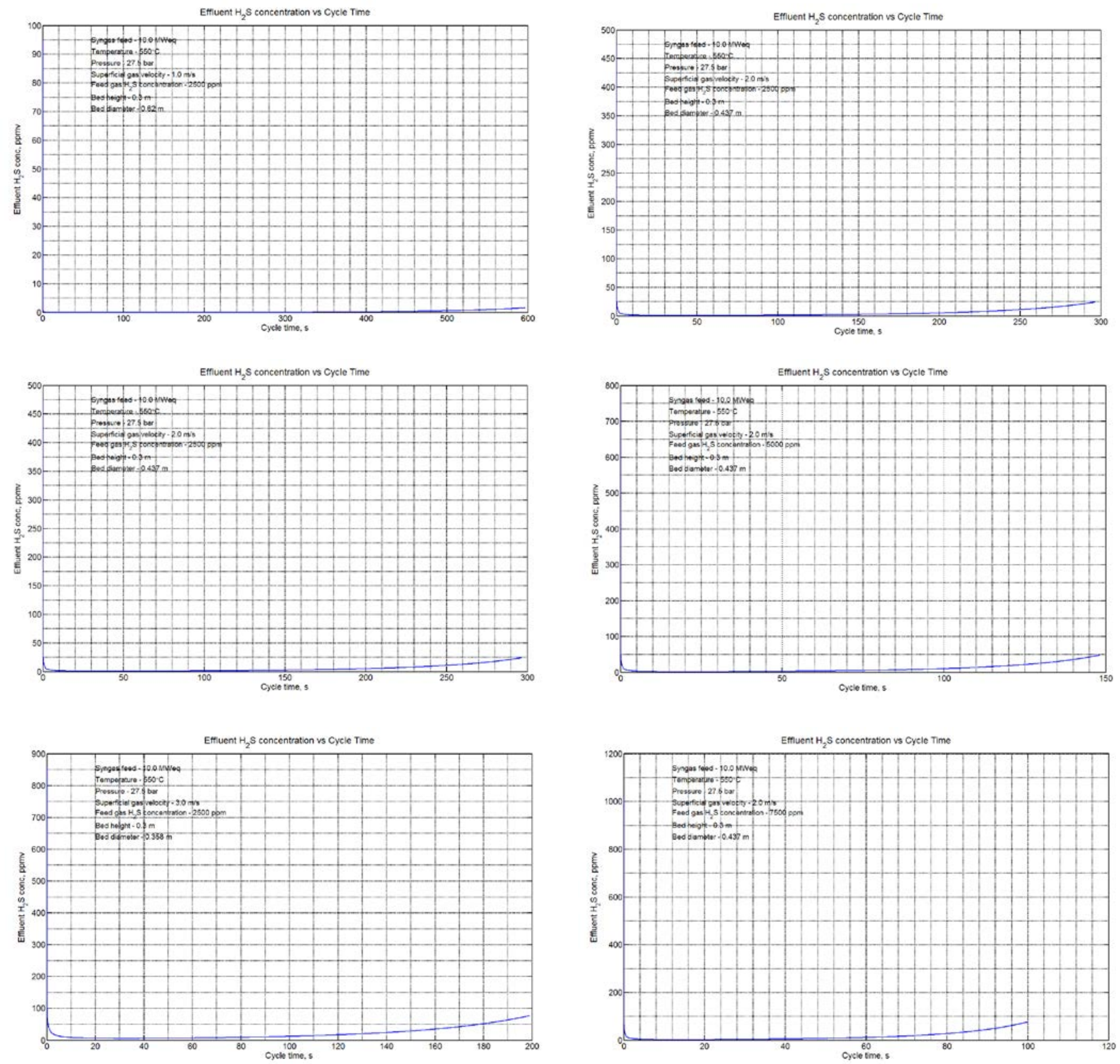


The mass transfer zone, indicated by the black diagonal line on each column, moves along the length of a fixed bed of adsorbent

- Iterative process of adsorption system design
- Adsorbent Particle Size
  - Smaller particle size lower mass transfer limitation but increase pressure drop
  - Preferred particle size is the smallest that still has a tolerable pressure drop
  - Common particle size range: 2-4 mm
- Superficial Gas Velocity
  - Length of MTZ increases with increasing gas velocity with a corresponding decrease in bed utilization
  - Typical velocity range: 0.15-0.45 m/s
- Bed Length
  - Longer bed allows for longer time-on-stream and higher bed utilization
  - However, it is more expensive and leads to higher pressure drop

Matlab Model to Simulate Fixed-Bed Reactors

- Developed a Matlab model to integrate:
  - Adsorption and desorption kinetics
  - WGS kinetics
  - Pressure drop
  - Heat transfer
  - Internal mass transfer diffusion
- Microreactor testing data will be used to estimate internal mass transfer diffusion coefficients
- Validated model will be used for reactor design, data for cycle development, and process optimization



Conclusions

- Proposed project builds on decades of effort invested in the development of RTI's Warm Syngas Cleanup technology
- Validated excellent performance of sorbent at low-sulfur syngas conditions extending its application to low-sulfur coals (Milestone 3)
- Completed generating ambient condition hydrodynamic data for the development of fluidized-bed regenerator at ambient conditions (Milestone 4)
- Currently working on studying the effect of pressure and temperature on sorbent hydrodynamics and optimizing fixed-bed sorbent extrudates and process
- Obtained pilot-scale fluidizable sorbent wet cake for the optimization of fixed-bed sorbent and process (Milestone 2)
- Currently optimizing fixed-bed sorbent and process
- Investigating commercial interest with varying sources for low sulfur, fixed-bed applications
- **Overall, the project is on track to meeting all project milestones and achieving the project objective of developing modular sorbent-based warm syngas cleanup designs that will be cost-competitive with large state-of-the-art commercial plants**

Acknowledgements

- U.S. Department of Energy Office of Fossil Energy
  - Co-operative agreement number: FE-0031522

- Steven Markovich – Project Manager

Questions?

Contact:
Atish Kataria
akataria@rti.org
919-541-6901