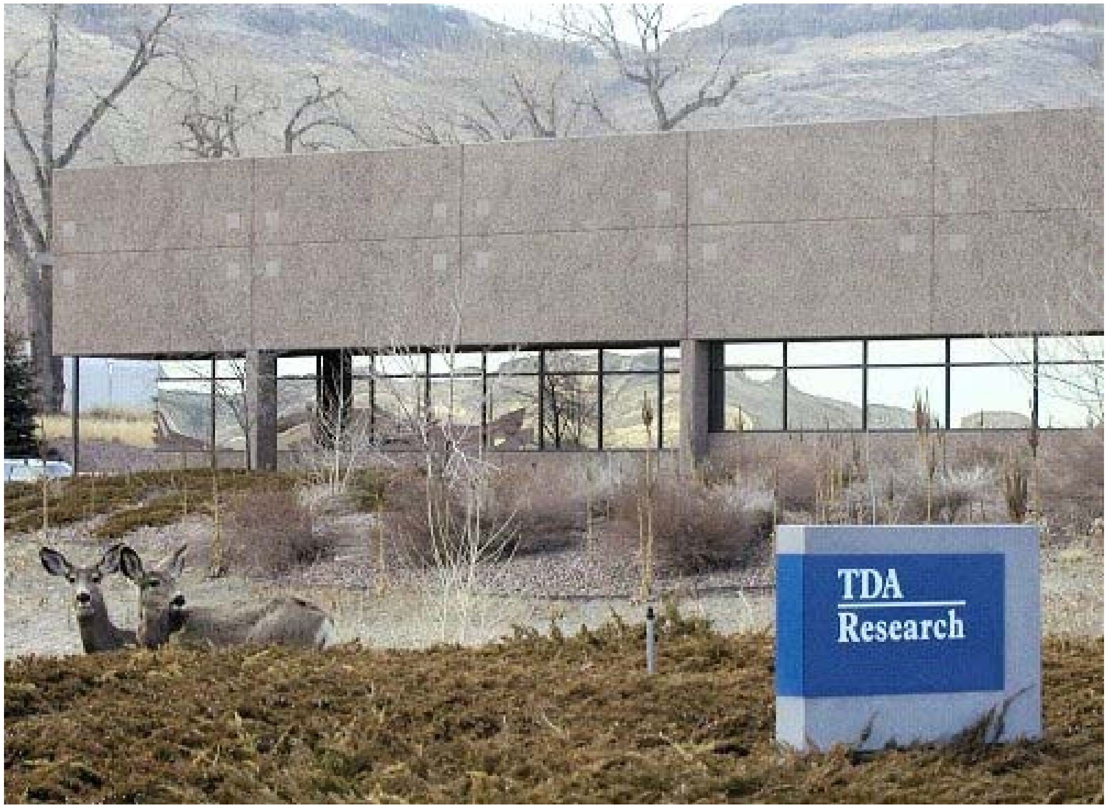
Integrated Water-Gas-Shift Pre-Combustion Carbon Capture Process



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2017 Gasification Systems Project Review

March 20, 2017

DE-FE0026142

October 1, 2015 – March 31, 2018

Project Objectives

- **The project objective is to demonstrate techno-economic viability of an integrated WGS catalyst/CO_2 removal system for IGCC power plants and CTL plants**
  - A high temperature PSA adsorbent is used for CO_2 removal above the dew point of the synthesis gas
  - A commercial low temperature catalyst is used for water-gas-shift
  - An effective heat management system
- **Project Tasks**
  - Design a fully-equipped slipstream test unit with 10 SCFM raw synthesis gas treatment capacity
  - Design and fabricate CFD optimized reactors capable of managing the exothermic WGS reaction while maintaining energy efficiency
  - Demonstrate all critical design parameters including sorbent capacity, CO_2 removal efficiency, extent of WGS conversion as well as H_2 recovery for over 2,000 hr using coal synthesis gas
  - Complete a high fidelity process design and economic analysis

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Project Partners

Project Duration

- **Start Date = October 1, 2014**
- **End Date = March 31, 2018 (no-cost extension requested)**

Budget

- **Project Cost = $5,632,619**
- **DOE Share = $4,506,719**
- **TDA and its partners = $1,125,900**

Presentation Outline

- **TDA's Approach**
- **TDA's Process**
- **Bench-Scale Results**
- **Modeling Results**
- **Prototype Unit Design and Fabrication**
- **Techno-economic Analysis**
- **Future Plans**

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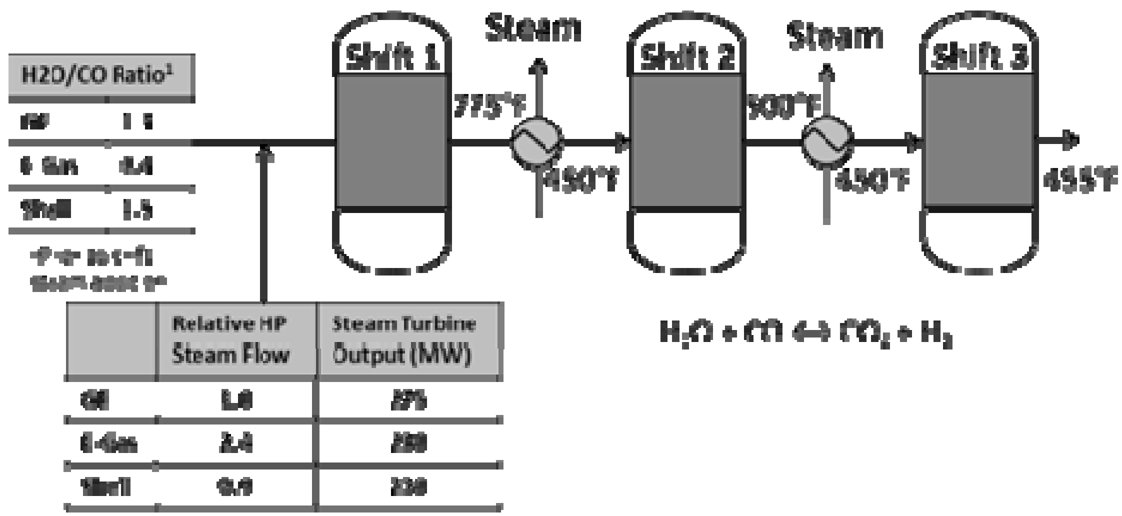
TDA's Approach

- **Conventional IGCC plants use multi-stage WGS with inter-stage cooling**
  - WGS is an equilibrium-limited exothermic reaction
- **Water is supplied at concentrations well above required by the reaction stoichiometry to completely shift the CO to CO_2**

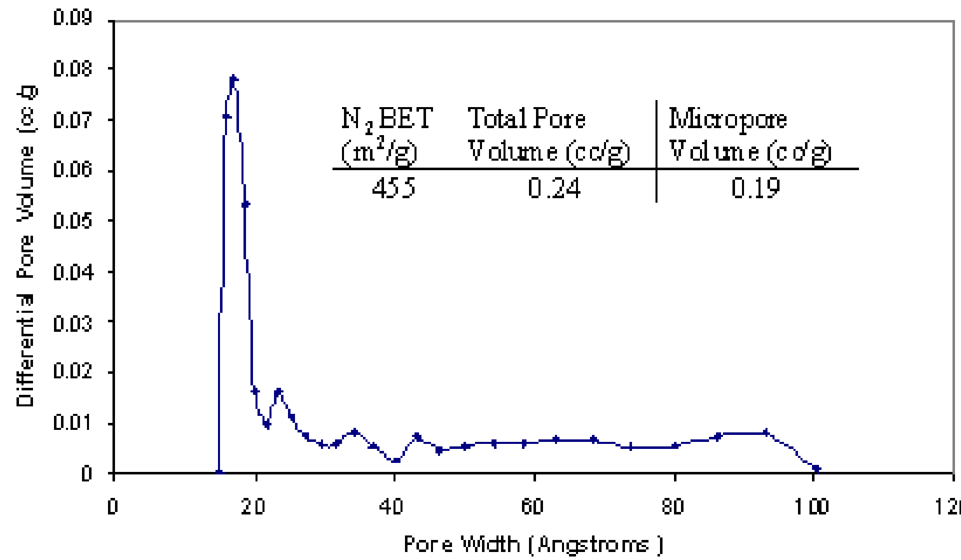


3-stage WGS unit as described in the DOE/NETL-2007/1281

- **In the process, high temperature CO_2 adsorbent is used to shift the CO *at low steam:carbon ratios***
- **Reduced water addition increases process efficiency**

TDA's Sorbent

- **TDA's uses a mesoporous carbon modified with surface functional groups that remove CO_2 via strong physical adsorption**
  - CO_2-surface interaction is strong enough to allow operation at elevated temperatures
  - Because CO_2 is not bonded via a covalent bond, the energy input for regeneration is low
- **Heat of CO_2 adsorption is 4.9 kcal/mol for TDA sorbent**
  - Comparable to that of Selexol
- **Net energy loss in sorbent regeneration is similar to Selexol, but a much higher IGCC efficiency can be achieved due to high temperature CO_2 capture**

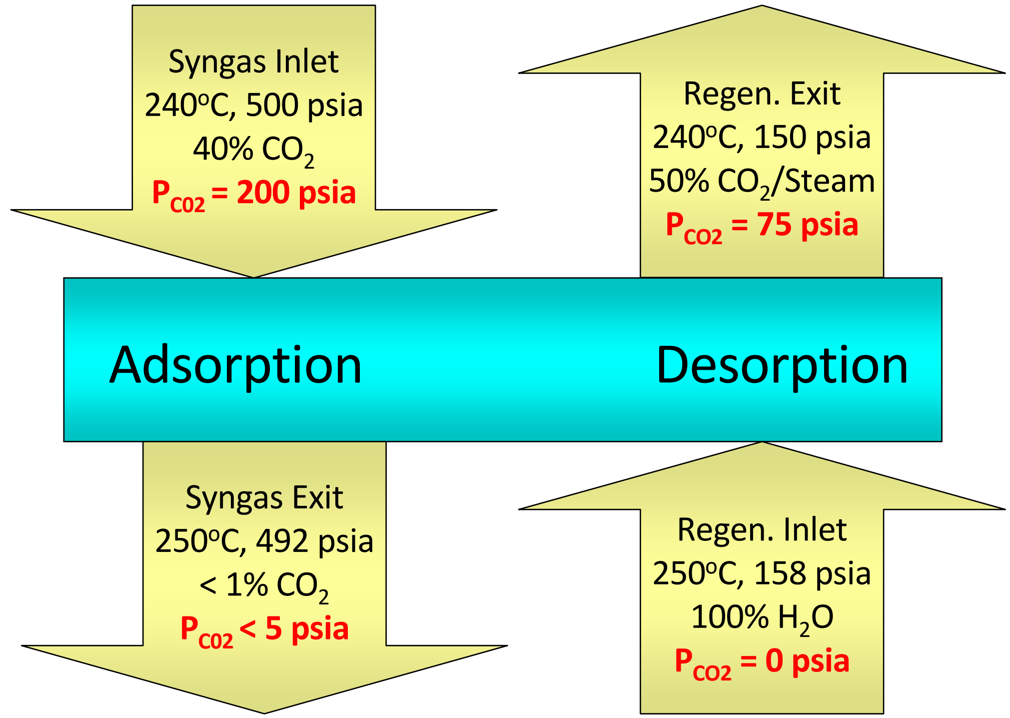


- **Pore size can be finely tuned in the 10 to 100 A range**
- **Mesopores eliminates diffusion limitations and rapid mass transfer, while enables high surface area**

US Patent 9,120,079, Dietz, Alptekin, Jayaraman "High Capacity Carbon Dioxide Sorbent", US 6,297,293; 6,737,445; 7,167,354
US Pat. Appl. 61790193, Alptekin, Jayaraman, Copeland "Pre-combustion Carbon Dioxide Capture System Using a Regenerable Sorbent"

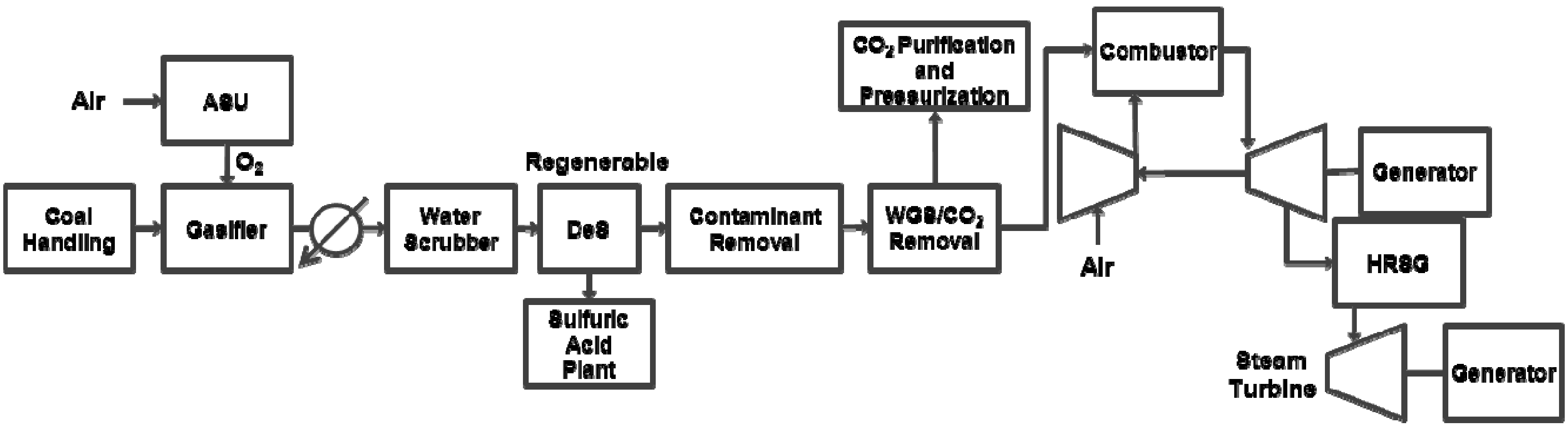
Operating Conditions

- CO_2 is recovered via combined pressure and concentration swing
  - CO_2 recovery at ~150 psia reduces energy need for CO_2 compression
  - Small steam purge ensures high product purity
- Isothermal operation eliminates heat/cool transitions
  - Rapid cycles reduces cycle time and increases sorbent utilization
- Similar PSA systems are used in commercial H_2 plants and air separation plants



Source: Honeywell/UOP

Integrated WGS/CO_2 Capture System

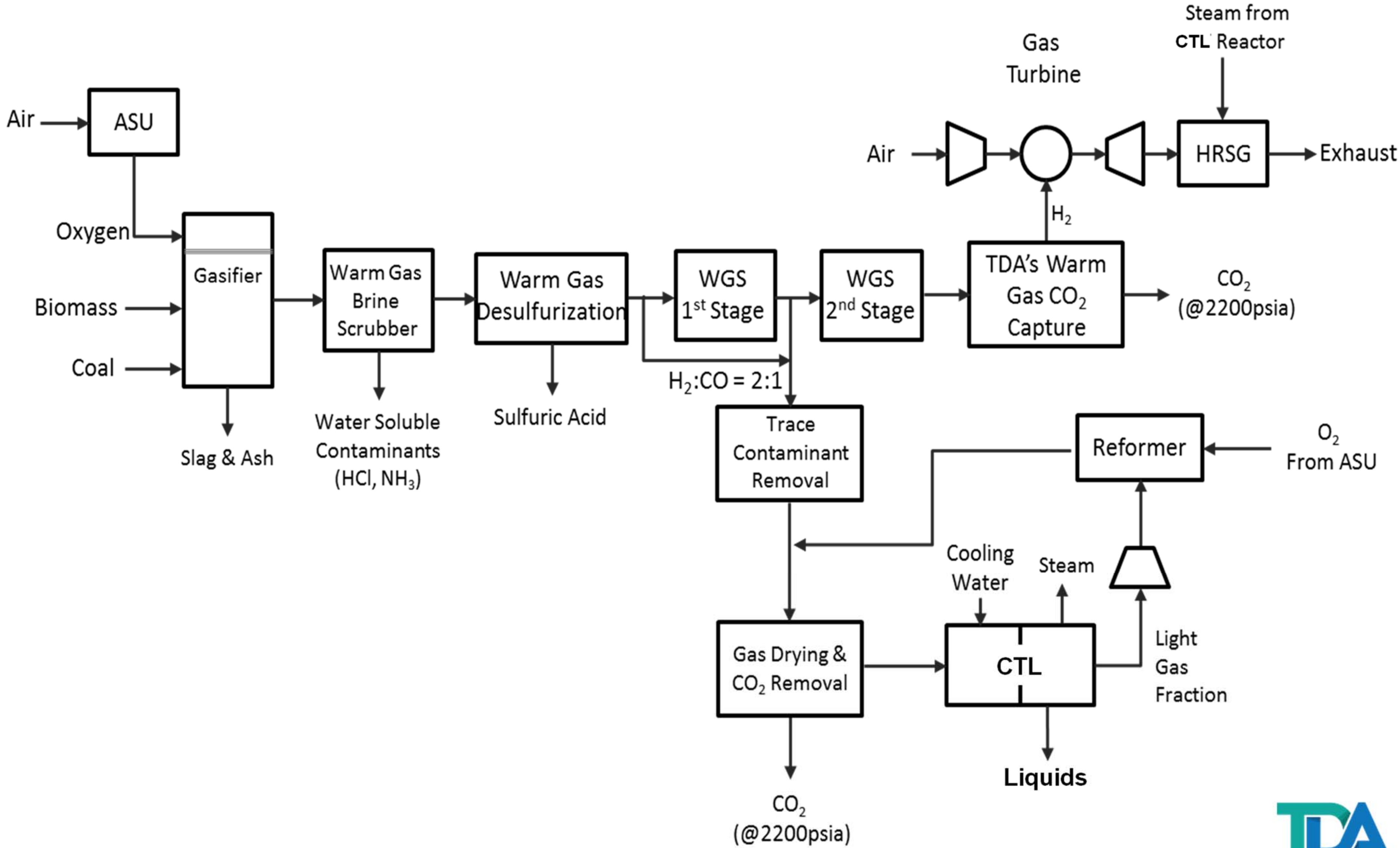


- **Reducing the use of excess steam improves power cycle efficiency**
  - Lower energy consumption to raise the steam
- **Process intensification could potentially reduce the number of hardware components and cost**

<u>Sorbent's point of view:</u>

- **Less dilution with water increases CO_2 partial pressure and in turn improves sorbent's working capacity**

Application to CTL



Sorbent Development Work

TDA 0.1 MW pre-combustion carbon capture unit installed at the National Carbon Capture Center

- **0.1 MW_e test in a world class IGCC plant to demonstrate full benefits of the technology**
  - Field Test #1 at NCCC
  - Field Test #2 at Sinopec Yangtzi Petro-chemical Plant, Nanjing, Jiangsu Province, China
- **Full operation scheme**
  - 8 reactors and all accumulators
  - Utilize product/inert gas purges
  - H_2 recovery/CO_2 purity

Yangtzi Petro-chemical Plant

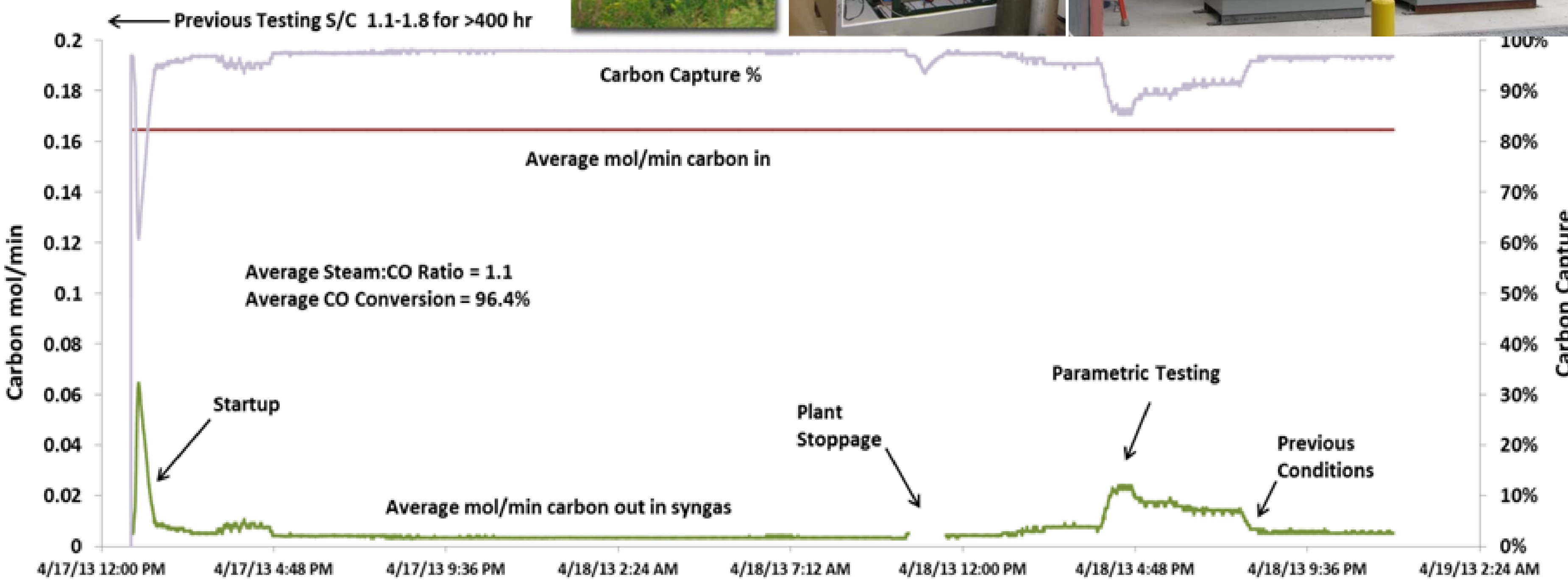
Sorbent and Catalyst for Field Tests

Sulfur Sorbent and WGS Catalyst

CO_2 Sorbent for Field Tests

- **3.5 m^3 of TDA's CO_2 sorbent has been produced for use in the field tests**
- **Warm gas Sulfur removal sorbent and High and Low Temperature WGS catalysts have been procured from Clariant**

NCCC Field Test – Early Work



- **90+% capture at steam:CO ratio= 1:1.1 with average 96.4% CO conversion**
- **All objectives met (no coking etc.) but high reactor T was observed**

Technology Status/R&D Needs

- **Sorbent is developed under a separate DOE project (DE-FE0000469)**
- **WGS catalyst is commercially available mature technology**
- **Early-stage concept demonstration has already been completed (DE-FE0007966)**
  - Integrated sorbent/catalyst operation
  - Pointed out the need to incorporate effective heat management
- **Key R&D need is the design/development of a high fidelity prototype to fully demonstrate the concept using actual coal-derived synthesis gas**
  - A 10 kg/hr CO_2 removal is being developed
  - Testing of the high fidelity system will be carried out at the NCCC and Praxair
  - Original test site Wabash River IGCC plant is no longer available

Project Structure

Year 1

- Design a field test unit including detailed design of the sorbent reactors, using multi-component adsorption and CFD simulation models
- Have the input and full approval of test sites
- Complete sorbent manufacturing based on the current Manufacturing Plan
- Initiate a long-term sorbent life evaluation (8,000 cycles)

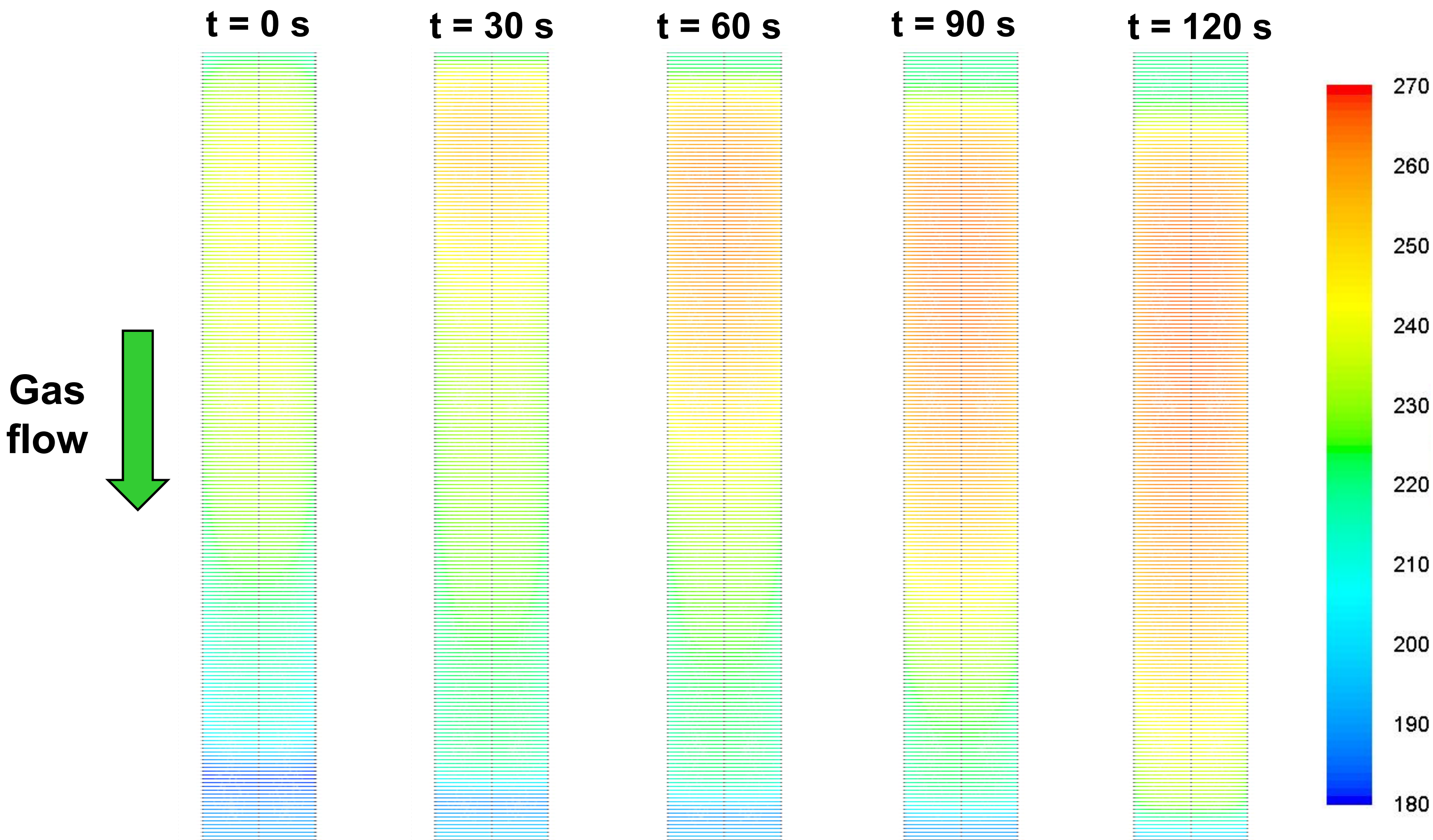
Year 2

- Complete evaluation of single integrated reactor with simulated syngas
- Revise our reactor design based on results from single reactor tests
- Complete fabrication of the slipstream test unit
- Continue long-term testing of the sorbent (20,000 cycles)

Year 3

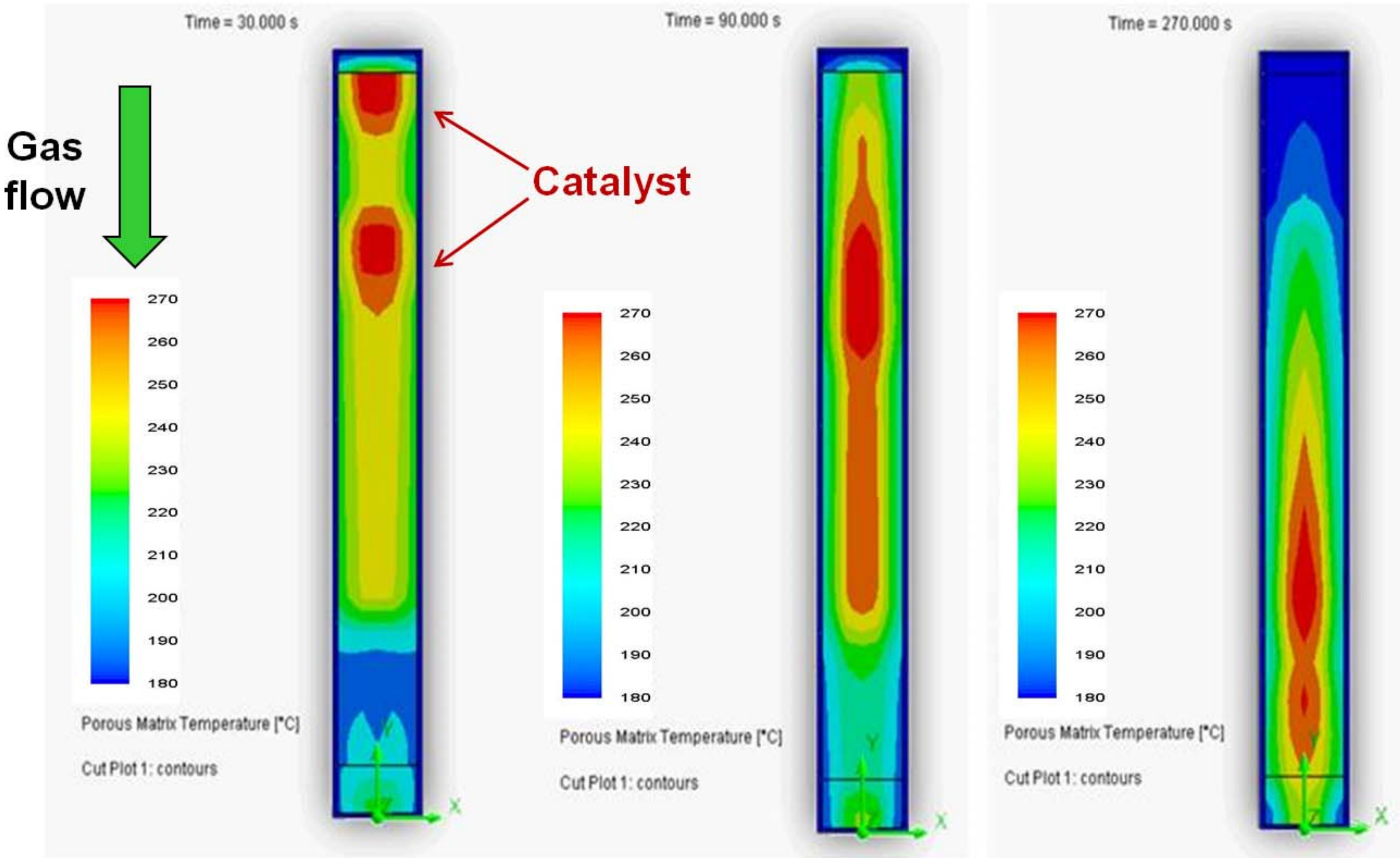
- Complete long-term testing of the sorbent (30,000 cycles)
- Complete field tests at the NCCC and Praxair Plants
- Complete a high-fidelity system design/analysis and cost estimate
- Complete an Environmental, Health and Safety (EHS) assessment

T Profiles - During CO_2 Capture Only



- **Heat generated during adsorption is removed during regeneration**
  - Near isothermal operation

Heat Wave WGS & CO_2 Capture

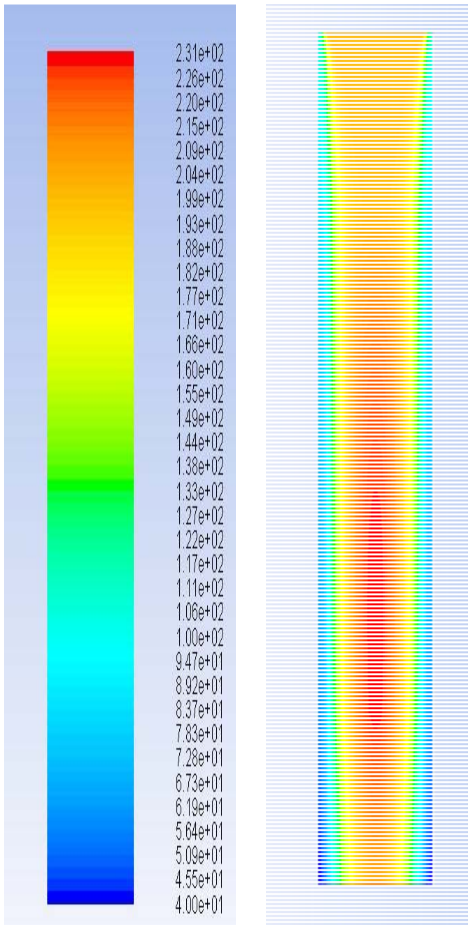


- Integrated WGS & CO_2 capture results in higher ΔT
- Not ideal for CO_2 capture (the WGS heat accumulates in the beds)

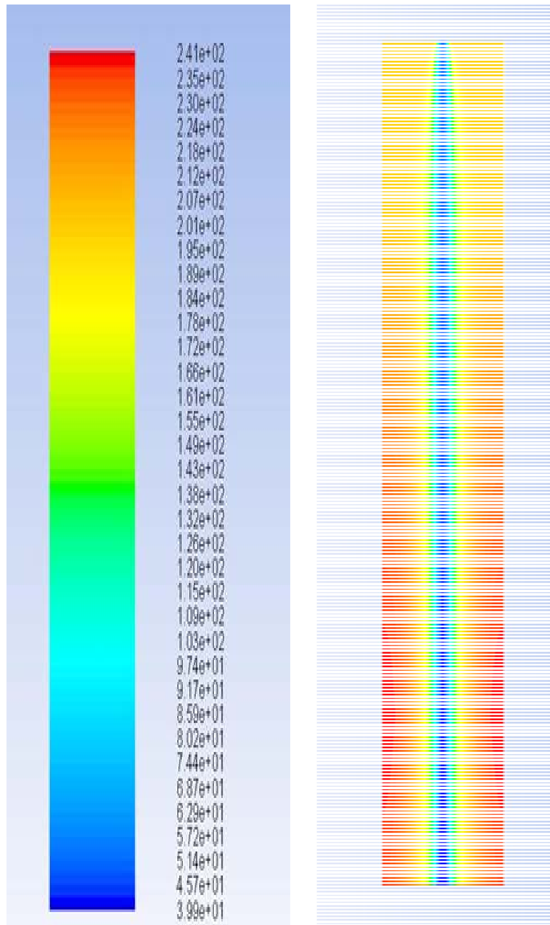
Conventional Heat Management Options

10 kg/hr CO_2 Removal Pilot Test System – 6” reactors

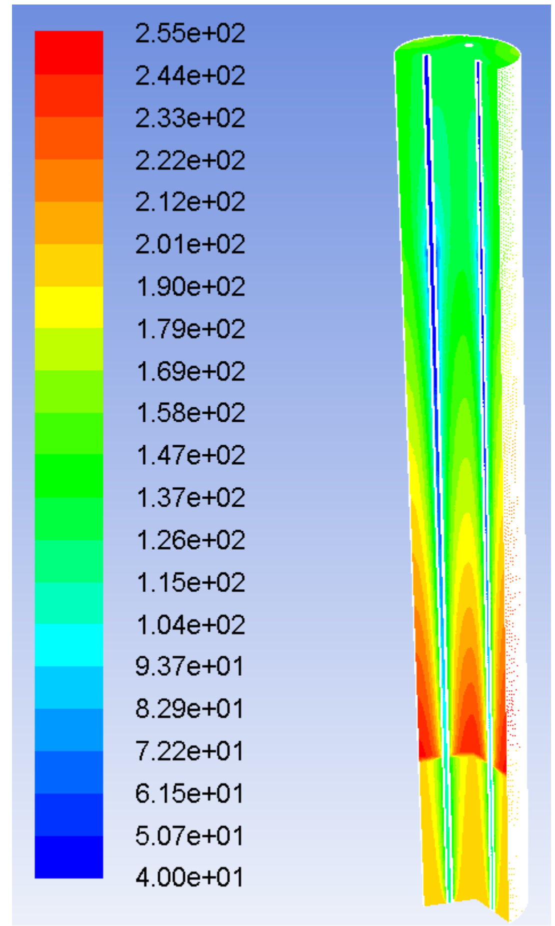
Cooling Jacket



Immersed Tube (1)



Immersed Tubes (3)



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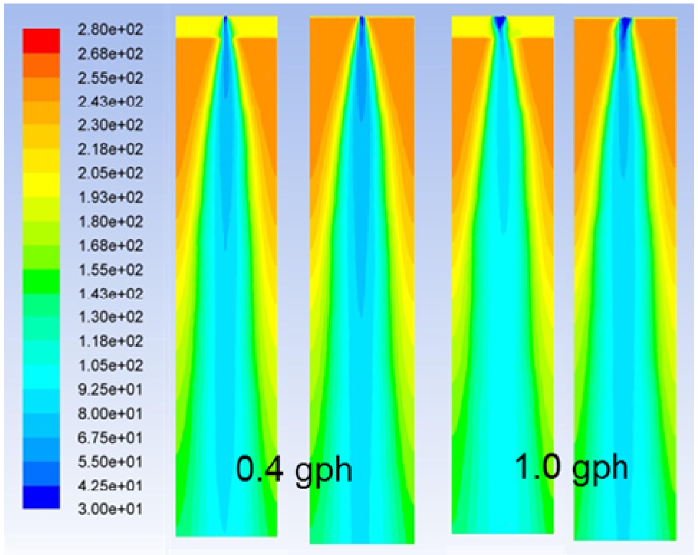
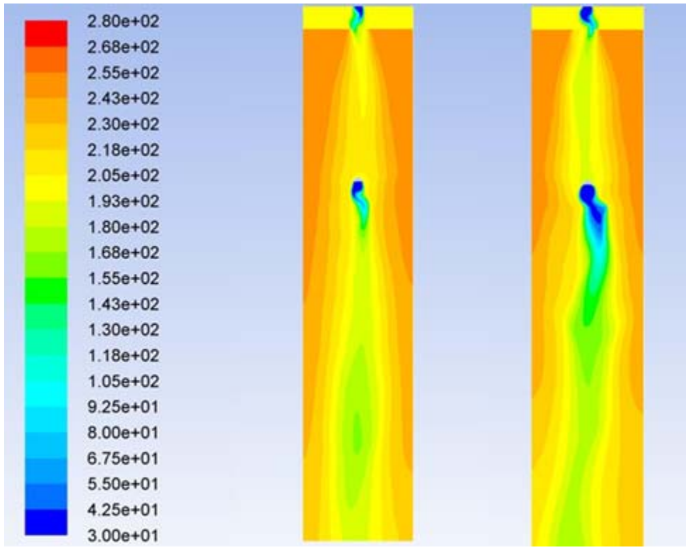
Heat Integrated WGS & CO_2 Capture

- **Advanced heat management concept based on direct water injection has proven to achieve much better temperature control**
  - Also much better heating efficiency (i.e., kJ heat removed per kg water)
- **Objective is to achieve a more uniform cooling without having hot or cold spots**
- **The temperature rise is optimal when the catalyst is distributed into two layers with water injections before each layer**

T Contours (°C) Single Injection Layer



T Contours (°C) Multiple Injection Layers



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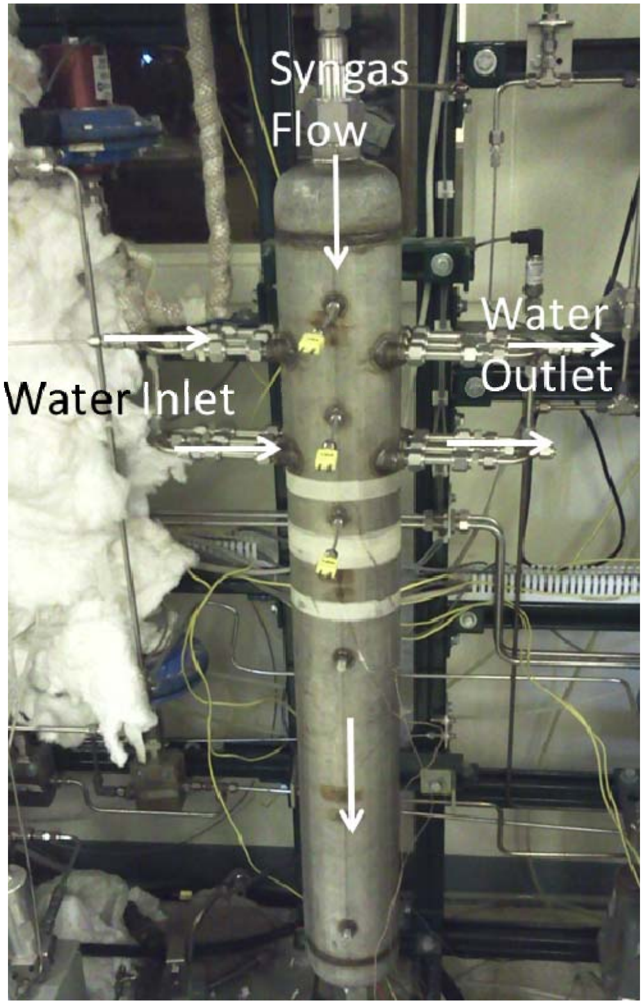
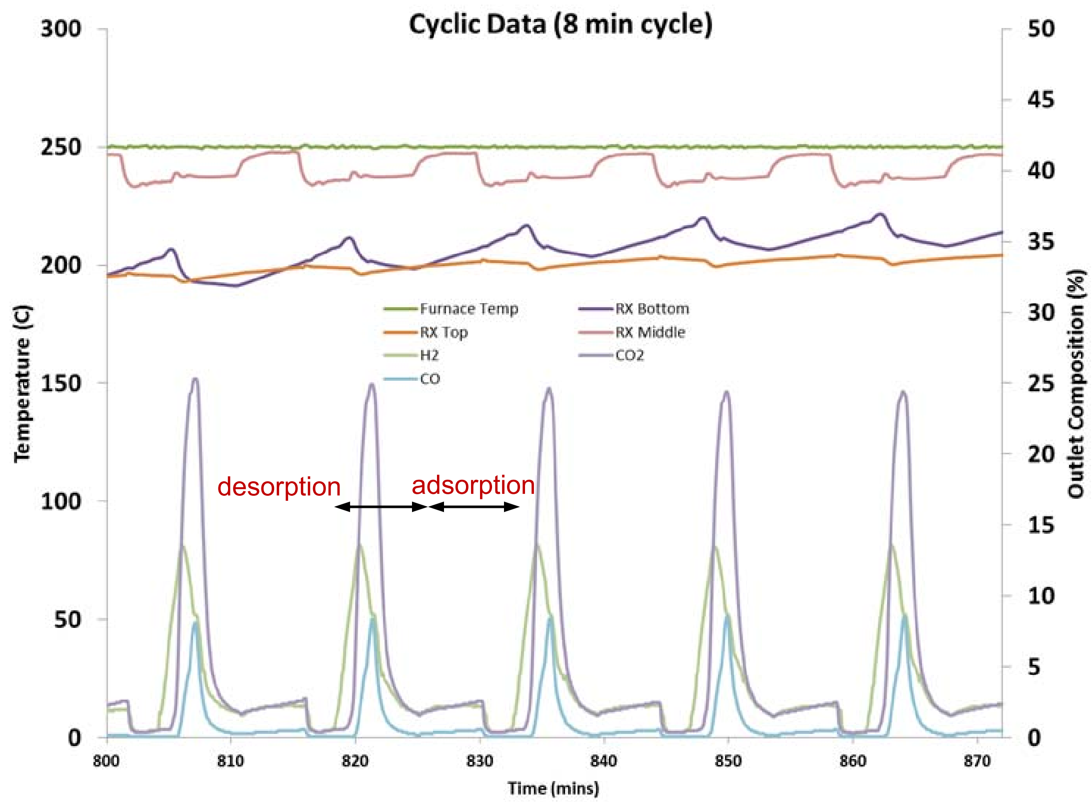
Bench-Scale Evaluations

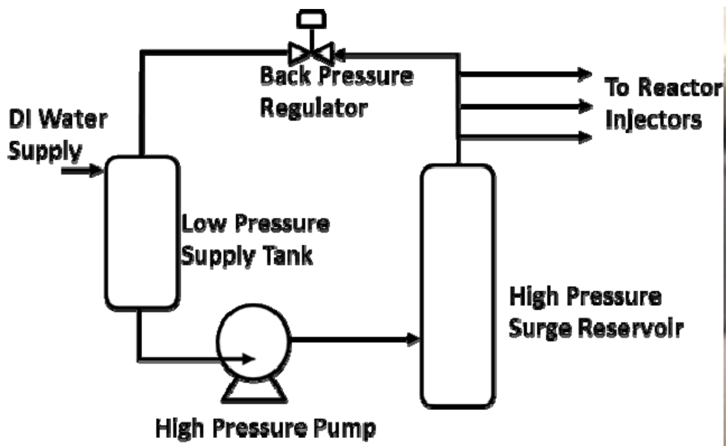


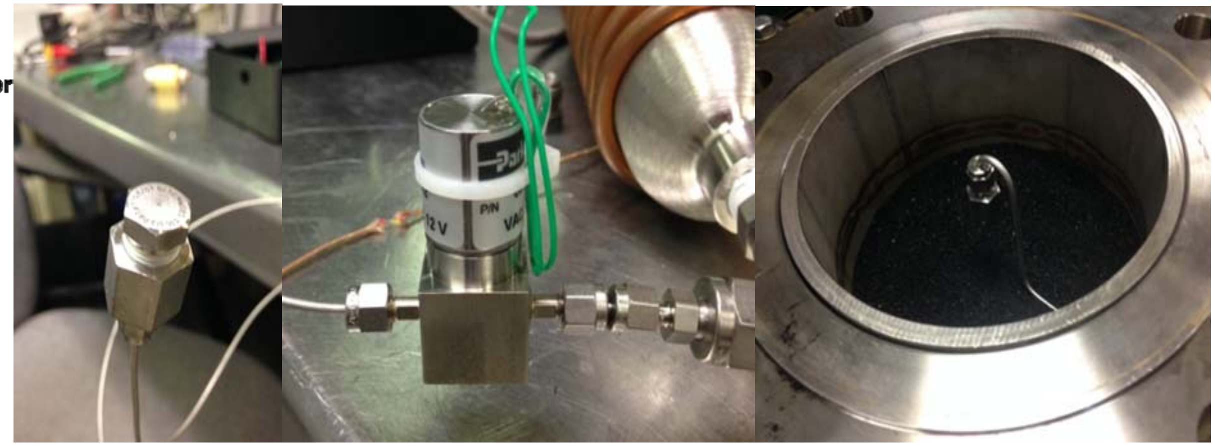


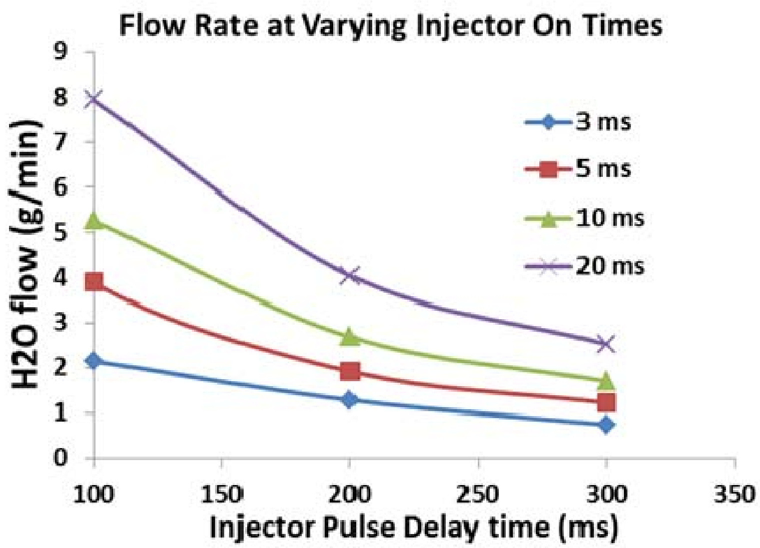
- **8L reactors were modified with the heat management options**
- **Successful proof-of-concept demonstrations have been completed**

- **ΔT <10°C was maintained over extended cycling (much lower than those observed in early field tests)**

Injector Design

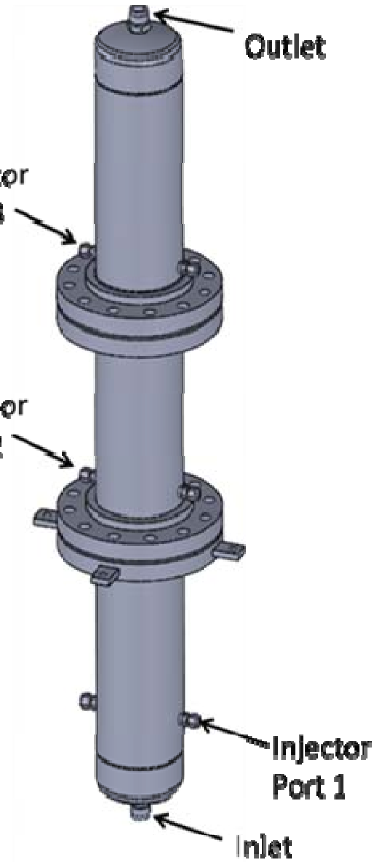


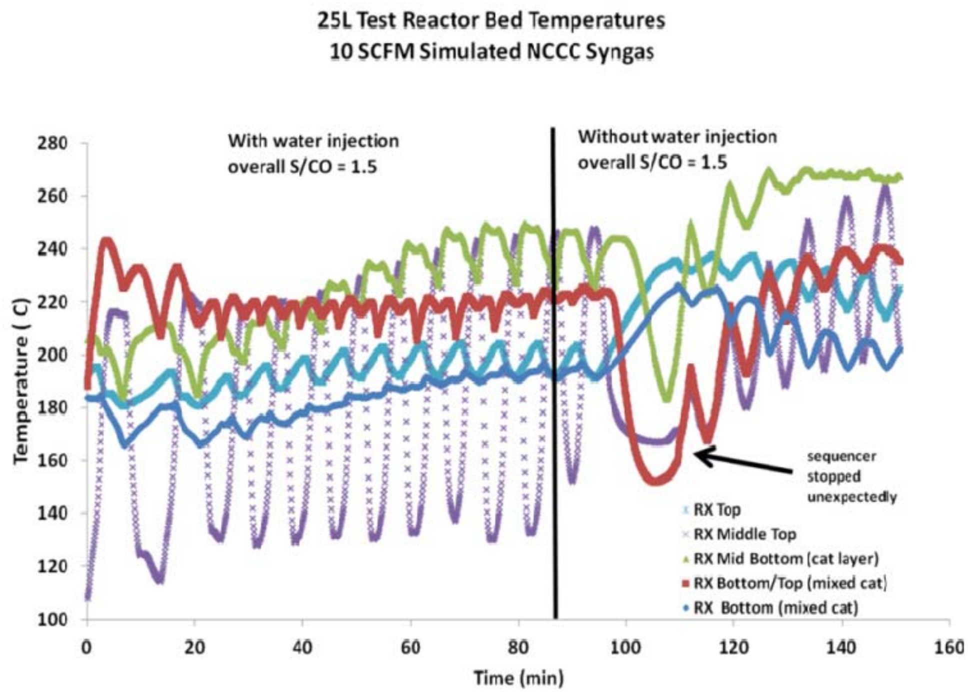


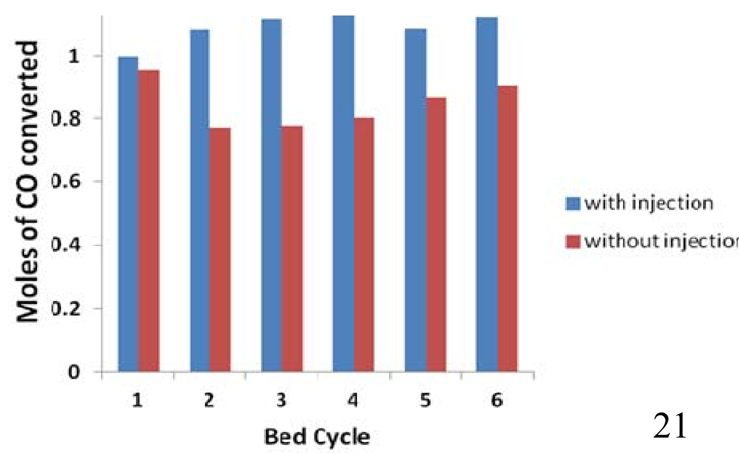


- **We designed our own injector nozzles and the water output control system that will allow these to effectively operate inside the reactor hot zone between 200-350°C**
- **The water flow rate is controlled by controlling injector pulse duration and pulse delay time**

Bench-scale Tests w/ Demo-size Reactor





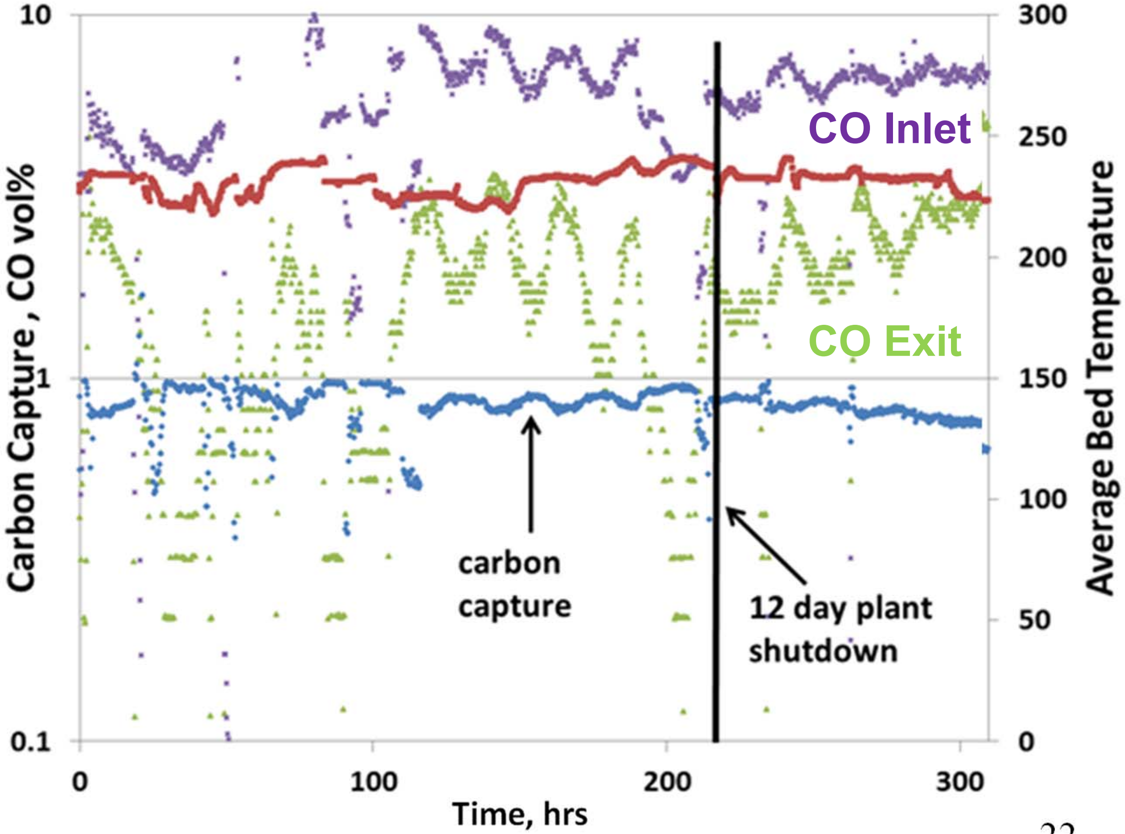


- Effective operation of the water injectors were demonstrated in a fully instrumented test reactor
- Sorbent & catalyst volume is the same as in the demo system

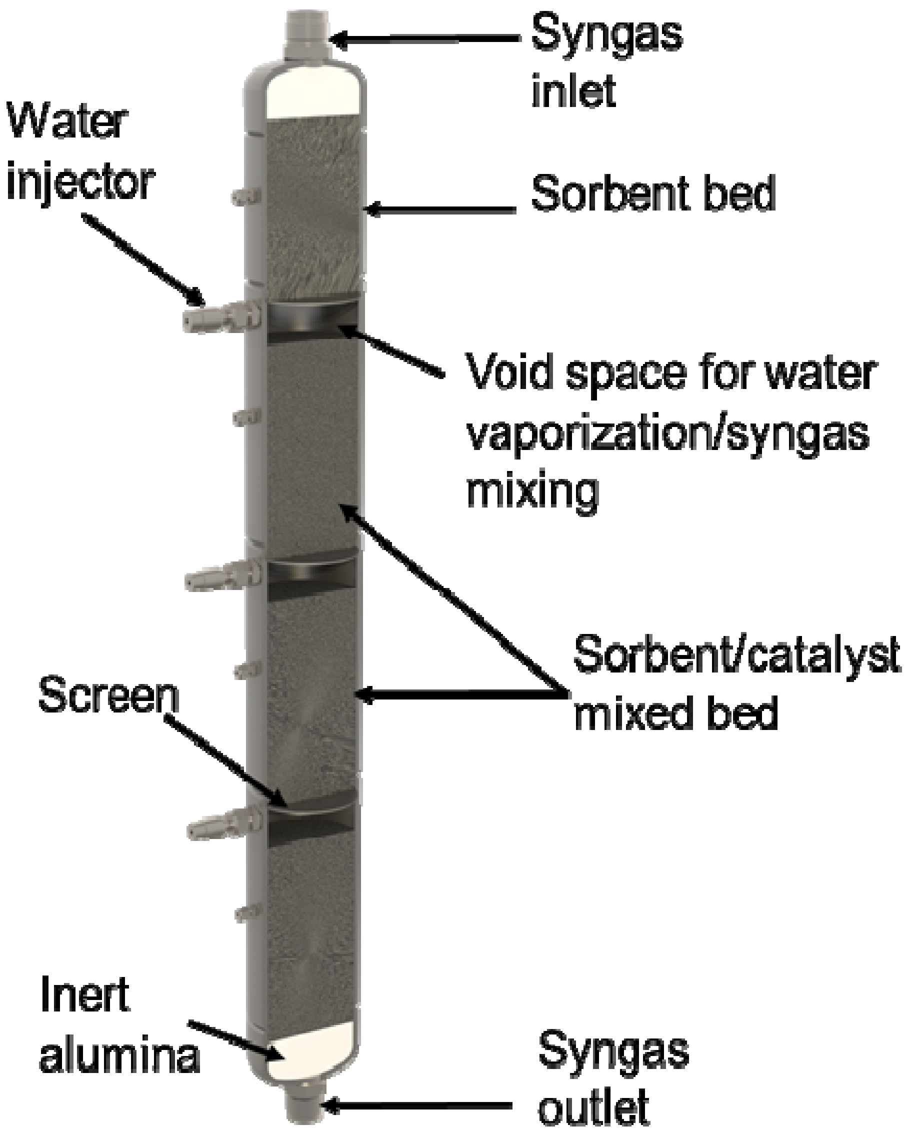
NCCC Testing

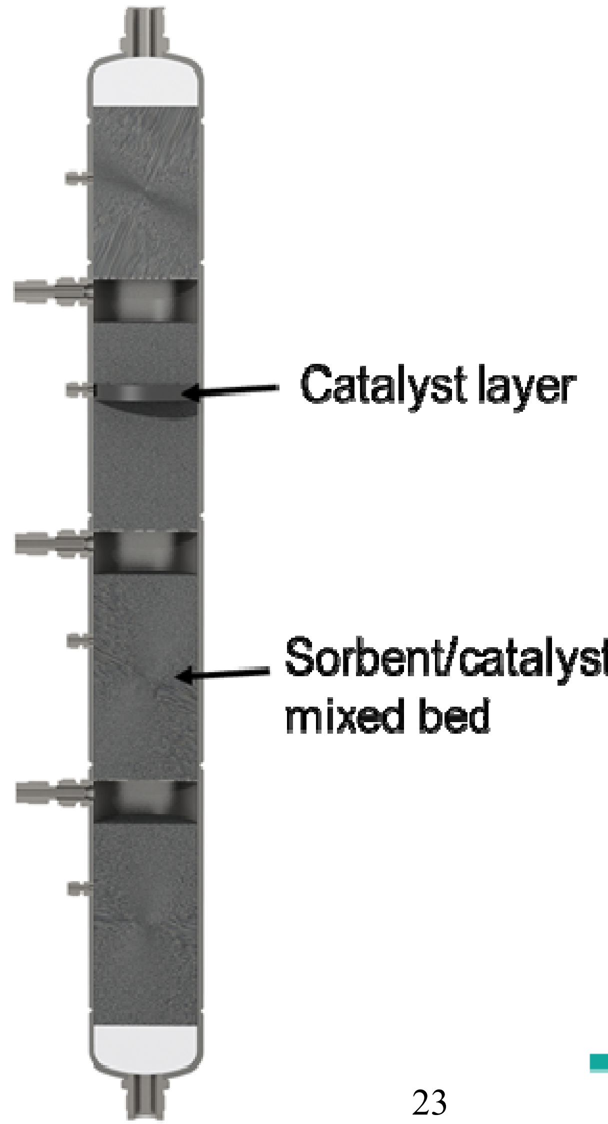
- **Testing during the G3 & G4 campaigns using at 1 SCFM scale validated the impact of water injection on bed temperature and CO conversion**
  - System was tested for over 650 hours
  - CO conversion, overall carbon capture, temperature, water injection functionality

CO Inlet Conc.= 6-8% vol.



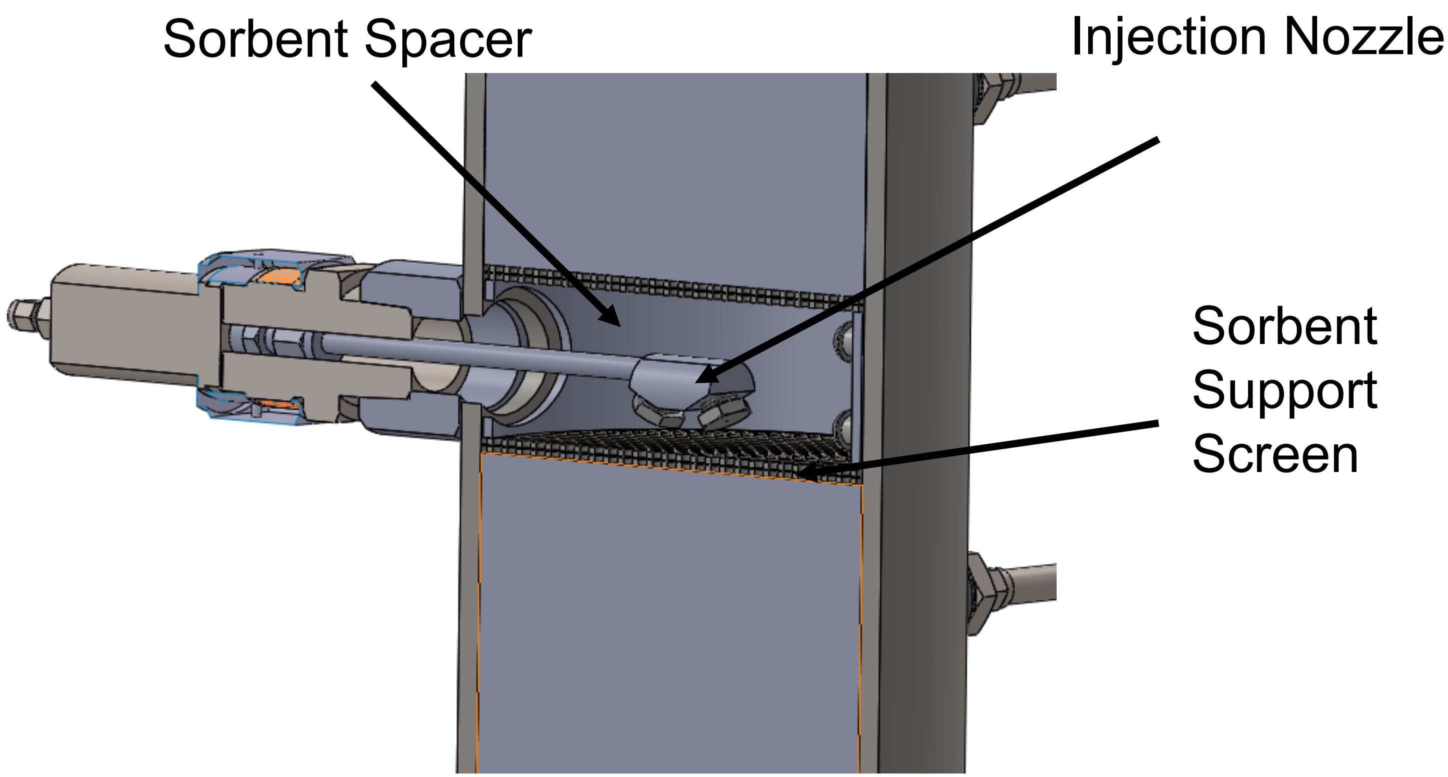
Reactor Design w/ Water Injectors

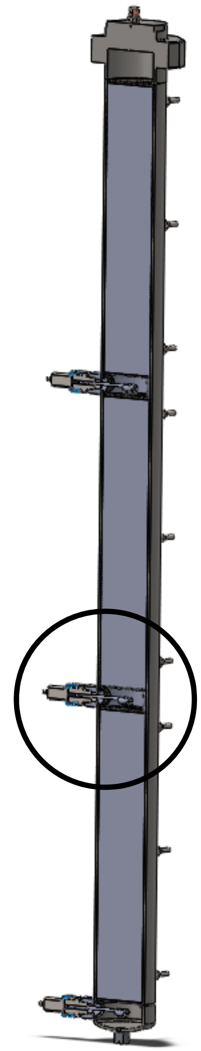




Water Injection System

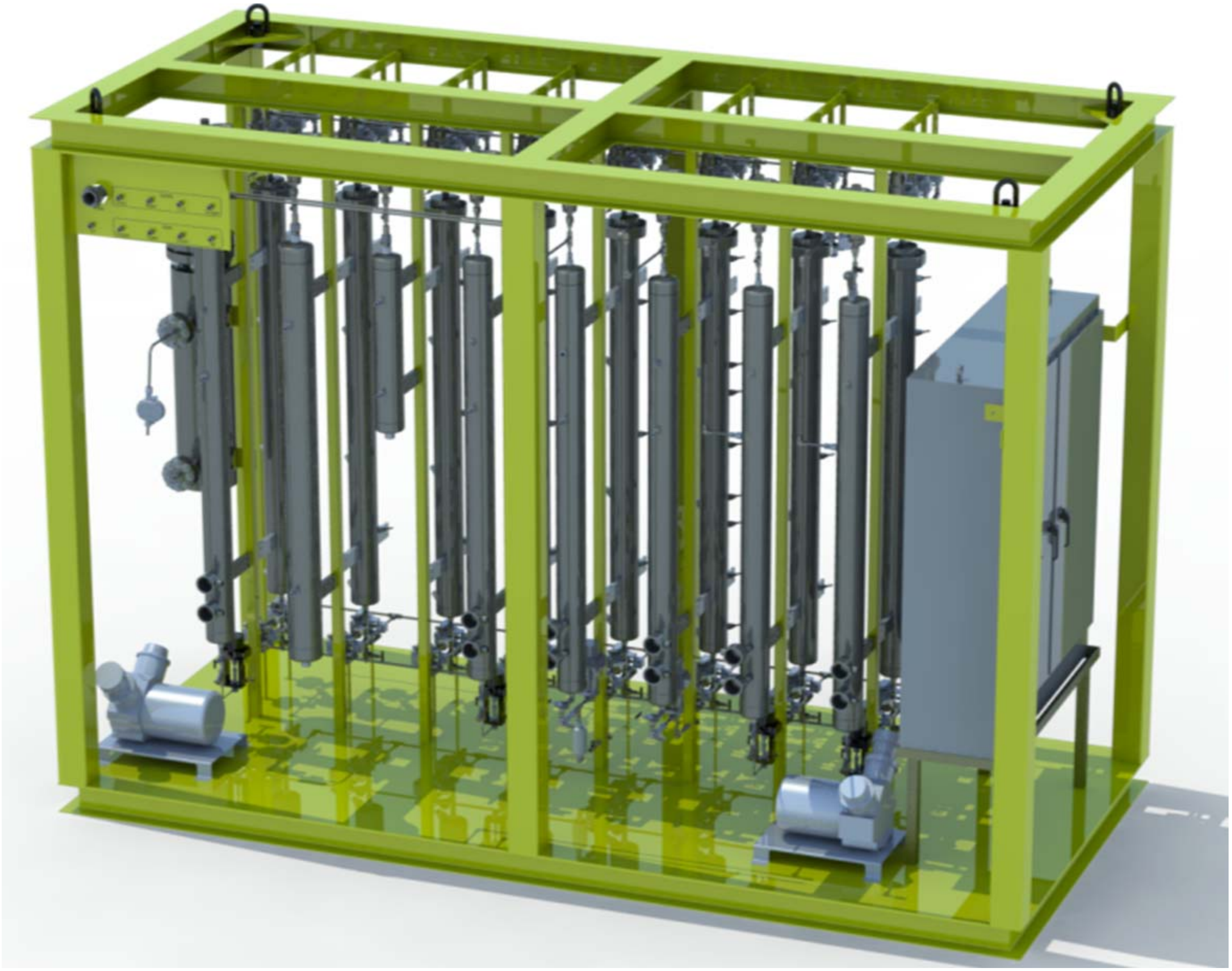
- **Water is injected in 3 locations along the bed**
- **A spacer will be inserted at each injector location to provide space for water vaporization and gas mixing**





TDA RESEARCH

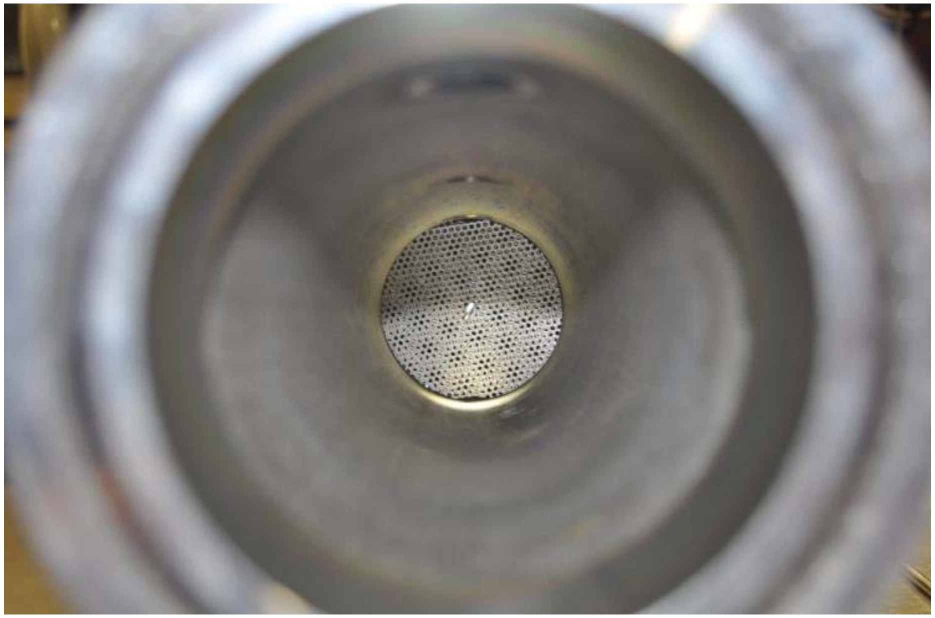
Integrated WGS/CO_2 Capture System



Fabrication of the Prototype

Reactor Vessel Fabrication

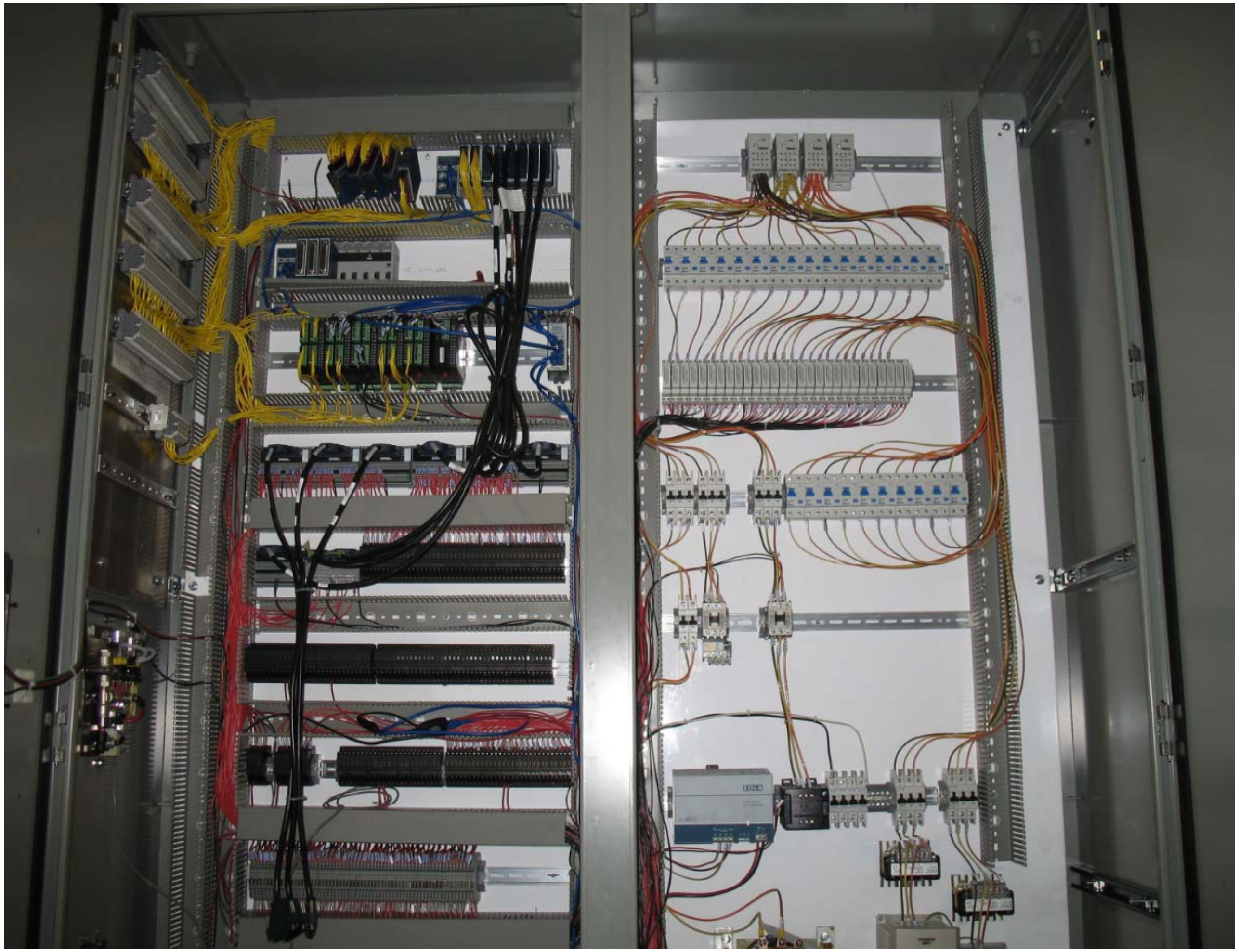
- **Vessel fabrication is completed**
- **Design allows easy replacement of media without removing the injector assembly**



Fabrication of the Prototype

- **All plumbing work is complete**

Electrical and Control Systems



- **Control box is completed (electrical, heating and insulation will be completed late April 2017**

Process Simulation and Analysis

IGCC plant with E-Gas™ Gasifier operating on Bituminous Coal

#	CO_2 Capture	Notes	Steam/ Water Addition	Overall Steam:CO Ratio	Net Efficiency % HHV
1	Conventional Technology	Reference IGCCCase with Steam addition to 1st WGS reactor feed	Steam	2.25	31.04
2	TDA/Advanced Technology	No steam addition to 1st WGS reactor feed; water injection into combined WGS+PSA reactor	Water	1.50	34.30
2-3	TDA/Advanced Technology	No 1st WGS reactor & water injection into combined WGS+PSA reactor	Water	2.21	33.73
2A	TDA/Previous Technology	Steam addition to 1st WGS reactor feed; no water injection into 2nd WGS reactor (not combined with PSA)	Steam	2.25	33.81

- **Reducing Steam:CO ratio to 1.50 w/ water addition to Integrated WGS/CO_2 Removal Reactor (2nd stage) provides a net plant efficiency of 34.30%**
  - **0.5% point improvement over TDA's sorbent-only technology**

IGCC plants with Shell Gasifier

Case #	Coal Type	CO_2 Capture	Notes	Overall Steam: CO Ratio	Net Efficiency % HHV
3	Bituminous	Conventional Technology	Reference IGCC Case (H2O/CO in 1st WGS reactor feed = 1.8 mole/mole per corresponding DoE case)	1.8	31.08
4	Bituminous	TDA/Advanced Technology	No steam addition to 1st WGS reactor feed (H2O/CO in 1st WGS reactor feed = 1.11 mole/mole); water injection into combined WGS+PSA reactor	1.38	33.71
5	Lignite	Conventional Technology	Reference IGCC Case (H2O/CO in 1st WGS reactor feed = 1.8 mole/mole)	1.8	30.89
6	Lignite	TDA/Advanced Technology	No steam addition to 1st WGS reactor feed (H2O/CO in 1st WGS reactor feed = 1.60 mole/mole); water injection into combined WGS+PSA reactor	1.78	32.79

- **Different gasifiers and coal are being evaluated**
  - **Better plant efficiency for all coals and gasifiers**

E-Gas™ & GE Gasifiers

Gasifier Type/Make	E-Gas			GE	
Case	1	2	2* (WGS/CO_2)	3	4
CO_2 Capture Technology	Cold Gas Cleanup Selexol™	Warm Gas Cleanup TDA's CO_2 Sorbent	Warm Gas Cleanup TDA's CO_2 Sorbent	Cold Gas Cleanup Selexol™	Warm Gas Cleanup TDA's CO_2 Sorbent
CO_2 Capture, %	90	90	90	90	90
Gross Power Generated, kW	710,789	670,056	693,542	727,633	674,331
Gas Turbine Power	464,000	425,605	427,980	464,000	417,554
Steam Turbine Power	246,789	244,450	265,562	257,657	246,746
Syngas Expander Power	-	-	-	5,977	10,031
Auxiliary Load, kW	194,473	124,138	138,741	192,546	120,661
Net Power, kW	516,316	545,917	554,801	535,087	553,671
Net Plant Efficiency, % HHV	31.0	34.1	34.7	32.0	34.5
Coal Feed Rate, kg/h	220,549	212,265	212,265	221,917	213,013
Raw Water Usage, GPM/MW	10.9	10.3	10.0	10.7	10.5
Total Plant Cost, $/kW	3,464	3,042	2,990	3,359	3,083
COE without CO_2 TS&M, $/MWh	136.8	120.5	118.8	133.0	121.8
COE with CO_2 TS&M, $/MWh	145.7	128.6	126.7	141.6	129.7
Cost of CO_2 Captured, $/tonne	53.2	37.4	35.8	47.3	36.1

- **Efficiency is increased to 34.7% with TDA's combined WGS/CO_2 system and reduced to $35.8/tonne**

Process Economic Analysis - CTL

- Integrated WGS with CO_2 capture reduced the required selling price (RSP) for Methanol to $438 per ST compared to $453 per ST for a CTL plant with Rectisol

Gasifier	Shell	
Coal	Bituminous	
Case	7	8
CO_2 Capture Technology	Cold Gas Cleanup Rectisol™	Warm Gas Cleanup TDA's CO_2 Sorbent
CO_2 Capture, %	90	90
Gross Power Generated, kW	320,514	292,457
Gas Turbine Power	130,684	130,114
Steam Turbine Power	189,830	162,342
Syngas Expander Power	-	-
Auxiliary Load, kW	310,729	276,851
Net Power, kW	9,785	15,606
Net Plant Efficiency, % HHV	-	0.35
Methanol Production rate, ST/D	11,094	10,934
Coal Feed Rate, kg/h	589,458	589,458
Raw Water Usage, GPM	6,529.0	5,405.0
Total Plant Cost, $/kg/D	357.26	345.27
1st year Required Selling Price (RSP) w/o CO2 TS&M, $/ST	453.0	438.0

Process Economic Analysis - CTL

Gasifier	Shell	
Coal	Bituminous	
Case	9	10A
CO_2 Capture Technology	Cold Gas Cleanup Rectisol[TM]	Warm Gas Cleanup TDA's CO_2 Sorbent
CO_2 Capture, %	90	90
Gross Power Generated, kW	462,568	458,830
Gas Turbine Power	130,283	130,519
Steam Turbine Power	332,285	328,311
Syngas Expander Power	-	-
Auxiliary Load, kW	397,803	365,956
Net Power, kW	64,764	92,875
Net Plant Efficiency, % HHV	1.08	1.55
Naphtha Production rate, ST/D	1,803	1,722
Diesel Production rate, ST/D	4,789	4,933
Coal Feed Rate, kg/h	793,864	793,864
Raw Water Usage, GPM	14,032.6	12,394.0
Total Plant Cost, $/kg/D	949.87	864.94
NAPHTHA		
1st year Required Selling Price (RSP) w/o CO2 TS&M, $/bbl	107.0	100.0
DIESEL		
1st year Required Selling Price (RSP) w/o CO2 TS&M, $/bbl	153.0	143.0

- **Integrated WGS with CO_2 capture reduced the required selling price for Naphtha to $100 per bbl compared to $107 per bbl for a CTL plant with Rectisol**
- **Integrated WGS with CO_2 capture reduced the required selling price for Diesel to $143 per bbl compared to $153 per bbl for a CTL plant with Rectisol**

TDA RESEARCH

Future Work

- Complete fabrication of the slipstream test unit – May 2017
- Testing of the unit at Praxair – June-August 2017
- Testing of the unit at NCCC – October-November 2017
- Complete long-term testing of the sorbent (30,000 cycles) – September 2017
- Complete a high-fidelity system design/analysis and cost estimate – March 2018
- Complete an Environmental, Health and Safety (EHS) assessment – March 2018