



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

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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.

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- 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

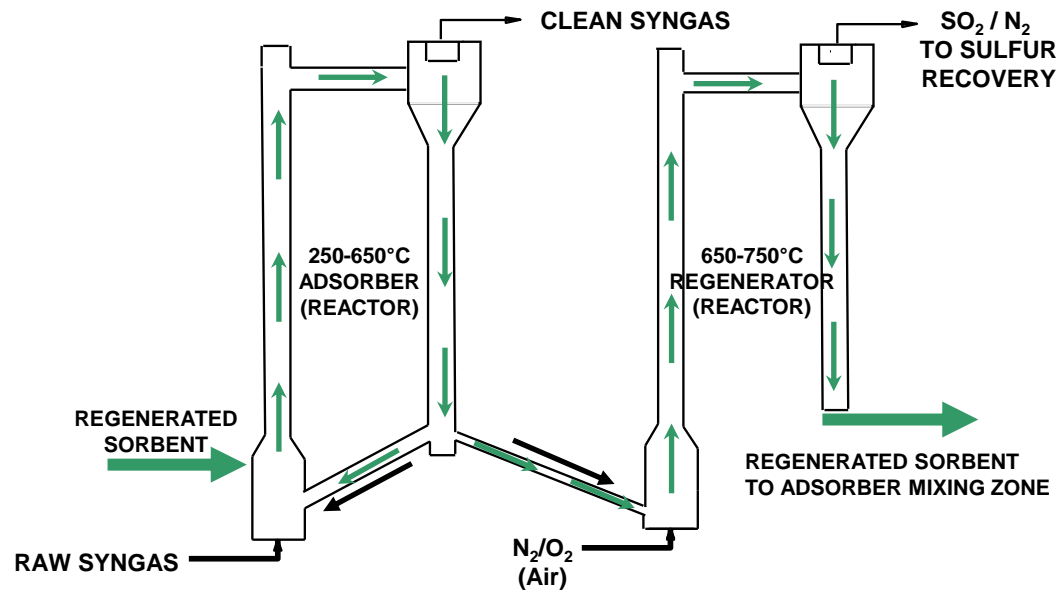
RTI Warm Gas Desulfurization Process (WDP) - Overview

Enables high removal of total sulfur ($\geq 99.9\%$) 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.

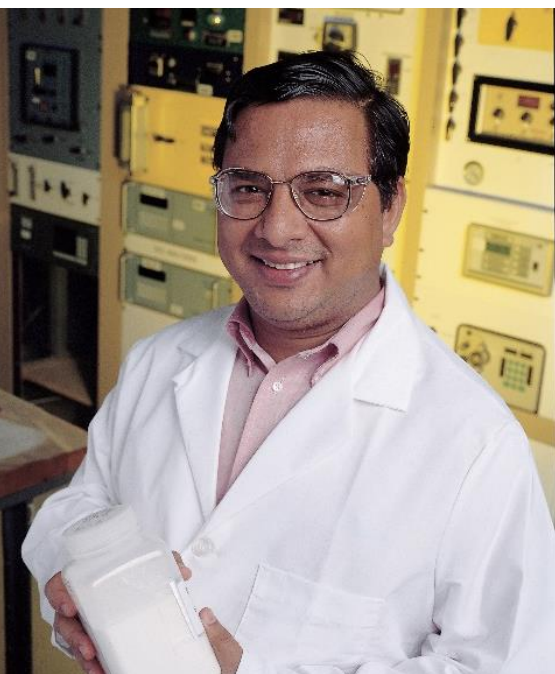


RTI Proprietary Desulfurization Sorbent

- 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

RTI Warm Gas Desulfurization Process (WDP)

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



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

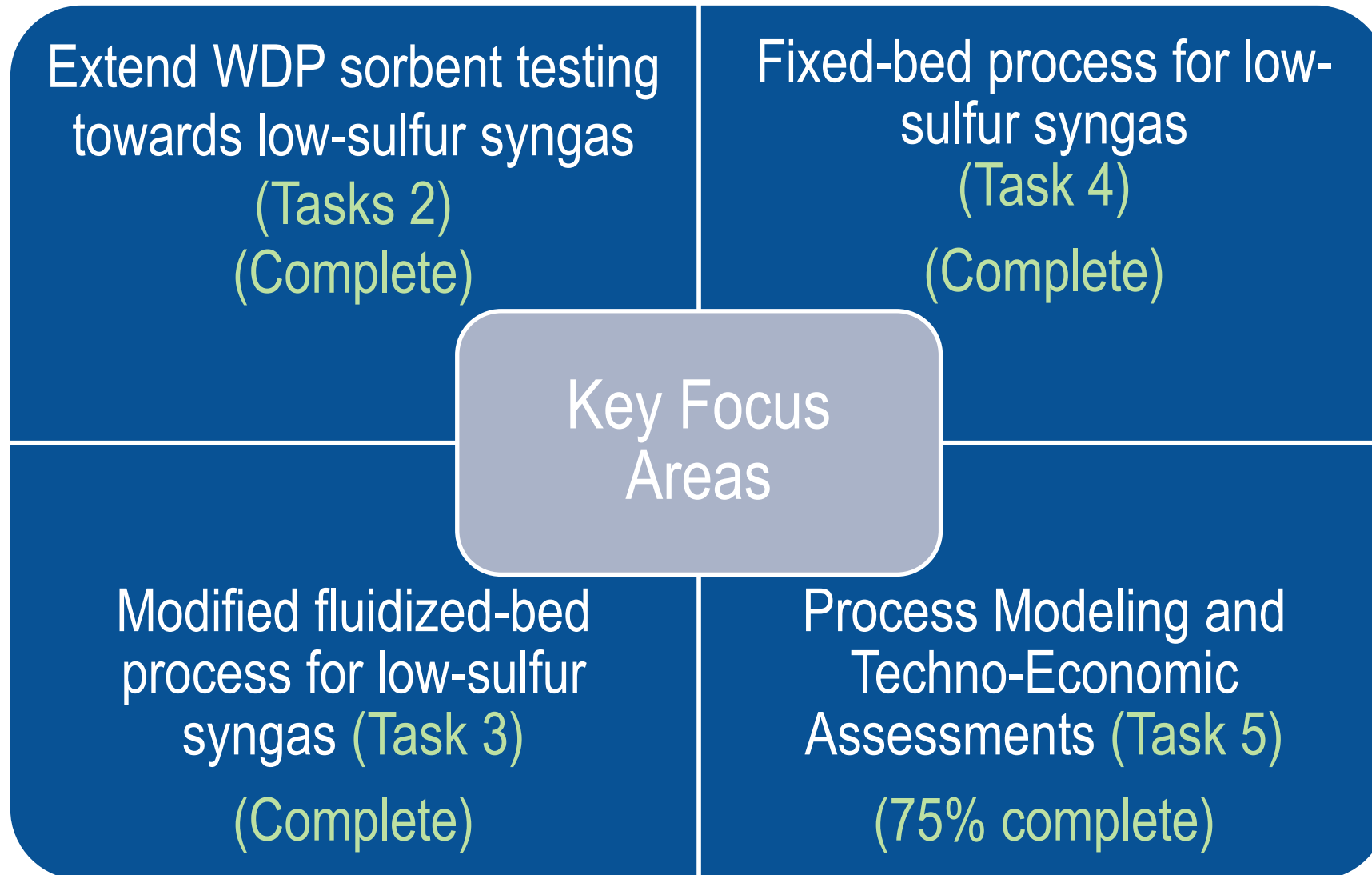
Key Strengths of WDP still apply

- 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

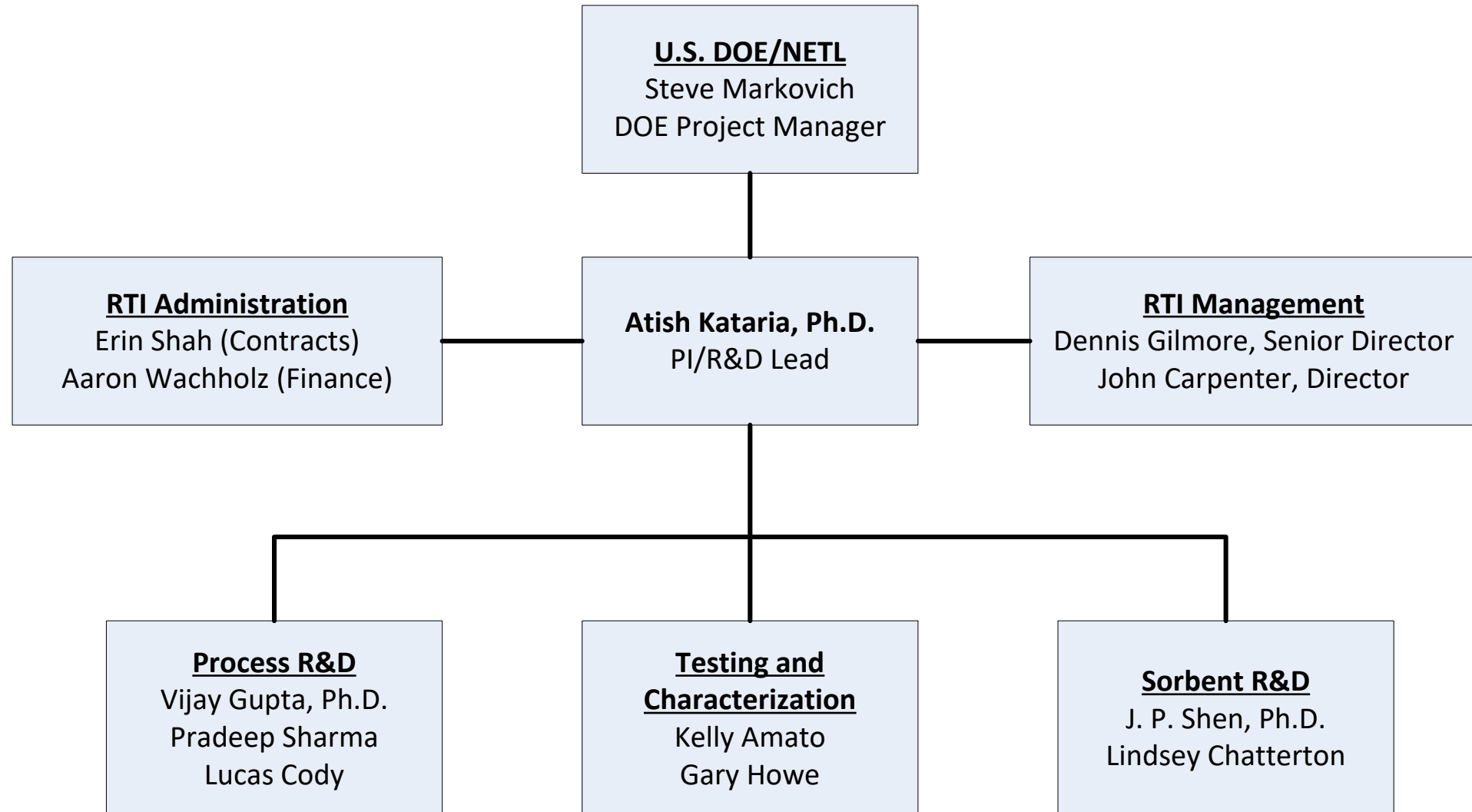
Knowledge gaps for application

- 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

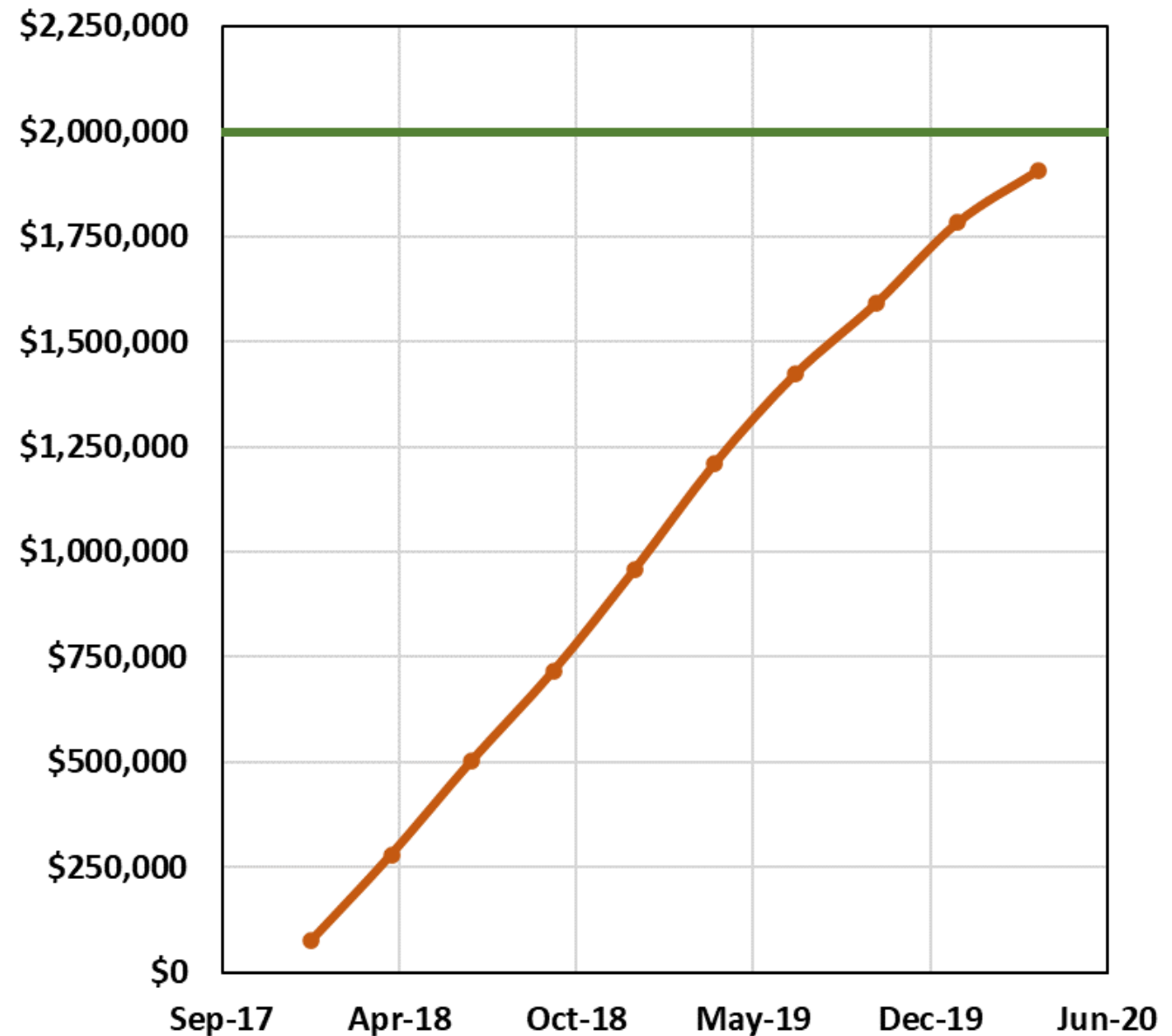


Task 1 – Project Management



Project Management Overview

- Project milestones on track
- On track with all the technical and financial reporting requirements
- Investigating commercial interest in the fixed-bed process



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. | 8/31/2030 | - |
| 6 | 2 | Demonstration testing of fixed-bed sorbent and process at simulated operating conditions validating design for techno-economic analysis completed. | 7/15/2020 | 7/15/2020 |
| 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 . | 9/30/2020 | - |

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

Atm-TGA and Bench-Scale Sorbent Testing System

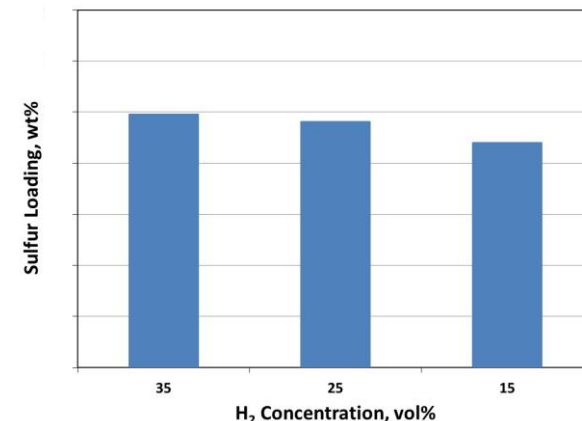
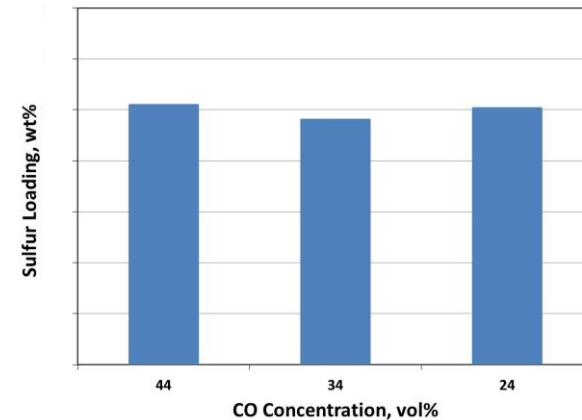
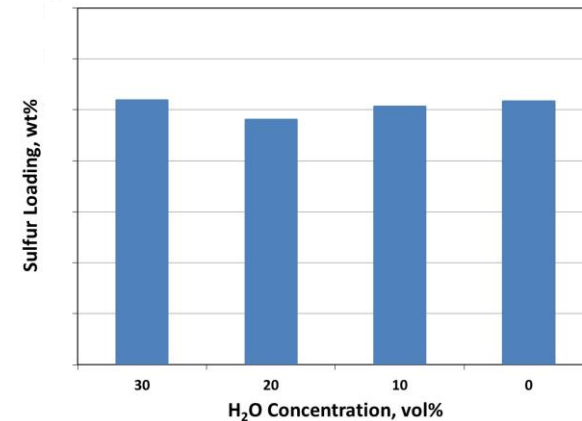
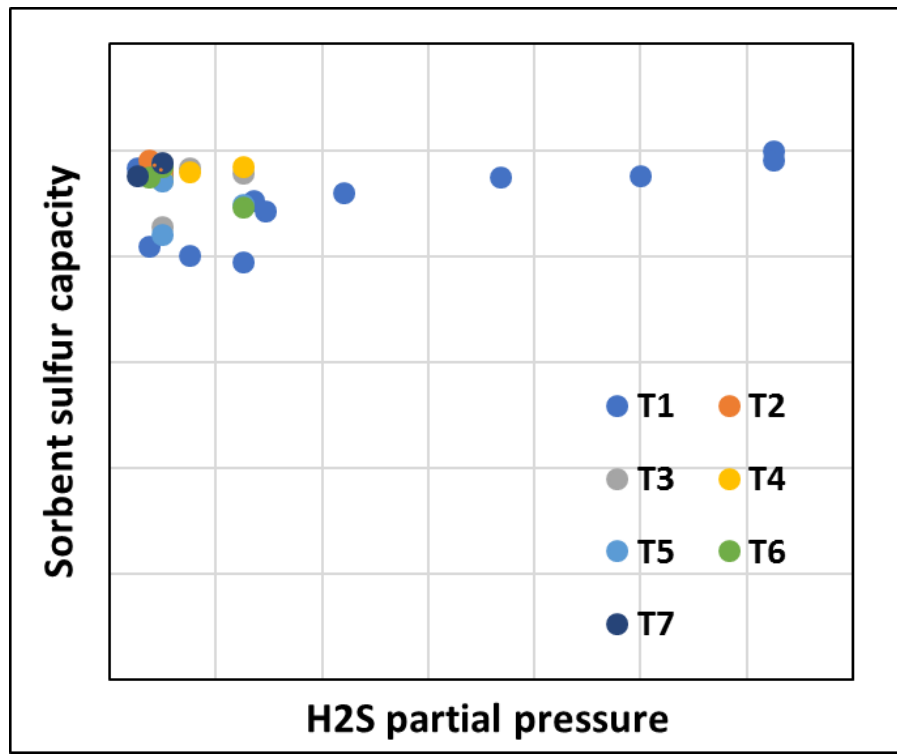
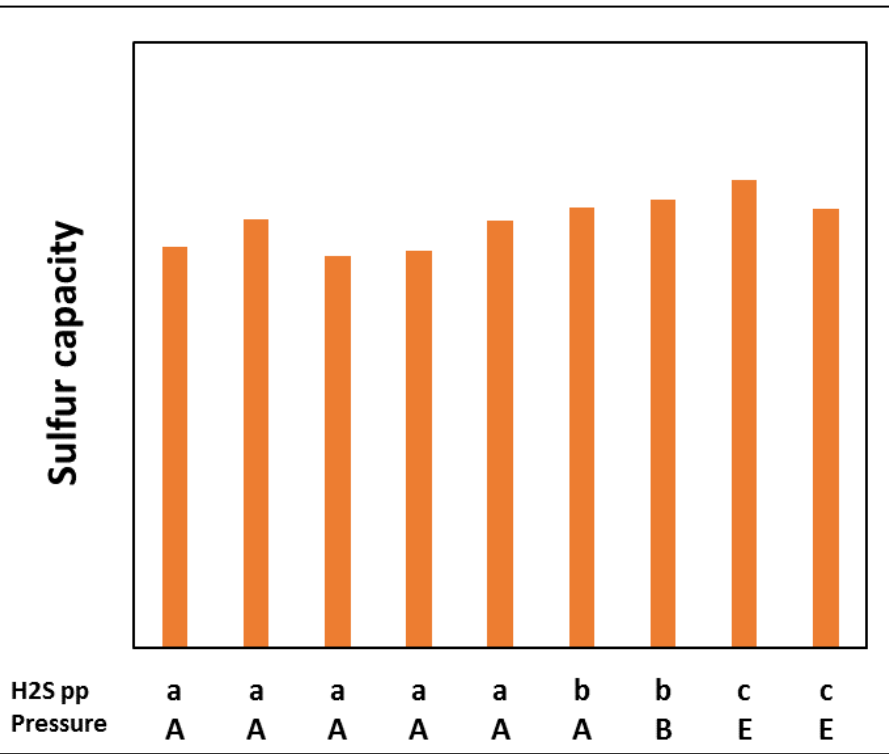


- Sorbent testing in simulated syngas and oxidation gases
- Operates at atmospheric pressure and up to 700°C
- Utilizes 5 to 20 mg of sorbent material
- Cross flow operation allows for kinetic measurements



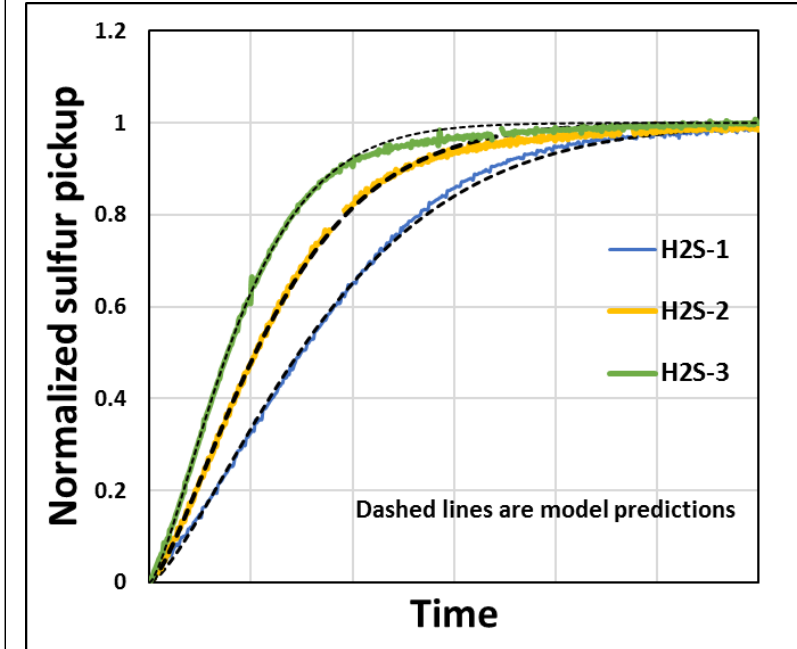
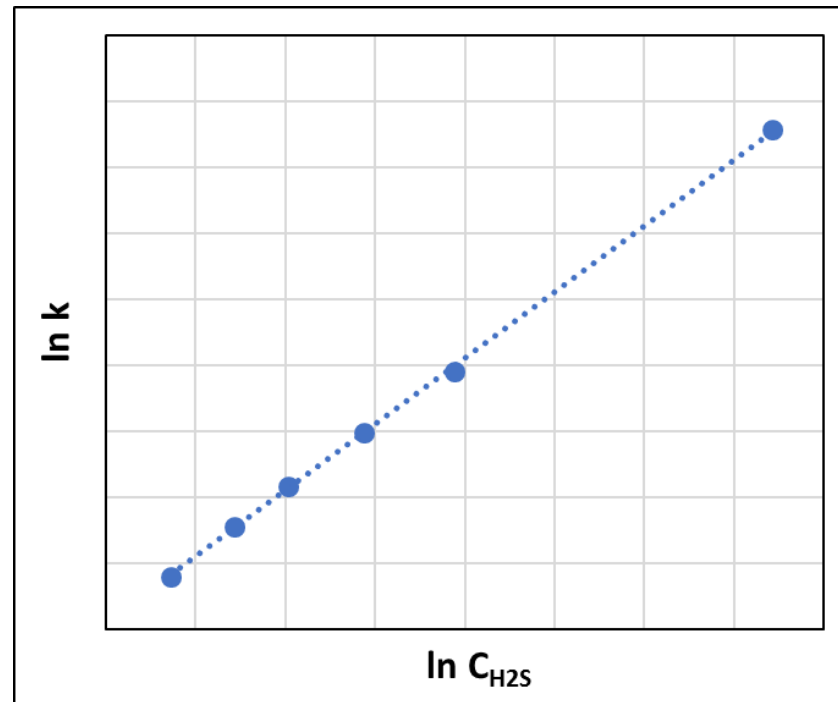
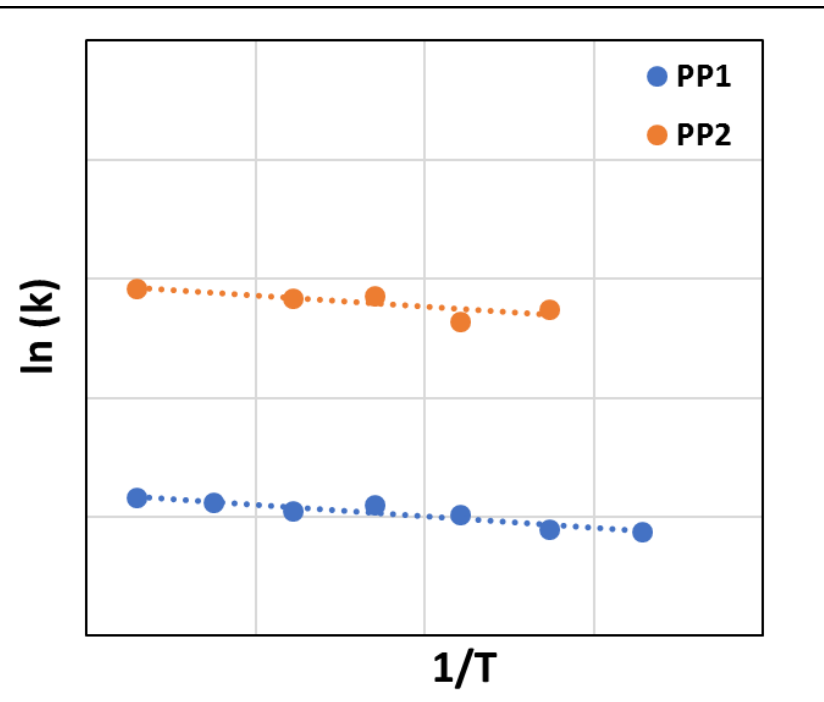
- Sorbent testing in simulated syngas and oxidation gases
- Operate up to 40 barg and 700°C
- Utilizes 100-300 g material
- Suspended quartz reactor inside stainless steel pressure vessel

Equilibrium Sorbent Sulfur Loading



- Tested performance of fluidizable RTI-3 sorbent under varying operating conditions – temperature, pressure, H₂S 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

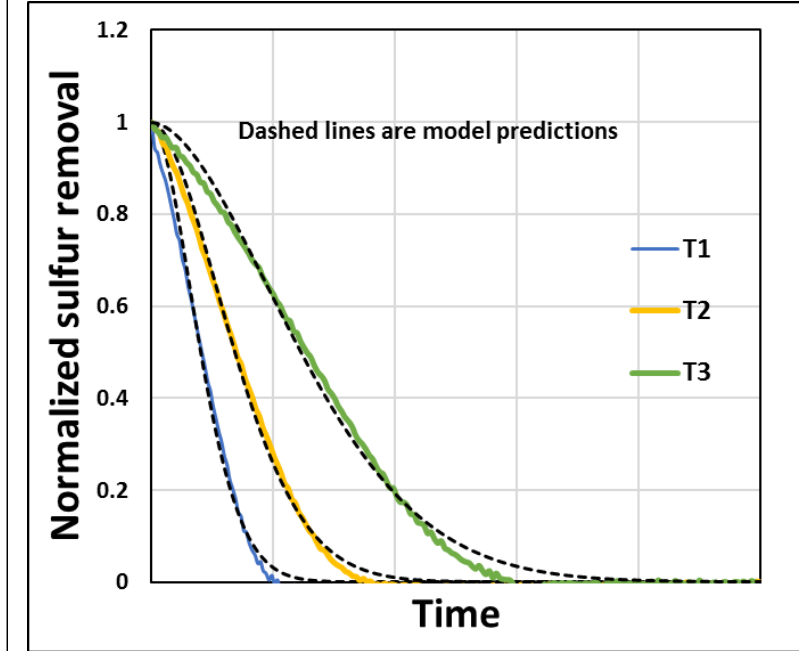
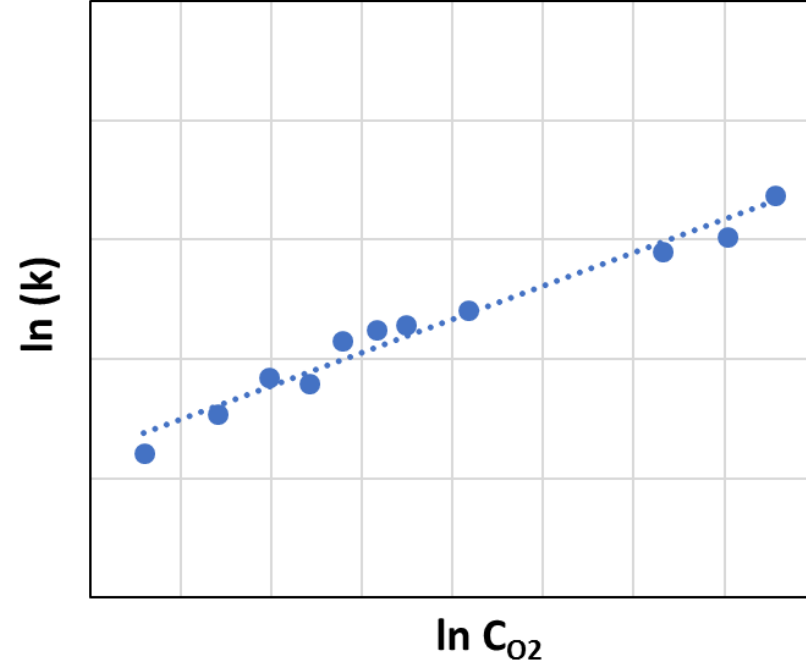
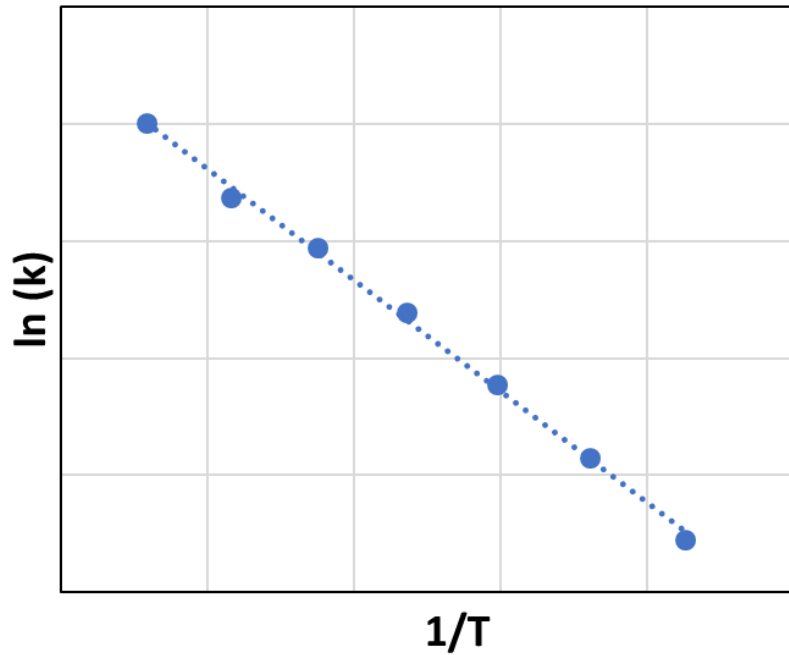
Adsorption Kinetics



- 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

$$\frac{q_t}{q_e} = 1 - \exp \left\{ - \left[C_1 P_{H_2S} \exp \left(\frac{-E_A}{RT} \right) t \right]^{C_2} \right\}$$

Desorption Kinetics



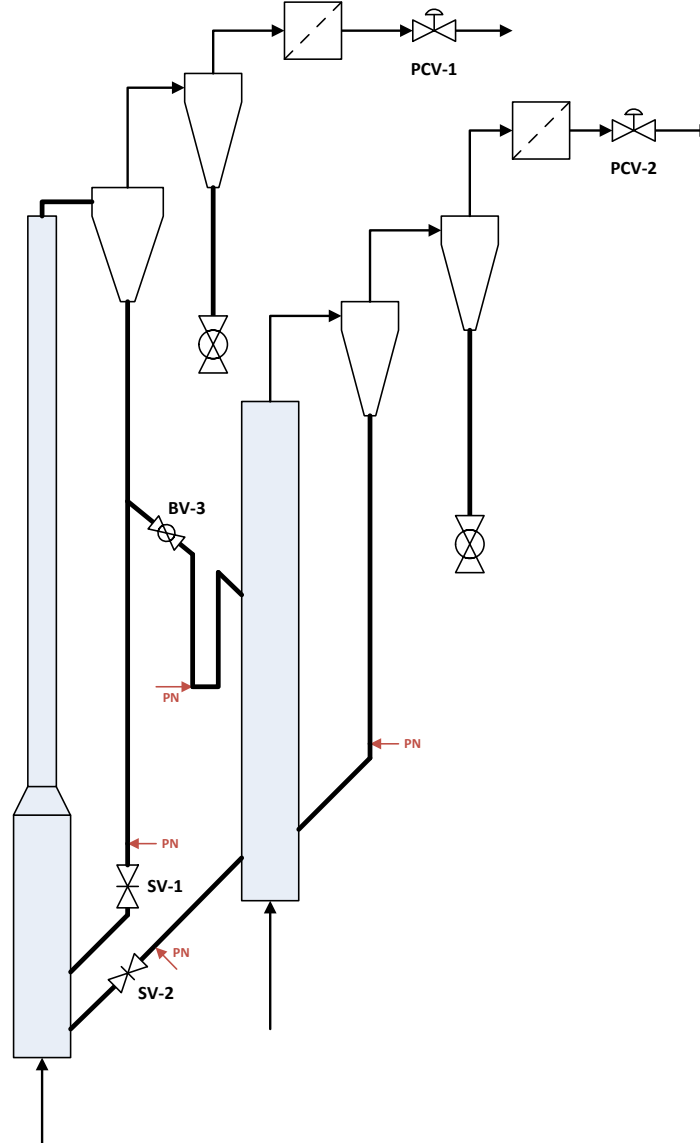
- A simplified kinetic expression was generated to incorporate the effect of regeneration operating parameters (temperature, O_2 partial pressure, etc.)
- Excellent agreement was observed between the experimental and model-predicted data

$$q_t = q_e \exp \left\{ - \left[C_1 \exp \left(\frac{-E_A}{RT} \right) t \right]^{C_2} \right\}$$

Task 3.0: Fluid-Bed Regenerator Development

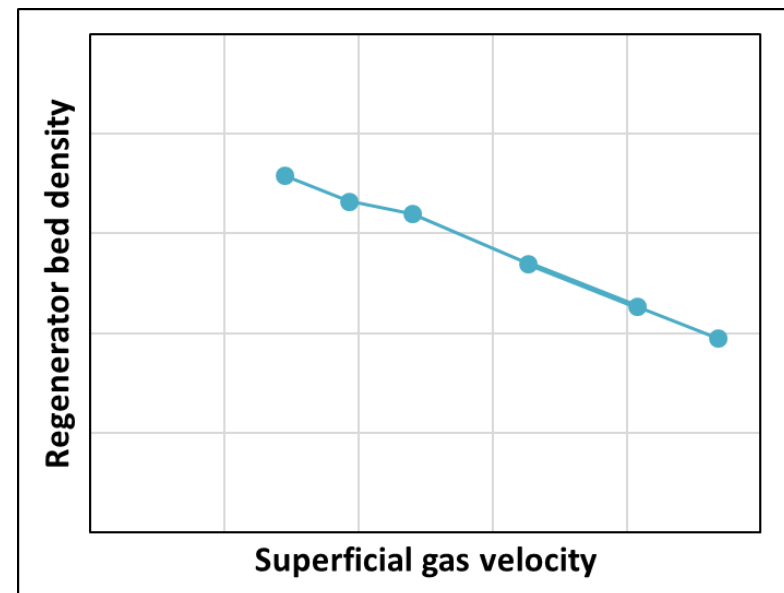
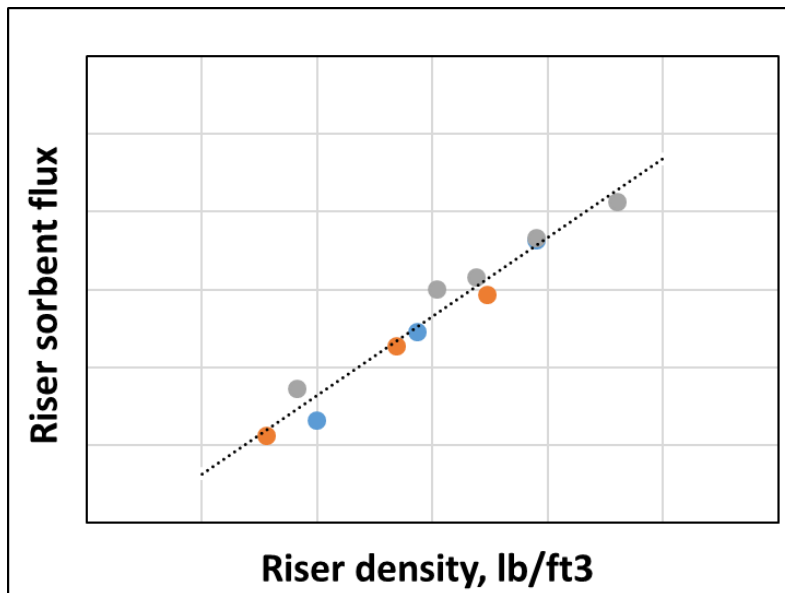
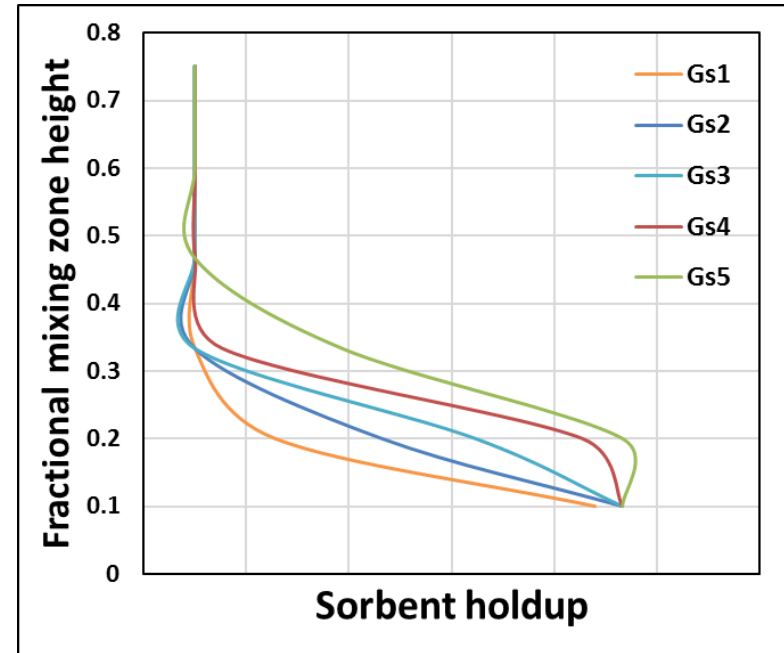
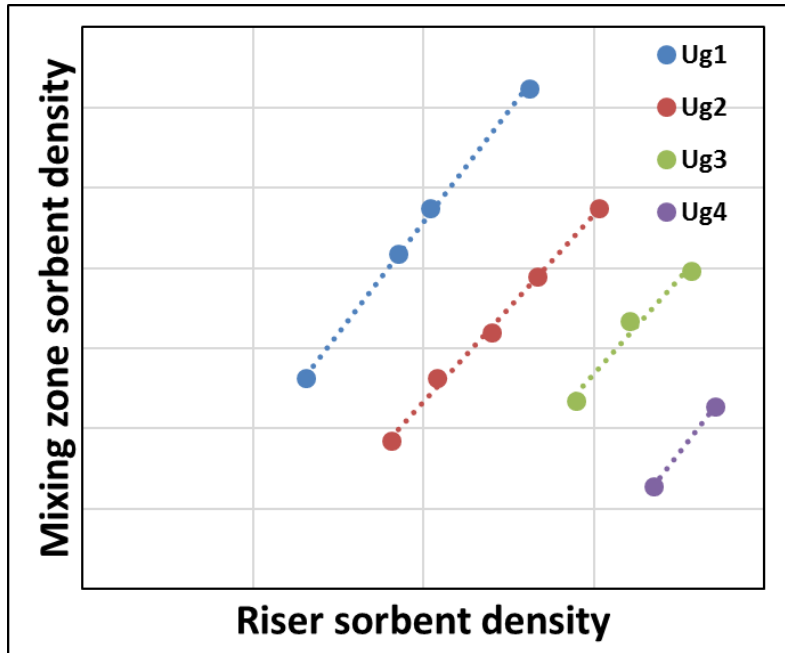
- Objective: Development of a fluid-bed regenerator for REMS application, especially with low-sulfur syngas
- Completed acquiring hydrodynamic data for the sorbent at key regions within the fluid-bed reactor system using the existing cold-flow unit (Milestone 4)
- Collected hydrodynamic data with effect of pressure and temperature in the hot-flow unit
- Data collected at a combination of pressure and/or temperature to enable extending the application of the data to commercially relevant operating conditions
- Performed cyclic sorbent sulfur testing in the hot-flow unit under simulated operating conditions to collect data for process modeling and techno-economic assessment

Subtask 3.1: Cold-Flow Testing

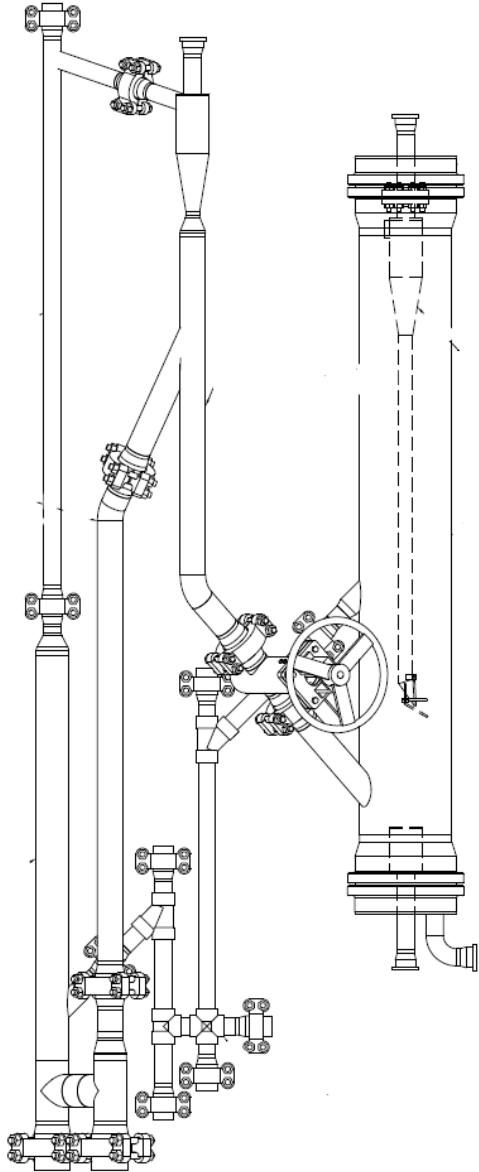


- Transport reactor absorber
 - Mixing zone-Riser Design
 - 8" mixing zone and 4" riser
- 6" fluidized bed regenerator
- 2" transfer lines
- Line size slide valves
 - Recirculation and transfer
- Two cyclones in series
- Extensively instrumented with dP transmitters

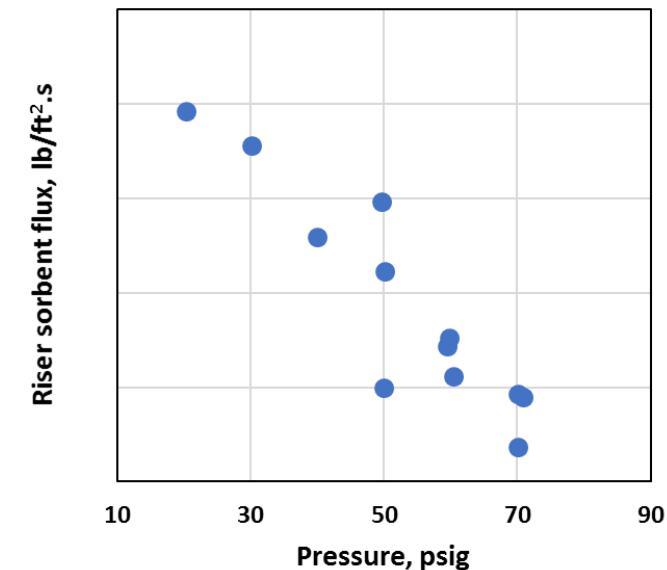
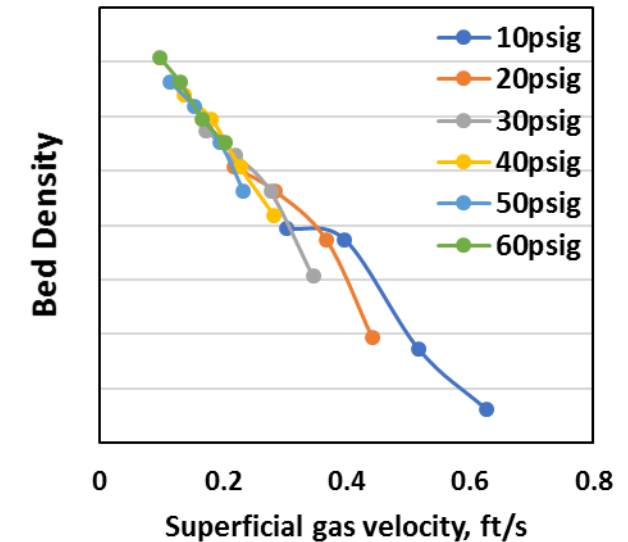
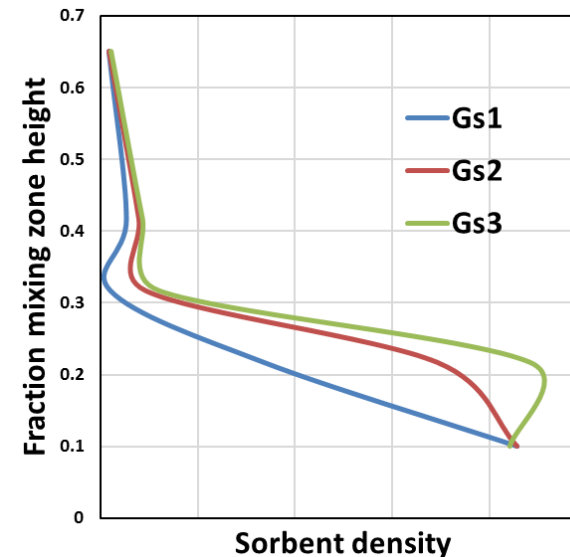
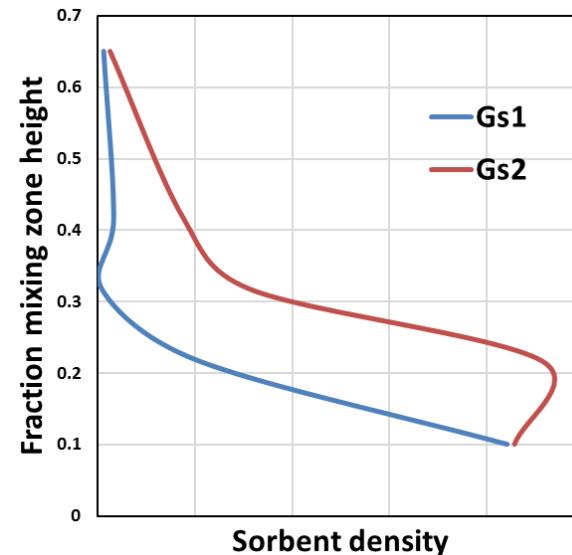
Milestone 4 Complete – Acquisition of Cold-Flow Hydrodynamic Data



Subtask 3.2 and 3.3: Hot-Flow Testing



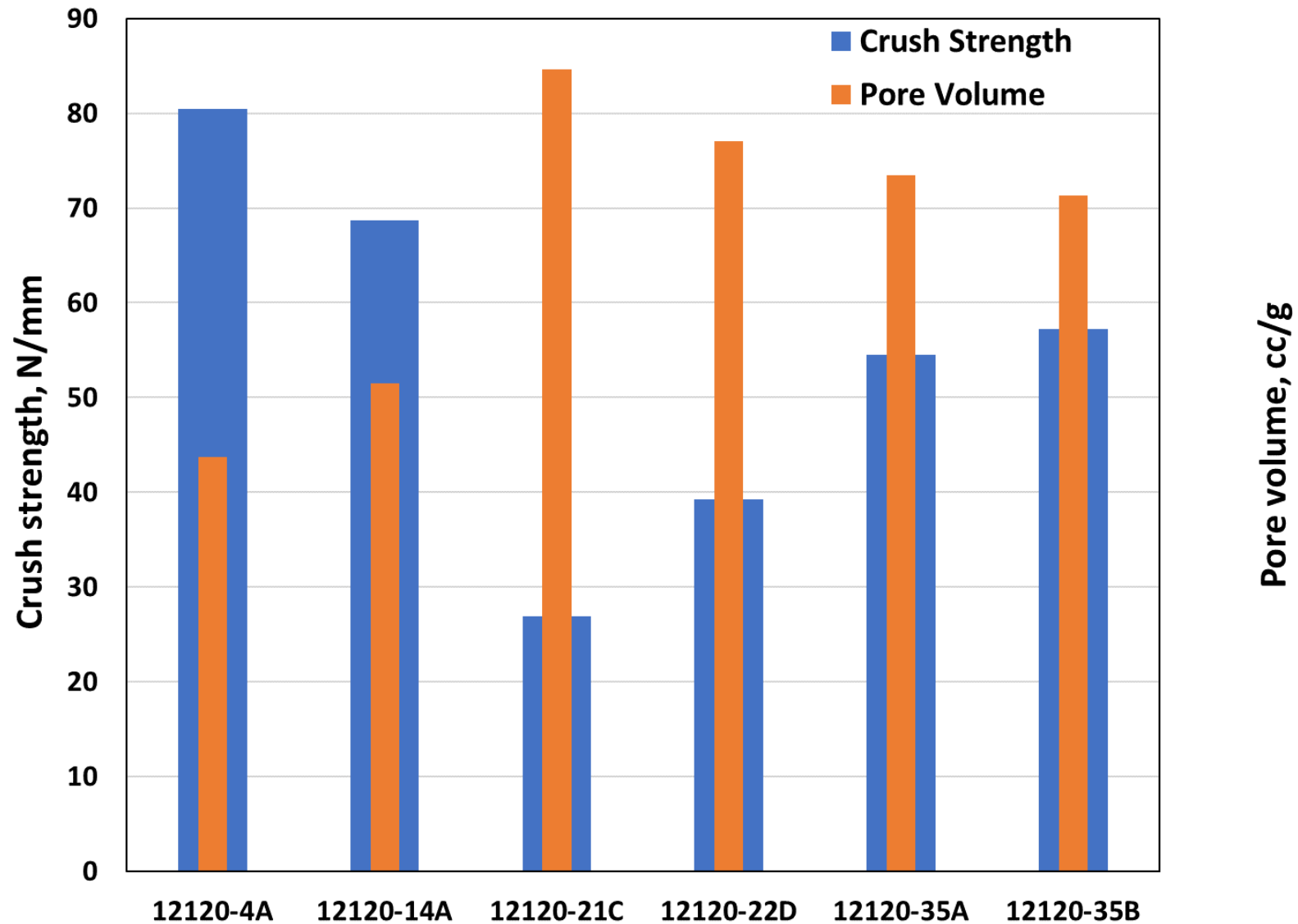
- Design similar to the cold-flow unit
- Operating limits of 150 psig and 650°C
- Generated hydrodynamic data at ambient conditions and by varying operating pressure and temperature
- Completed cyclic adsorption-regeneration testing in August 2020



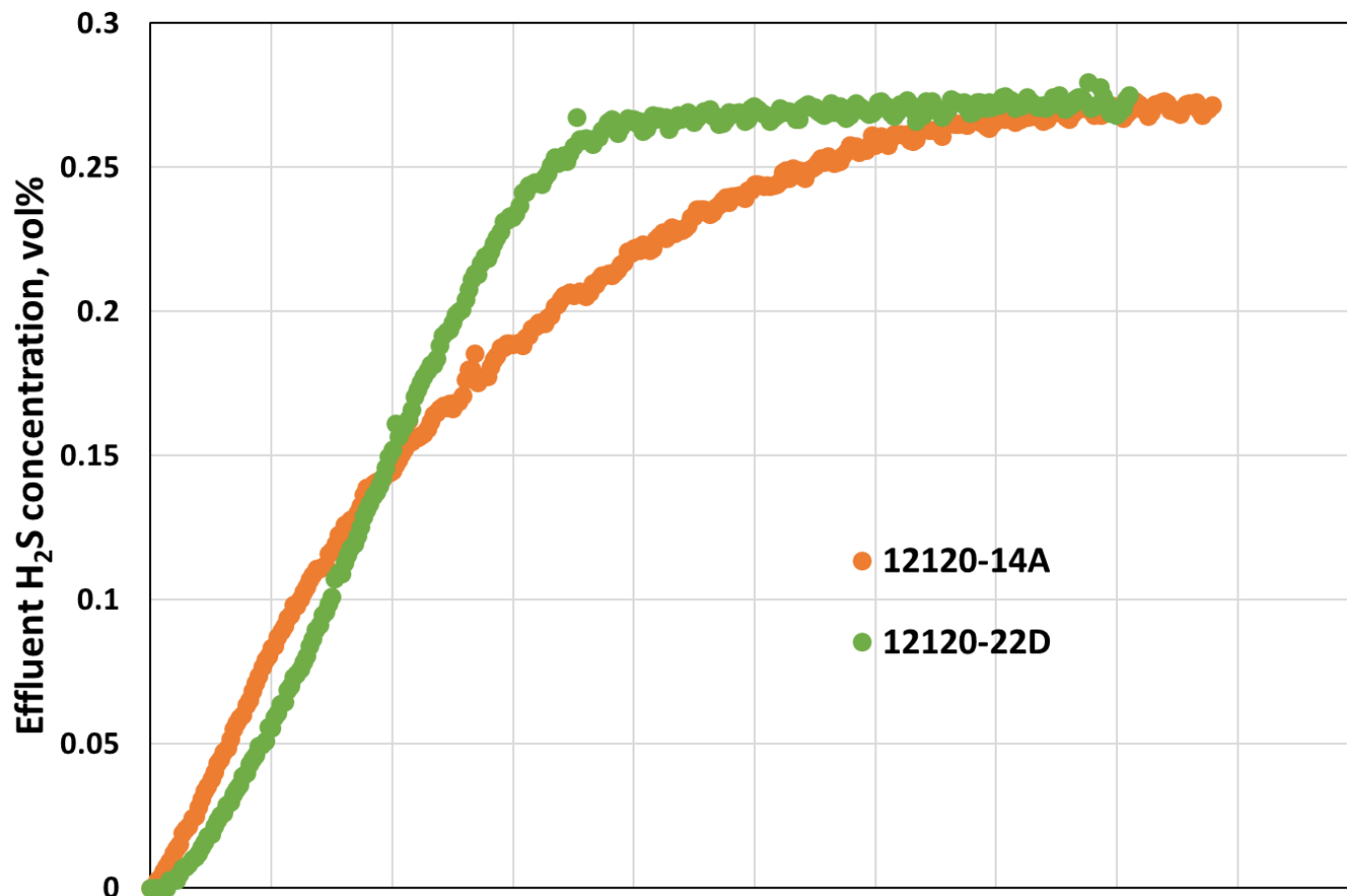
Task 4.0: Fixed-Bed Sorbent Development

- 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 used to optimize fixed bed process parameters (time sequences, regeneration conditions, purge, etc.)
- Multicycle stability of the optimized fixed-bed sorbent tested for >20 cycles

Promising Extrudates Synthesized



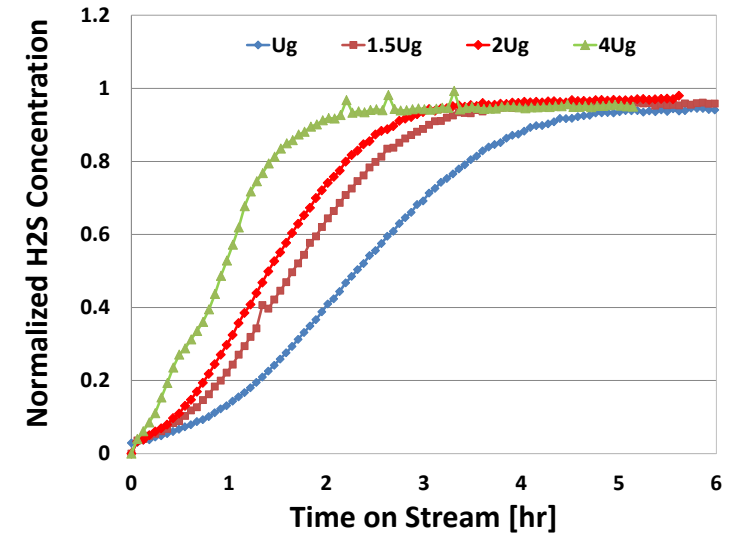
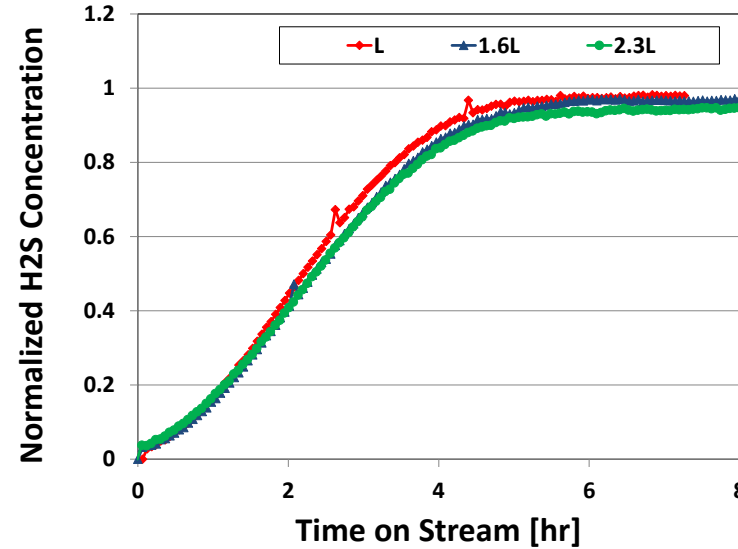
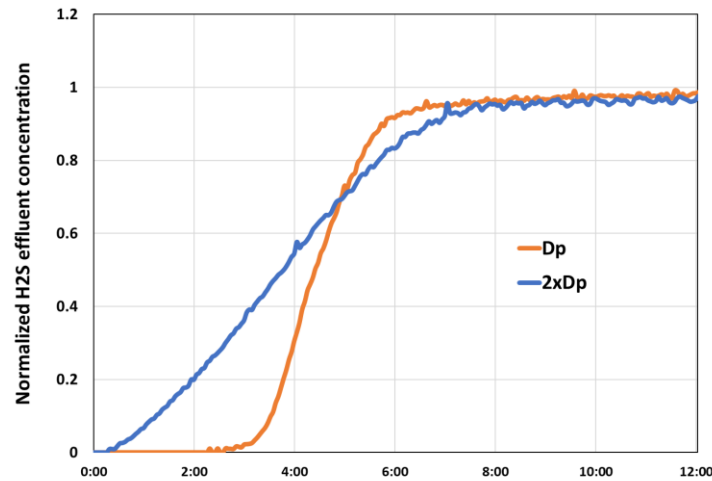
Balancing Crush Strength and Porosity



- Crush strength represents mechanical strength against compression
- Porosity improves internal mass transfer diffusion and shrinks the length of MTZ
- Balancing is key to achieving extrudates of optimal performance
- Use of pore formers to strike the desired balance

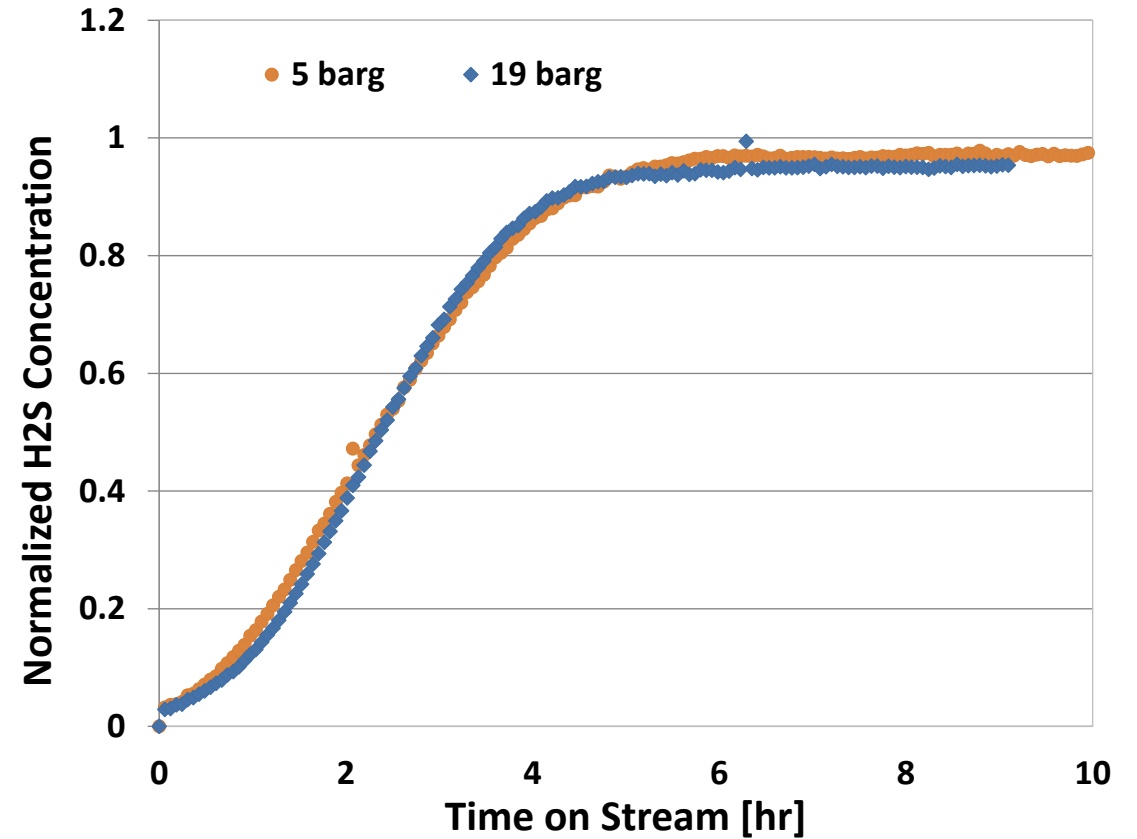
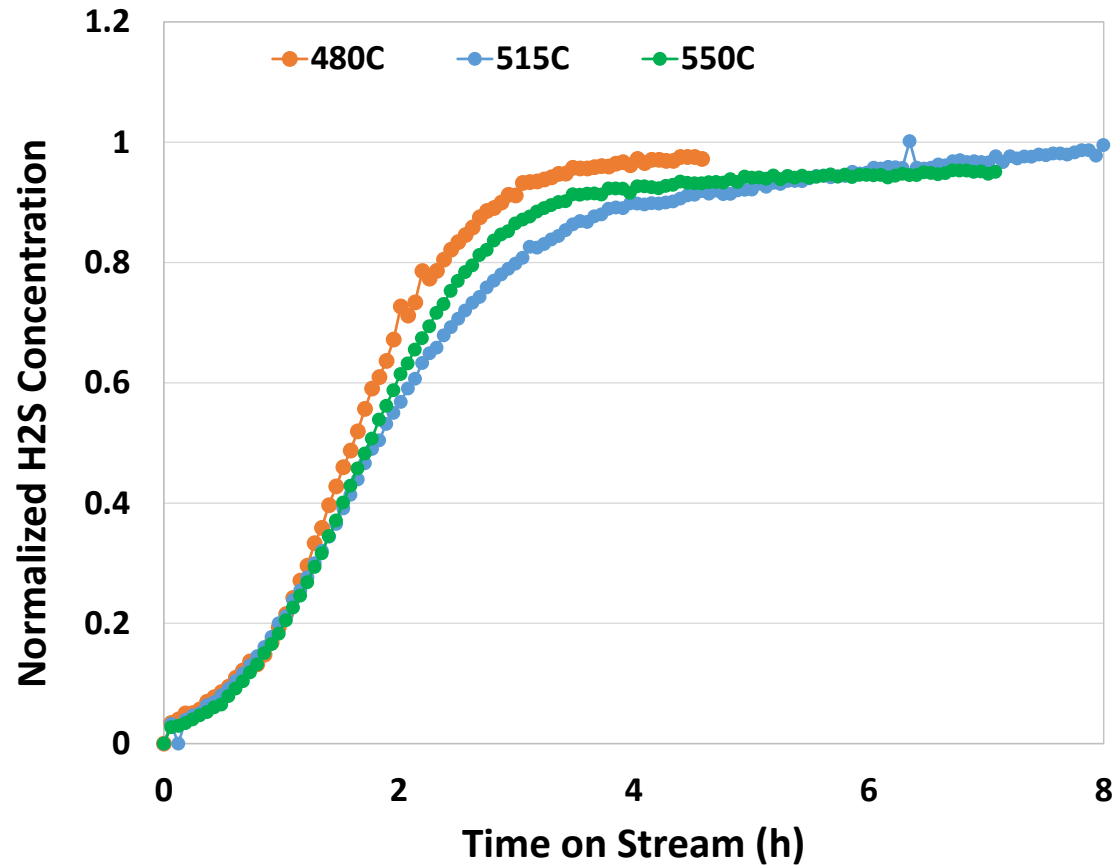
| | 12120-14A | 12120-22D |
|----------------------|-----------|-----------|
| Crush strength, N/mm | 69 | 39 |
| Surface area | X | 1.7X |
| Pore volume | Y | 1.5Y |

Balancing Pressure Drop and Internal Mass Transfer Diffusion

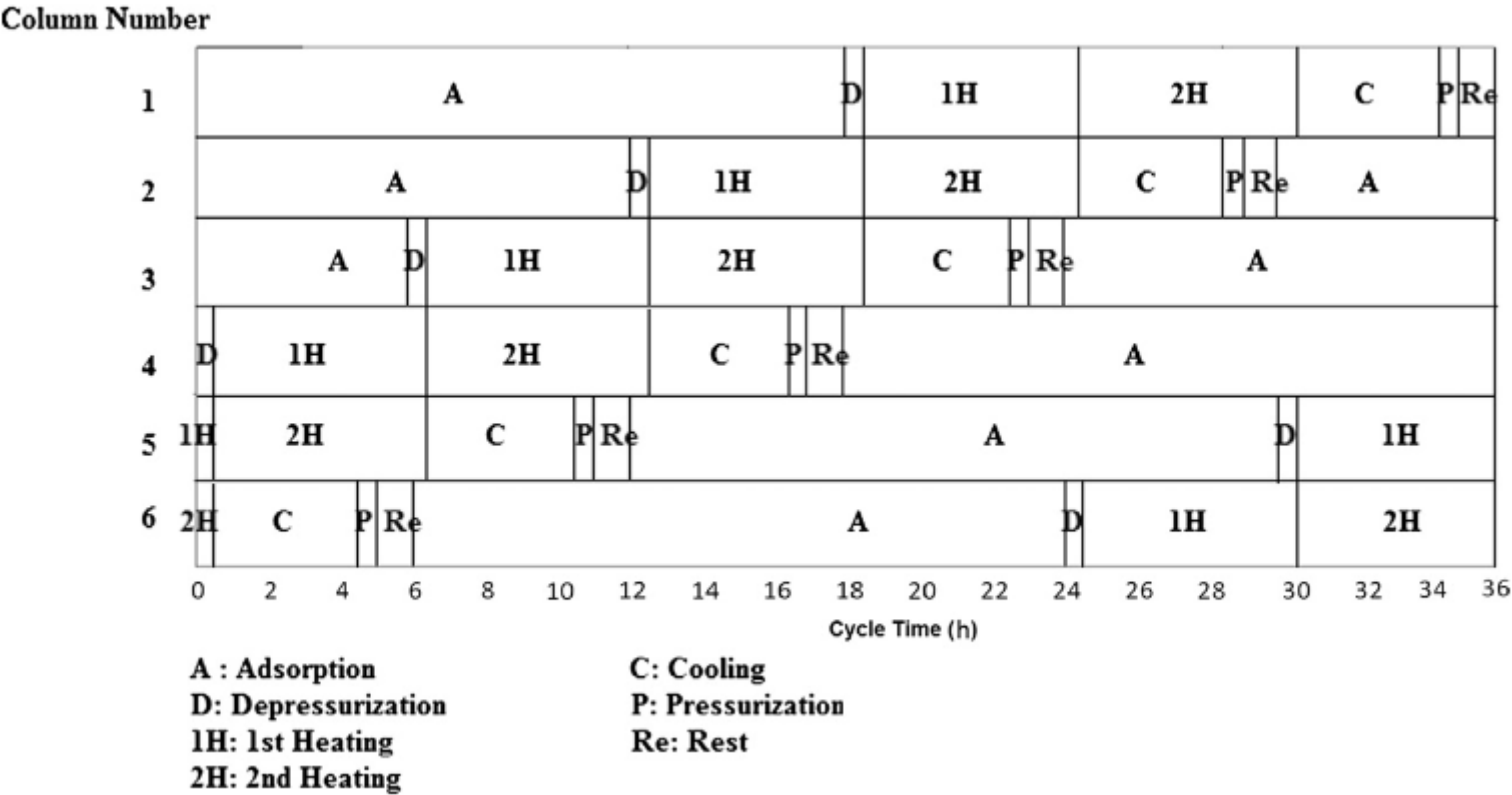


- Smaller particle size lower mass transfer limitation but increase pressure drop
- Preferred particle size is the smallest that still has a tolerable pressure drop. Common particle size range: 2-4 mm
- Bed length did not impact the MTZ, while increasing bed utilization. Higher bed length increase pressure drop.
- Higher space velocity helped decrease the length of MTZ, while increasing the pressure drop.

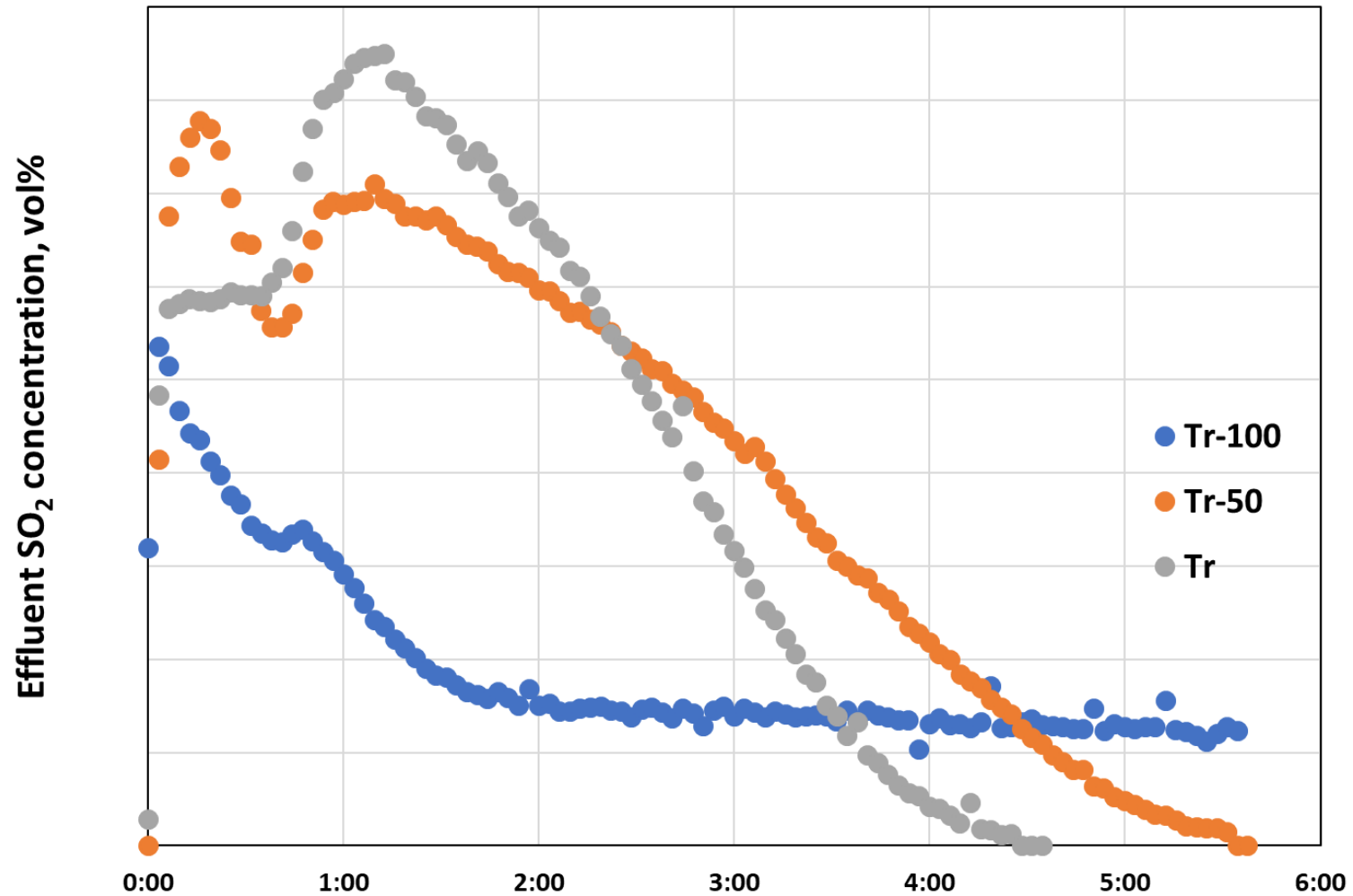
Impact of Adsorption Temperature and Pressure



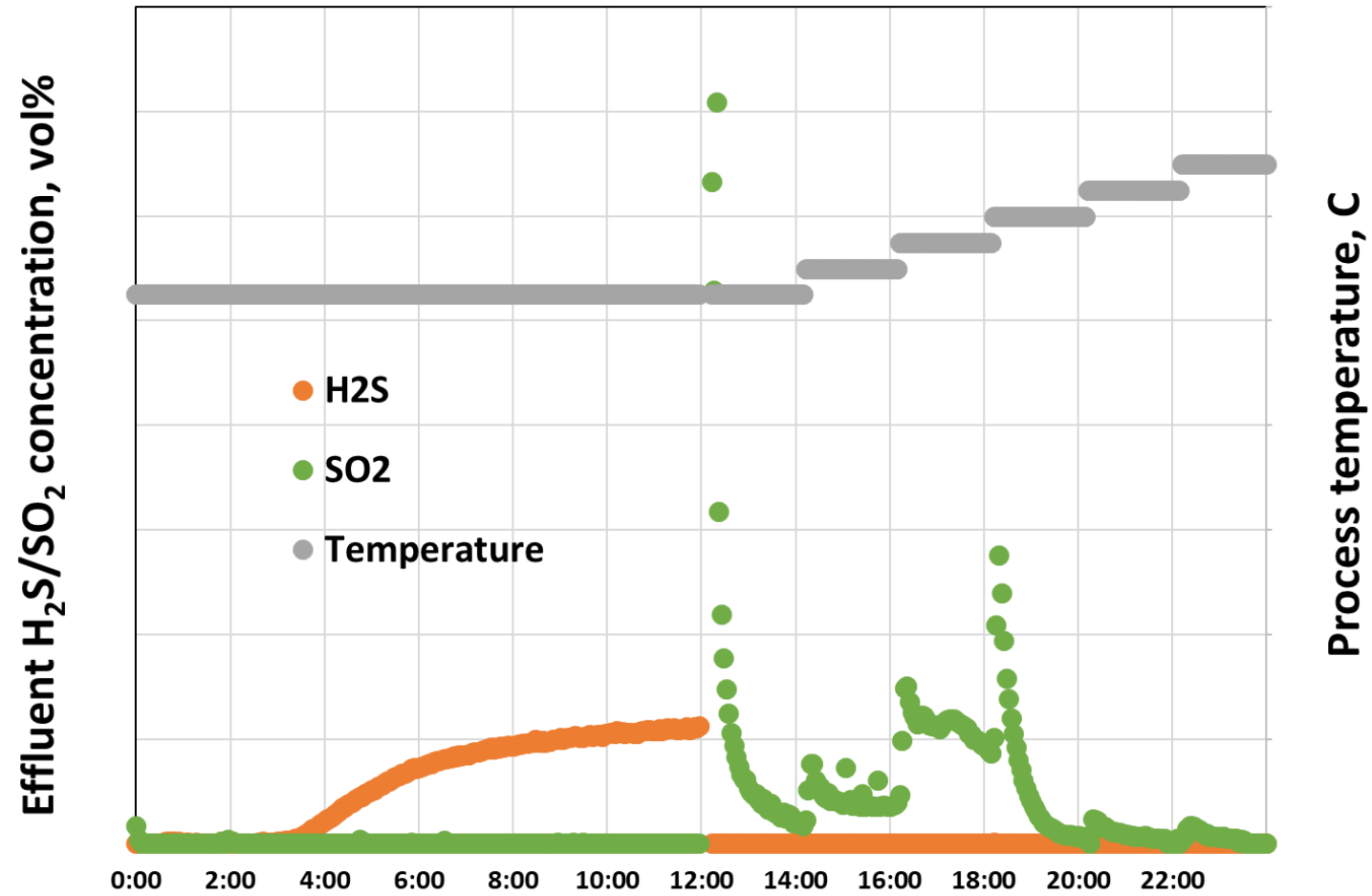
PTSA Process Can Get Complicated



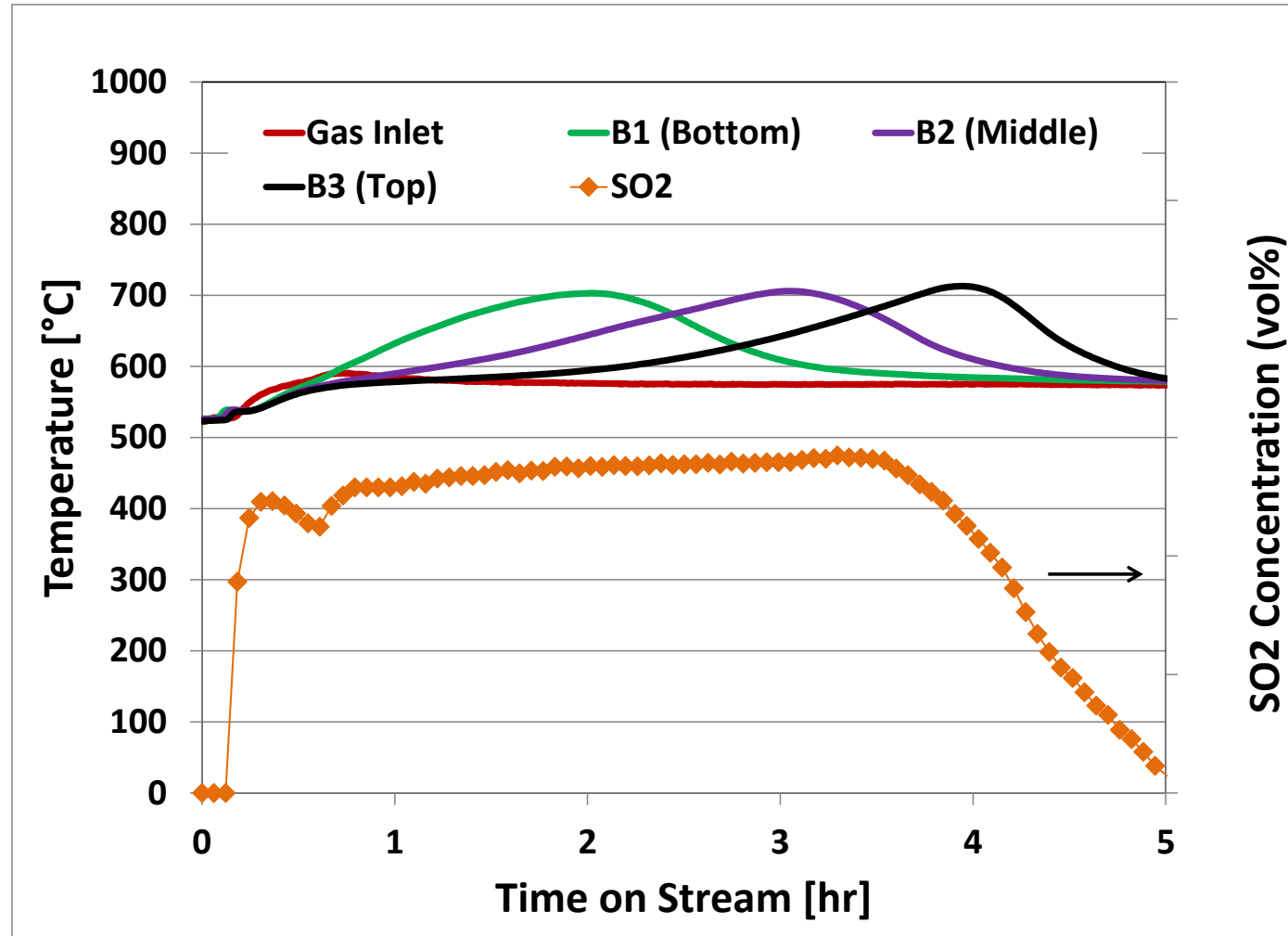
Sorbent Regeneration Temperature



Adsorption – Regeneration Transition

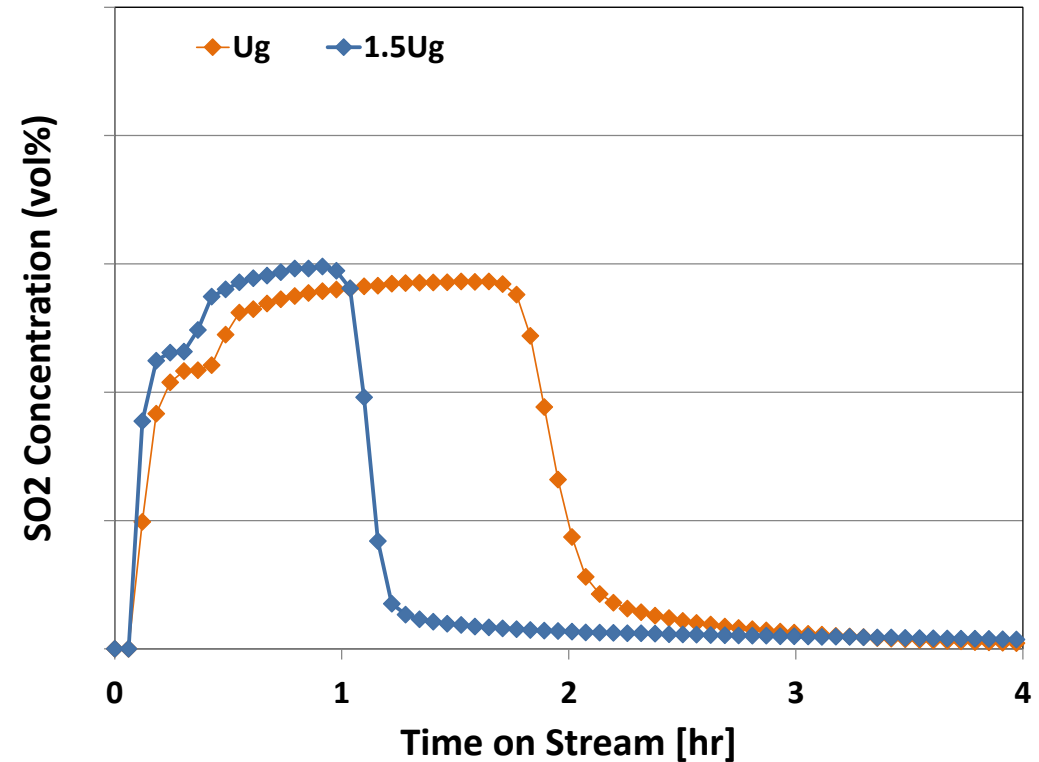
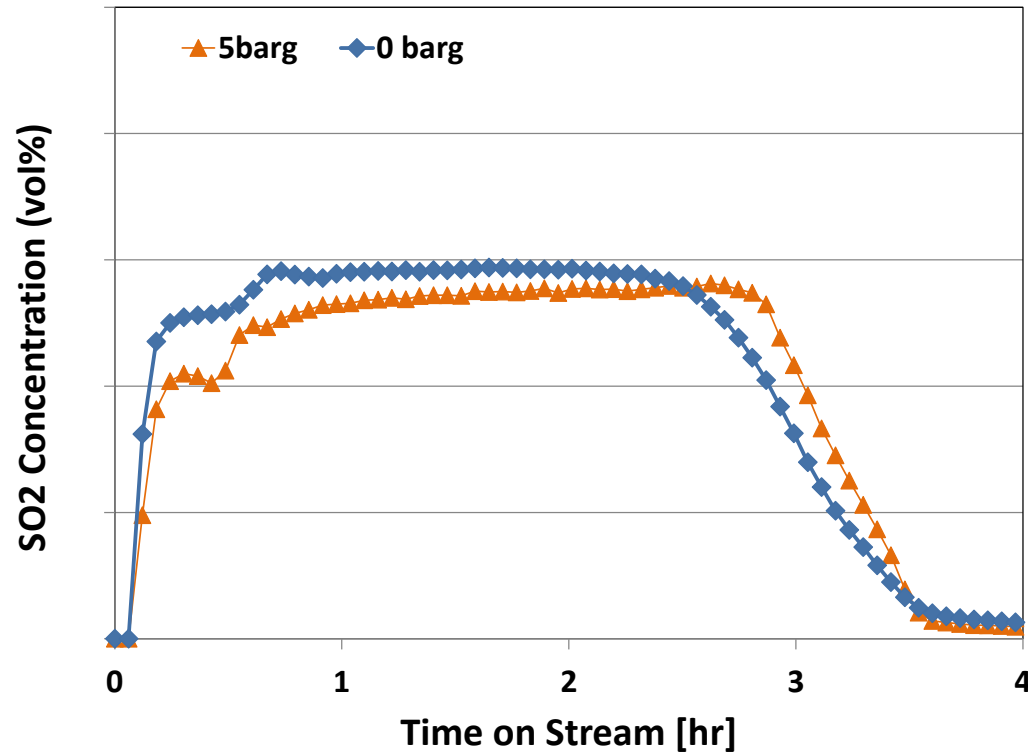


Sorbent Regeneration



- Regeneration Exotherm was captured in the scaled-up sorbent testing
- Results were used to identify the minimum temperature requirement to light off the sorbent regeneration process

Regeneration – Pressure and Space Velocity



- Pressure did not impact the kinetics of sorbent regeneration. Atmospheric regeneration will help save on the energy required for feed gas compression

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 being 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
- TEAs developed in this task are 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

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)
- Studied the effect of pressure and temperature on sorbent hydrodynamics and recently completed cyclic sorbent sulfur testing in the hot-flow unit under simulated operating conditions
- Successfully used pilot-scale fluidizable sorbent wet cake for the optimization of fixed-bed sorbent and process (Milestone 2)
- Currently finalizing conceptual designs for desulfurization processes based on fluidized-bed and fixed-bed reactors to support TEA
- Investigating commercial interest with varying sources for low sulfur, fixed-bed applications

Acknowledgements

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Questions?

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

