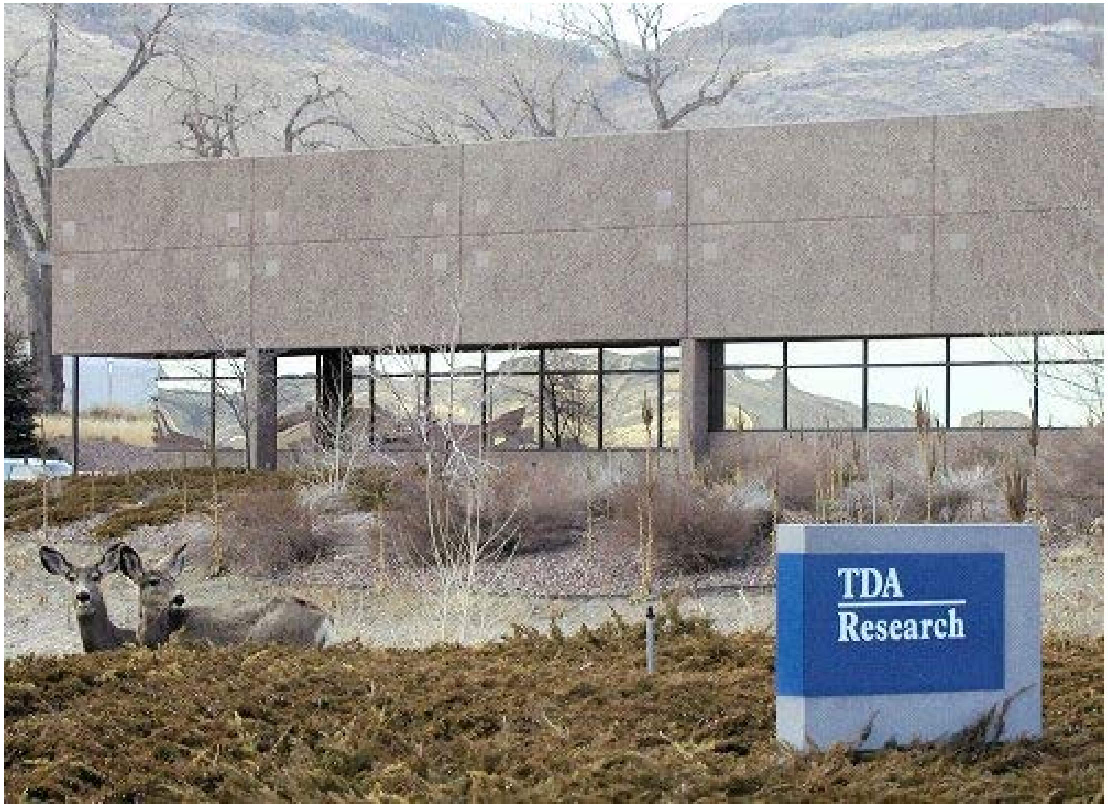
Integrated Water-Gas-Shift Pre-Combustion Carbon Capture Process (Contract No. DE-FE0023684)



Gökhan Alptekin, PhD
TDA Research, Inc.
Wheat Ridge, CO
galptekin@tda.com

2019 Crosscutting Research Program
Gasification Systems Project Review

April 9, 2019

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 is developed
- **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 exotherm of the WGS reaction while maintaining energy efficiency
  - Demonstrate critical design parameters including sorbent capacity, CO_2 removal efficiency, extent of WGS conversion as well as H_2 recovery using coal synthesis gas
  - Complete a high fidelity process design and economic analysis

Project Partners

Project Duration

- **Start Date = October 1, 2014**
- **End Date = September 30, 2019**

Budget

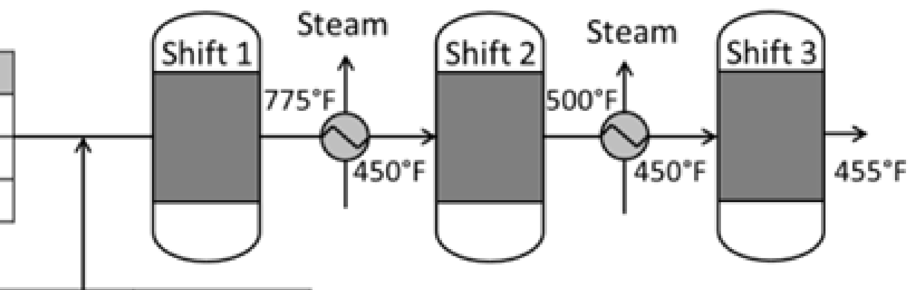
- **Project Cost = $5,632,619**
- **DOE Share = $4,506,719**
- **TDA and its partners = $1,125,900**

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**

H2O/CO Ratio[1]	
GE	1.3
E-Gas	0.4
Shell	1.5

[1]Prior to shift steam addition



	Relative HP Steam Flow	Steam Turbine Output (MW)
GE	1.0	275
E-Gas	2.4	230
Shell	0.9	230

$H_2O + CO \leftrightarrow CO_2 + H_2$

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

- **In our process, the WGS catalyst is combined with a high temperature CO_2 adsorbent to achieve high CO conversion *<u>at low steam:carbon ratios</u>***
- **Reduced water addition increases process efficiency**

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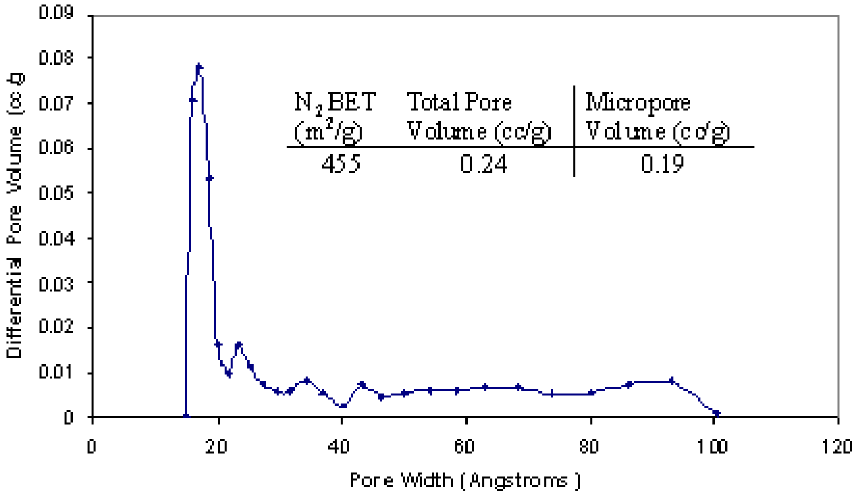
TDA’s Sorbent

- **TDA’s uses a mesoporous carbon 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, energy input for regeneration is low
- **Heat of CO_2 adsorption is 4.9 kcal/mol for TDA sorbent**
  - Net energy loss in sorbent regeneration is similar to Selexol; much higher IGCC efficiency can be achieved due to high temperature CO_2 capture
- **Favorable material properties**
  - Pore size is tuned to 10 to 100 A
  - Mesopores eliminates diffusion limitations



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 CO_2 Capture System Using a Regenerable Sorbent”

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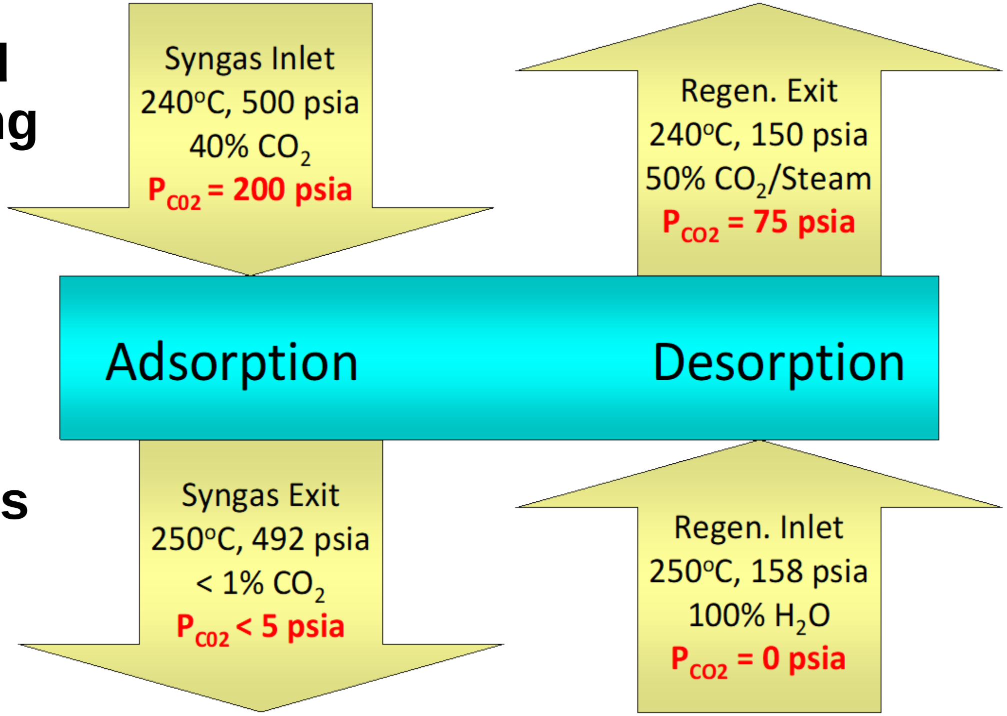
Operating Conditions

- CO_2 is recovered via combined pressure & 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
- The WGS catalyst was subjected to the same cycle



Source: Honeywell/UOP

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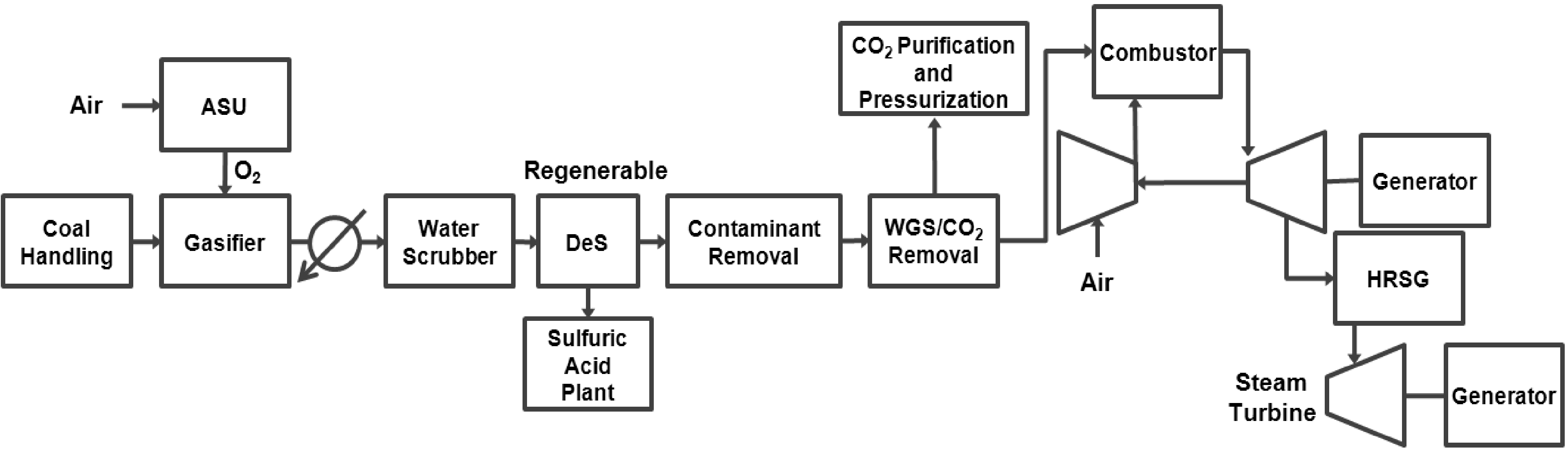
Integrated WGS/CO_2 Capture System

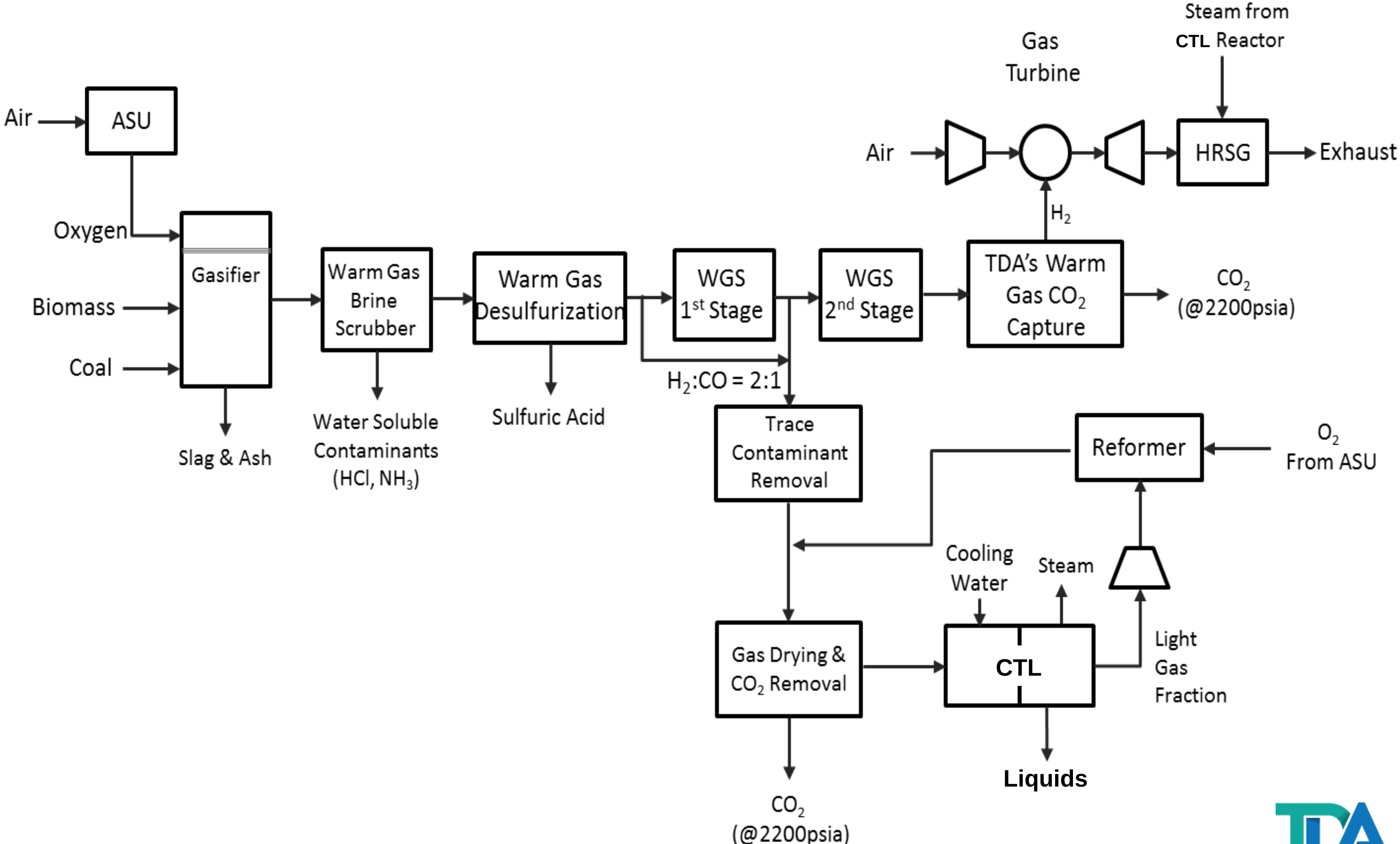


- **Reducing the use of excess steam improves power cycle efficiency**
  - Lower energy consumption to raise the steam
- **Process intensification could potentially reduce the number of hardware components and cost**

<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 of the Technology to CTL



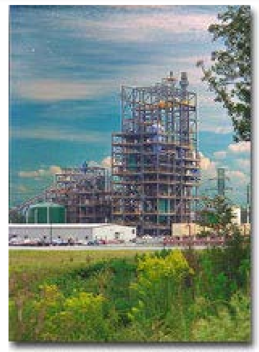
Sorbent Development Work

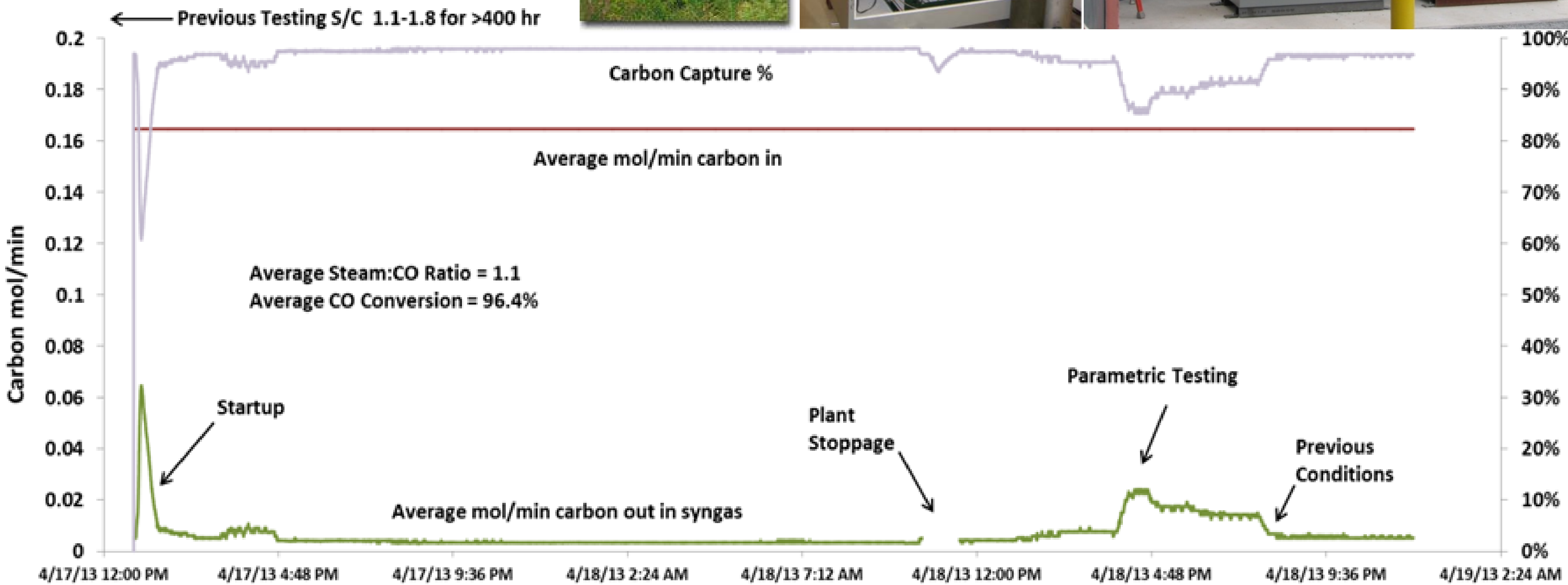
TDA 0.1 MW pre-combustion carbon capture unit installed at the National Carbon Capture Center

- **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

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 and DE-FE0012048)**
  - Integrated sorbent/catalyst operation
  - Pointed out the need to incorporate effective heat management
  - Implemented the heat management scheme in a 4-bed PSA system using coal derived synthesis gas at 1 kg/hr CO_2 removal
- **Key R&D need is the design/development of a high fidelity prototype to fully demonstrate the concept using actual coal-derived synthesis gas**
  - Reactor design to address the heat management needs
  - A 10 kg/hr CO_2 removal is being developed
  - Testing of the high fidelity system will be carried out at Praxair

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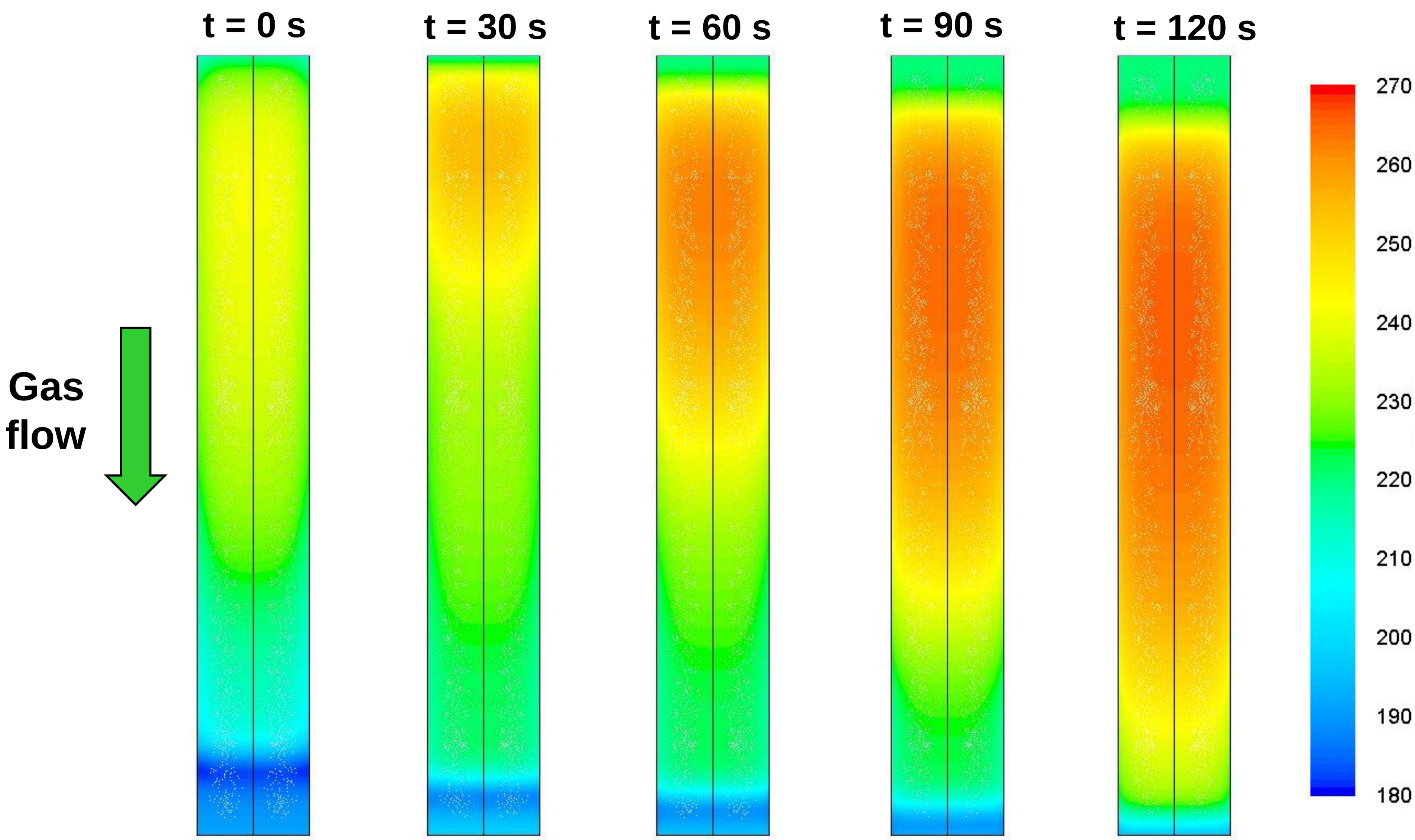
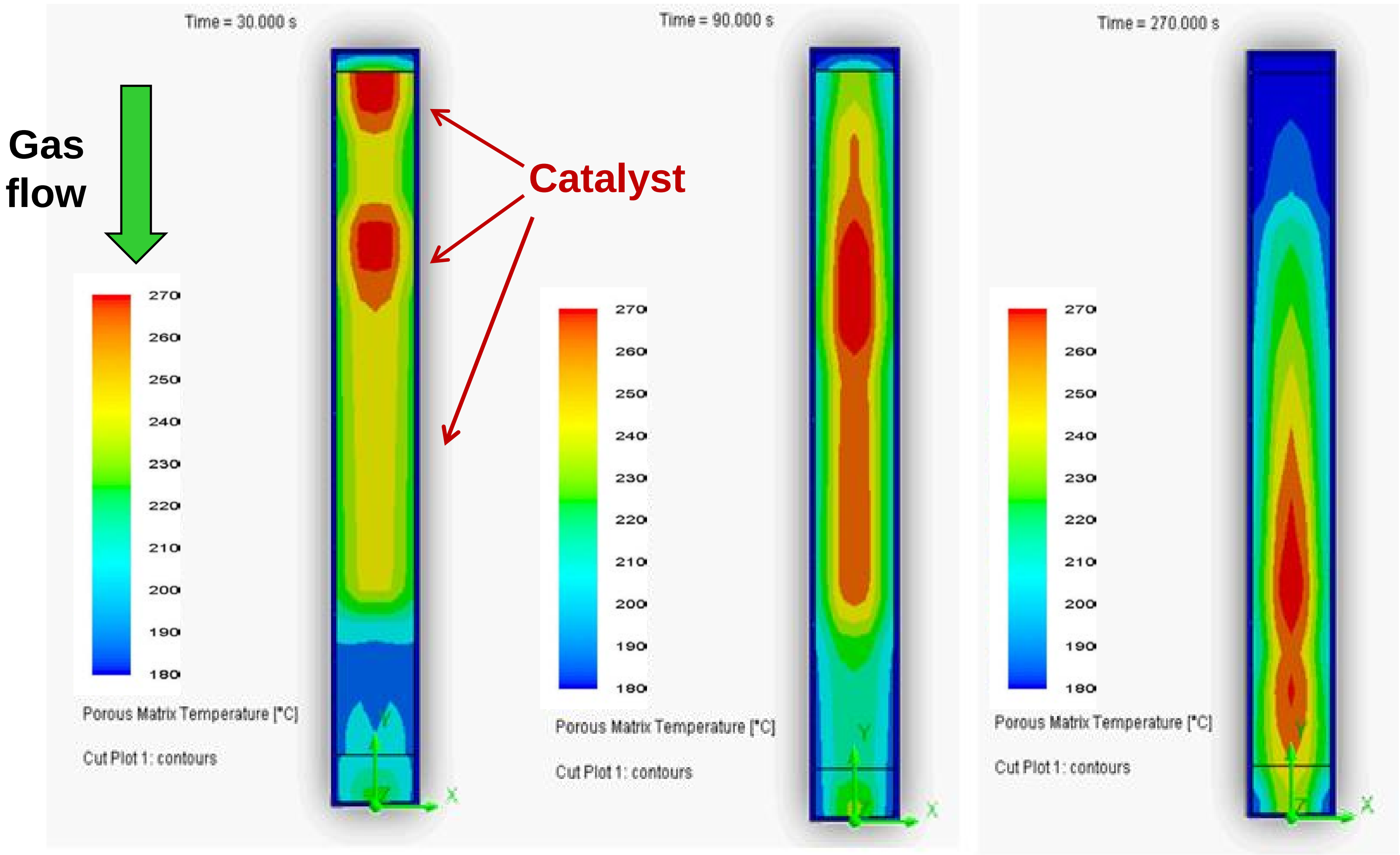
T Profiles - During CO_2 Capture Only



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

Heat Wave WGS & CO_2 Capture

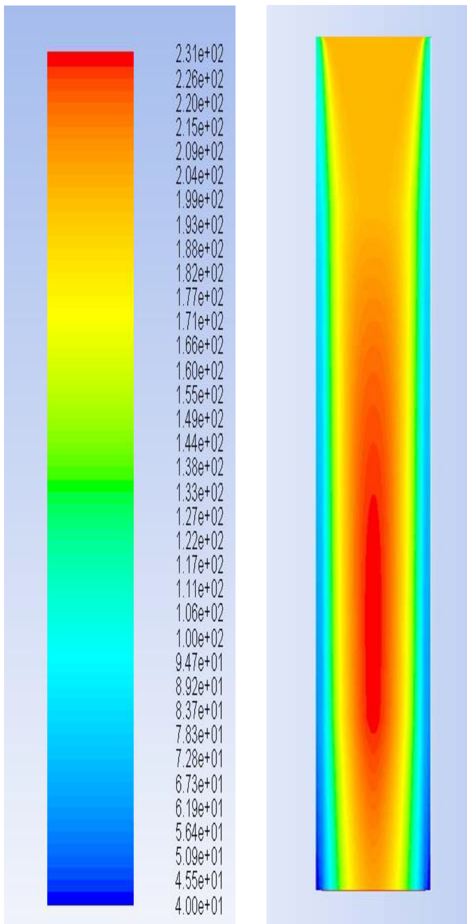


- **Integrated WGS & CO_2 capture results in higher ΔT**
- **Not ideal for CO_2 capture (the WGS heat accumulates in the beds)**

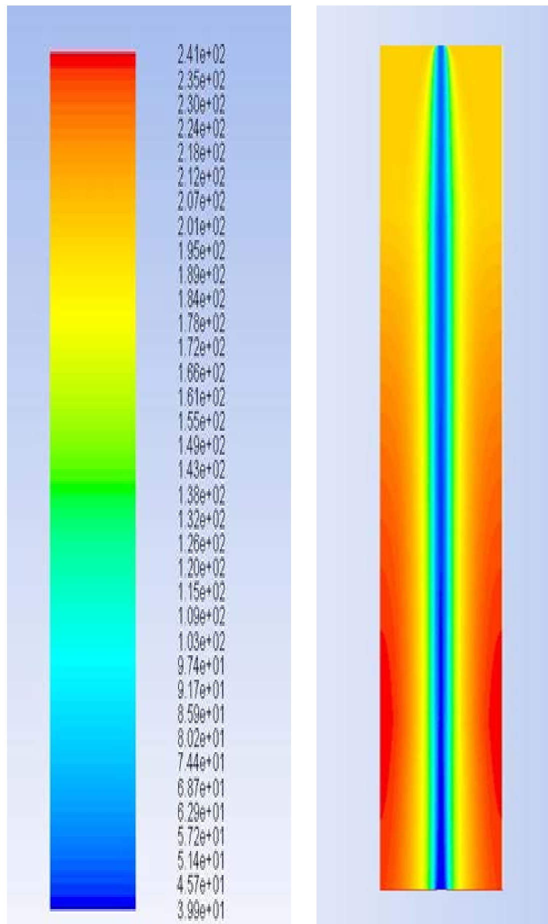
Conventional Heat Management Options

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

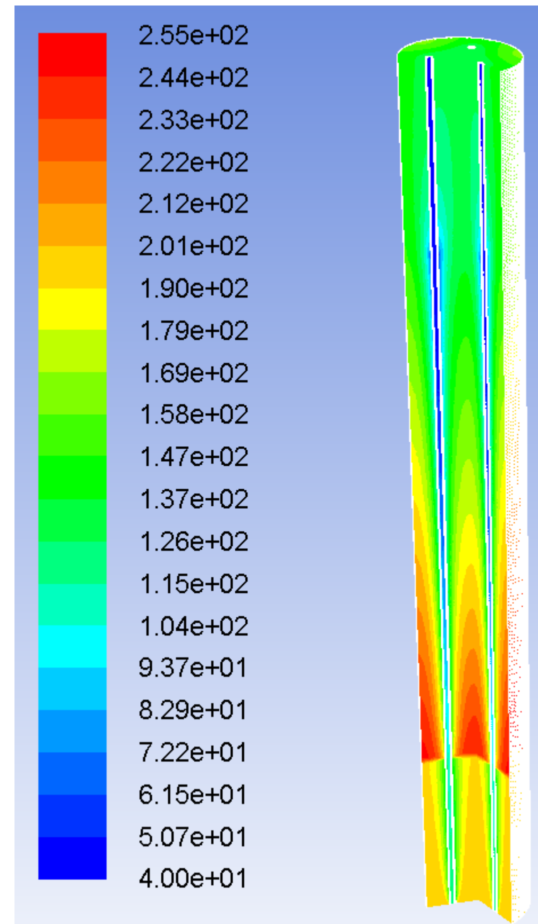
Cooling Jacket



Immersed Tube (1)



Immersed Tubes (3)



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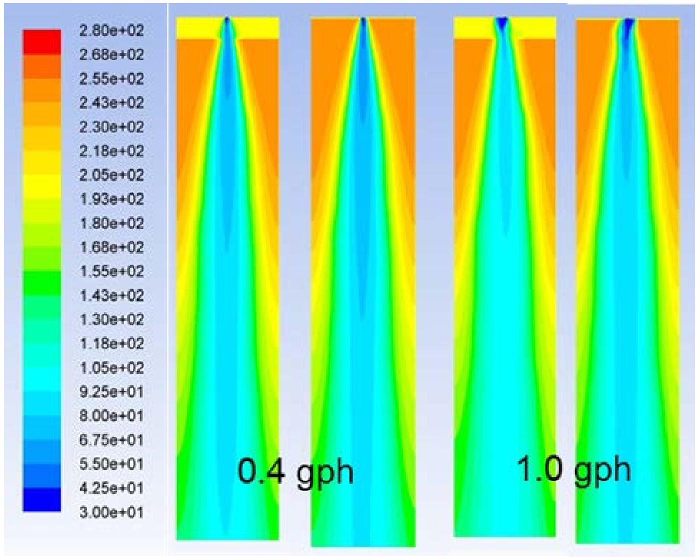
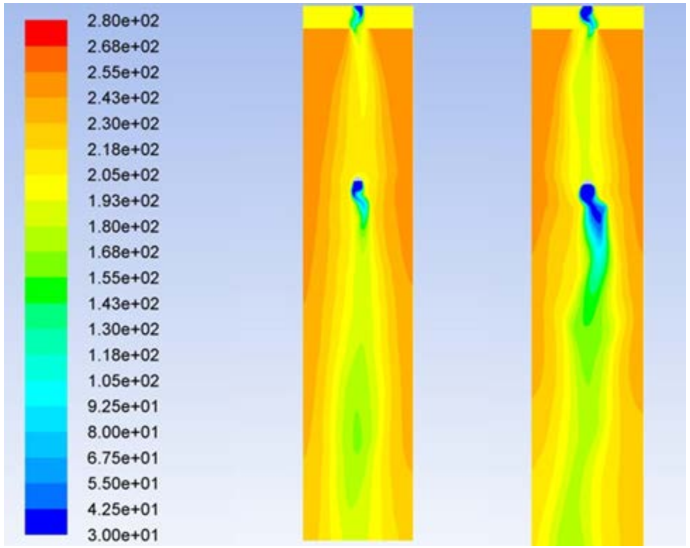
Heat Integrated WGS & CO_2 Capture

- **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**

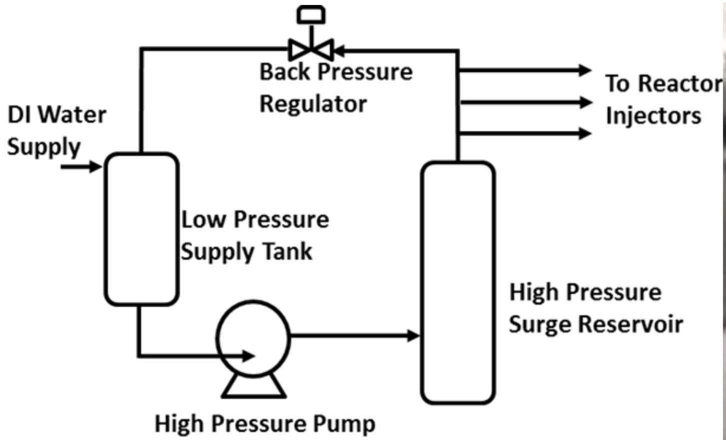
T Contours (°C) Single Injection Layer

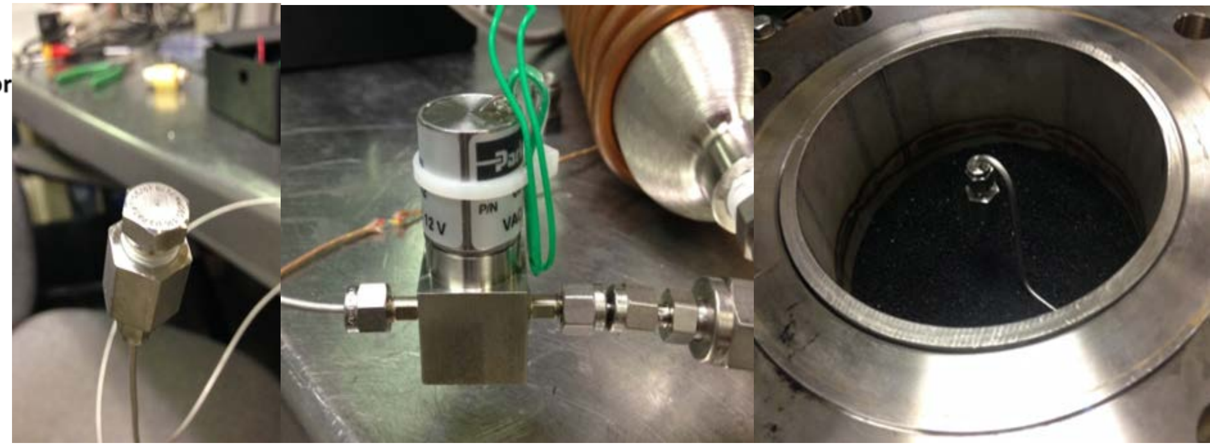


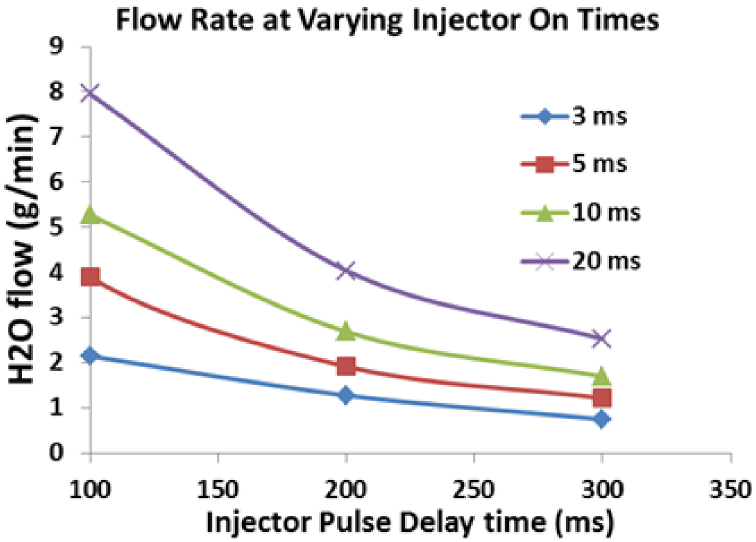
T Contours (°C) Multiple Injection Layers



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**

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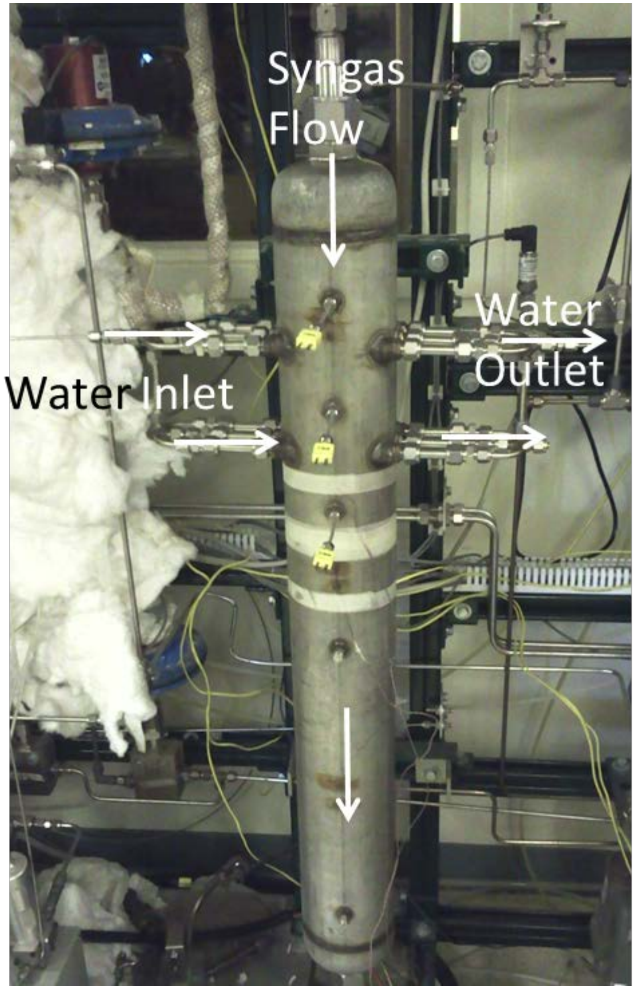
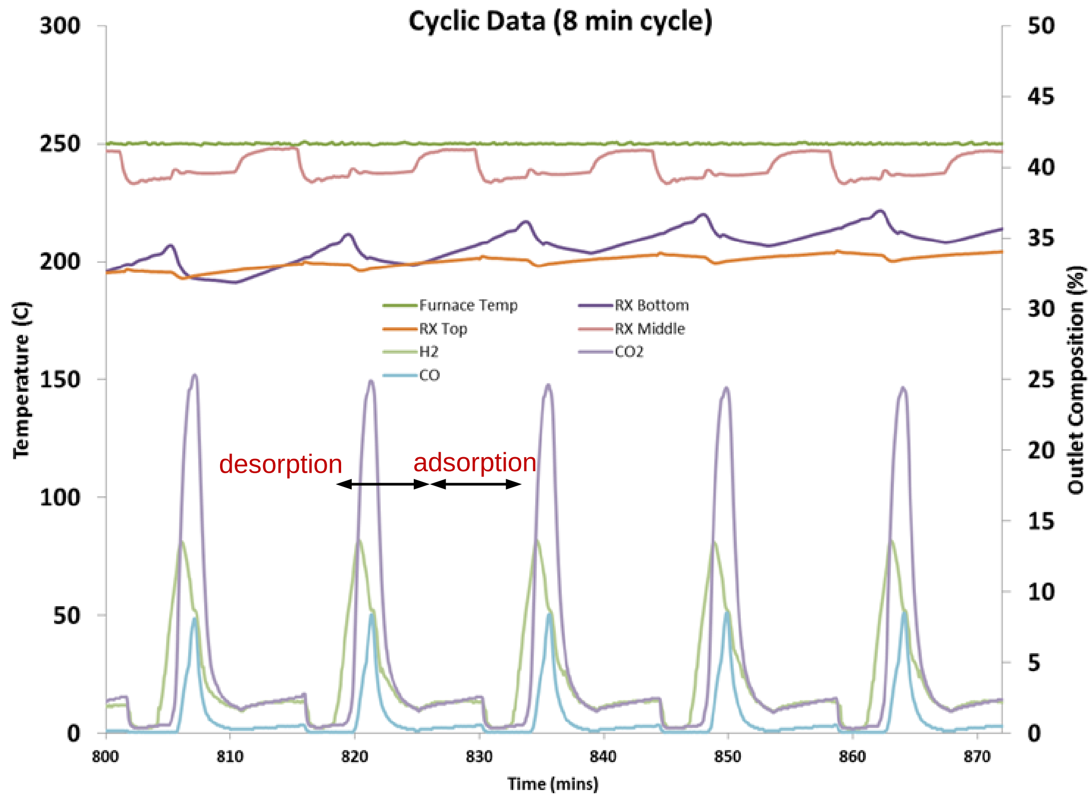
Bench-Scale Evaluations

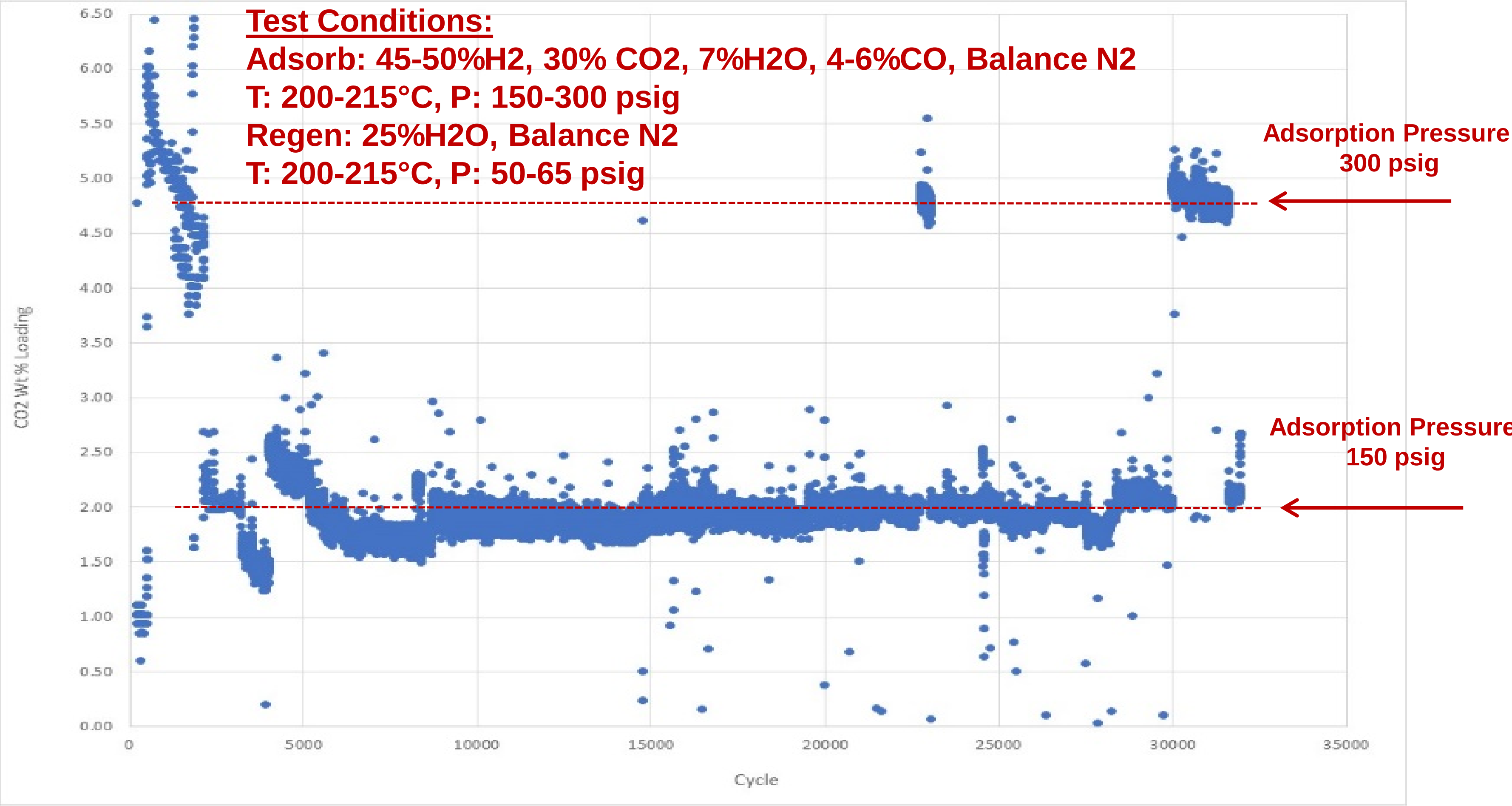




- **8L reactors were modified with water injectors**
- **Successful proof-of-concept demonstrations have been completed**

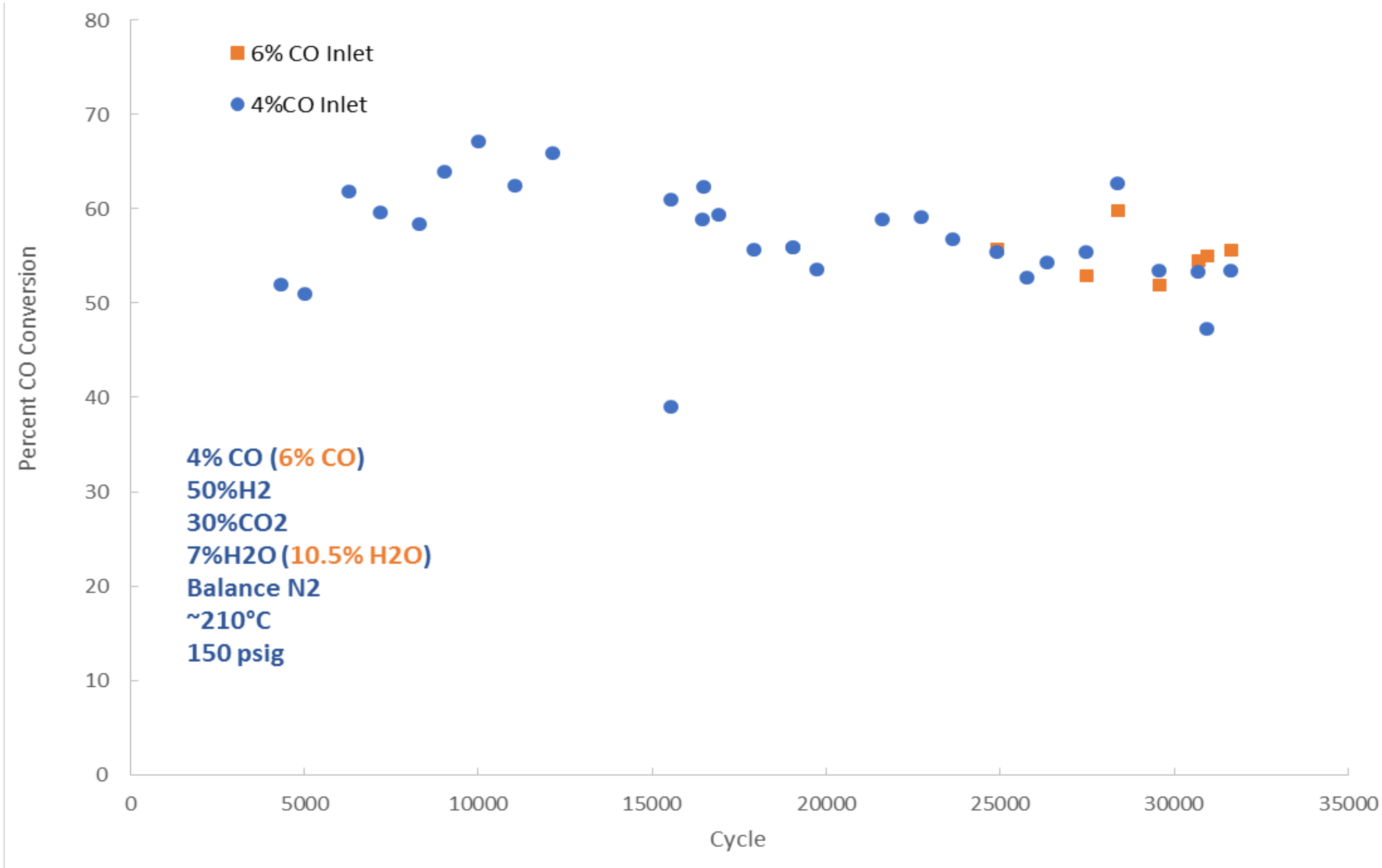
- **ΔT <10°C was maintained over extended cycling (much lower than those observed in the early field tests)**

Life Tests – Sorbent Activity



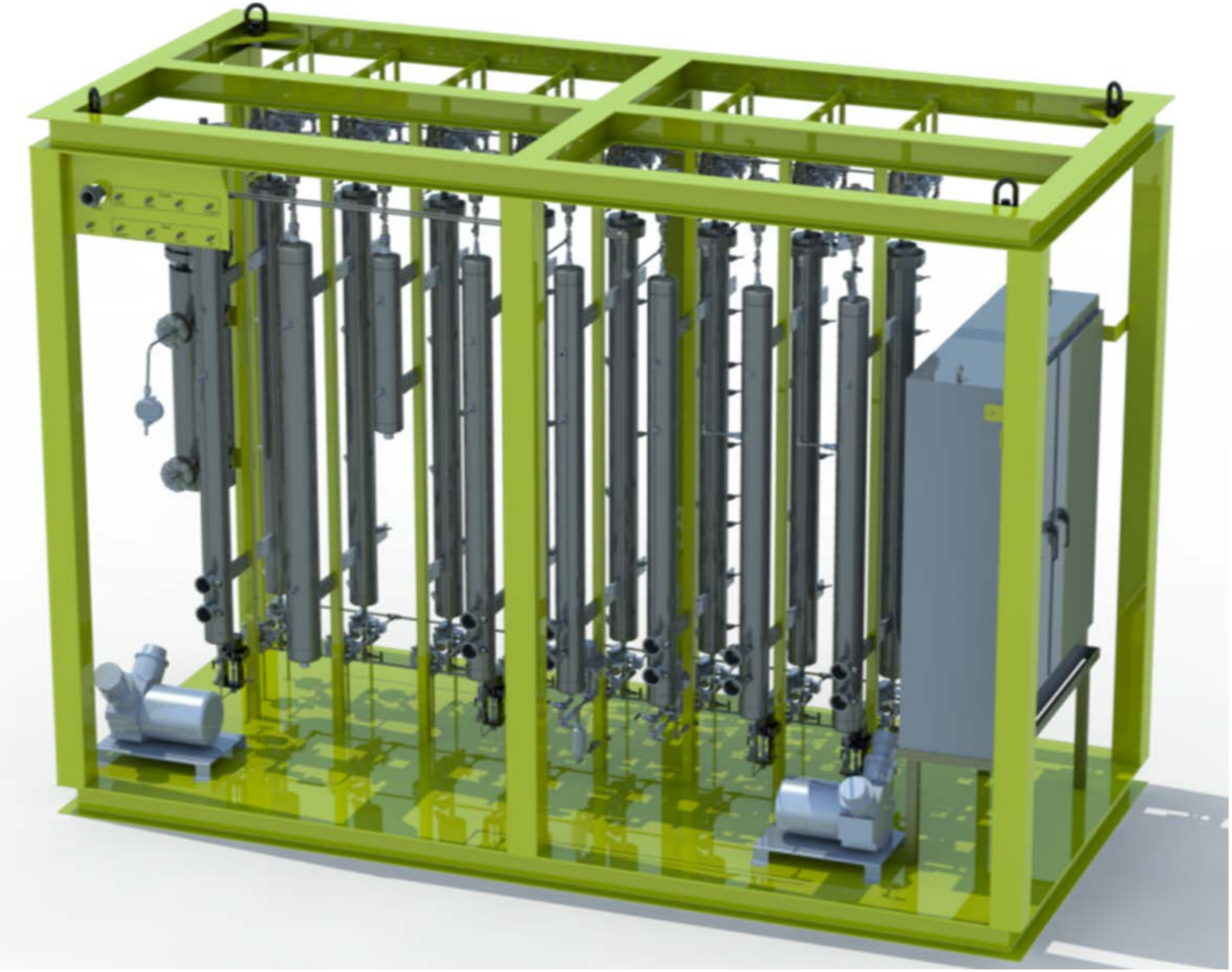
- We completed 32,000 cycles showing stable performance for the WGS catalyst and CO_2 sorbent

Life Tests – Catalyst Activity



- **By evaluating continuous catalytic activity (alone) we showed that cycling between reducing and oxidizing conditions (i.e., steam exposure) had no adverse effect on the WGS catalyst**

Integrated WGS/CO_2 Capture System



Fabrication of the Prototype

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Installation at Praxair

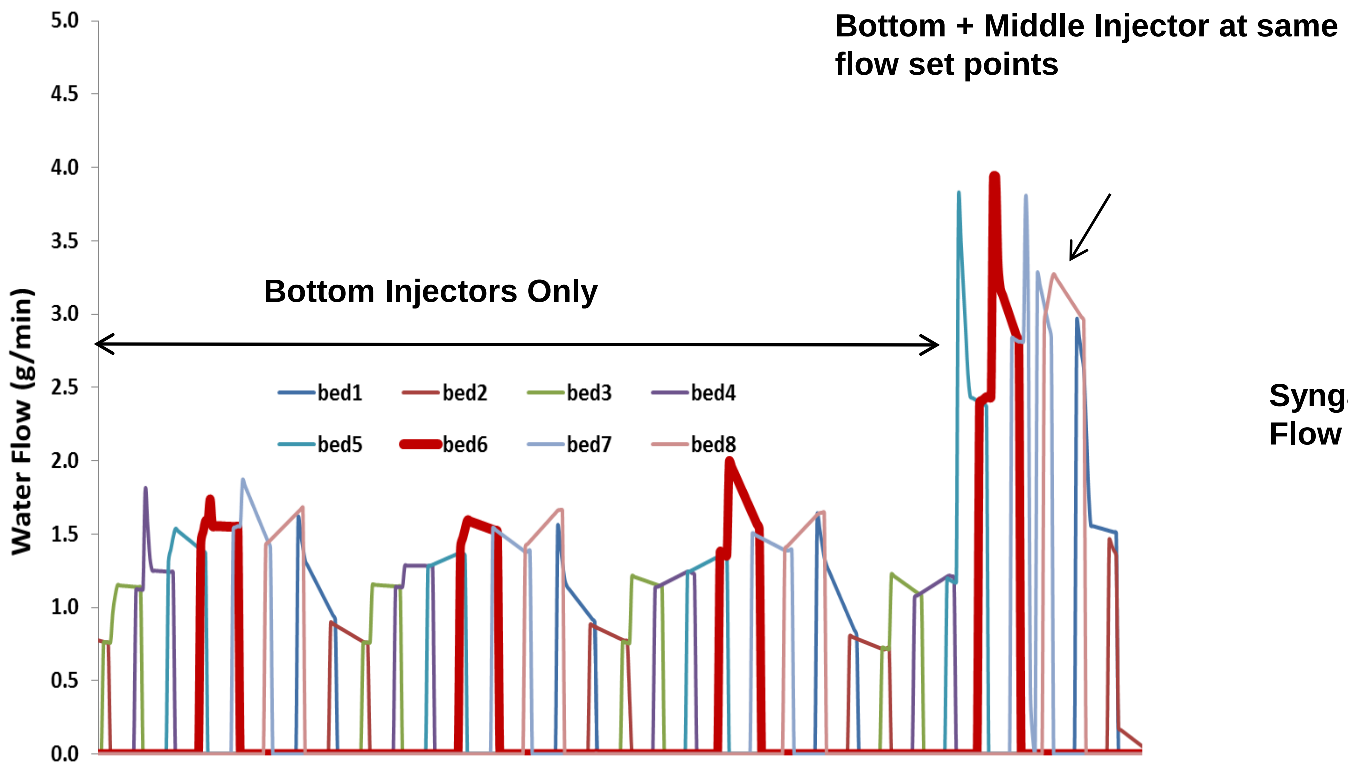
- **Fabrication of the Prototype unit was completed in 2018 Q2 and installation at Praxair R&D Center (Tonawanda, NY) was completed in 2018 Q3**

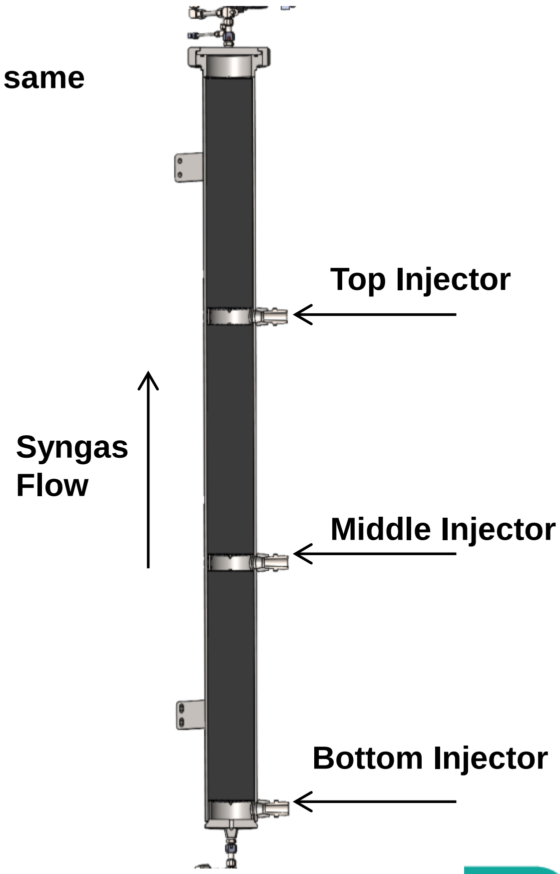
Reactor Loading at Praxair

- **Reactors were loaded with the catalyst and the sorbent in 2018 Q2**
- **Catalyst has been reduced**
- **Shakedown tests and preliminary experiments were completed in 2018 Q3**

Control of Water Injection

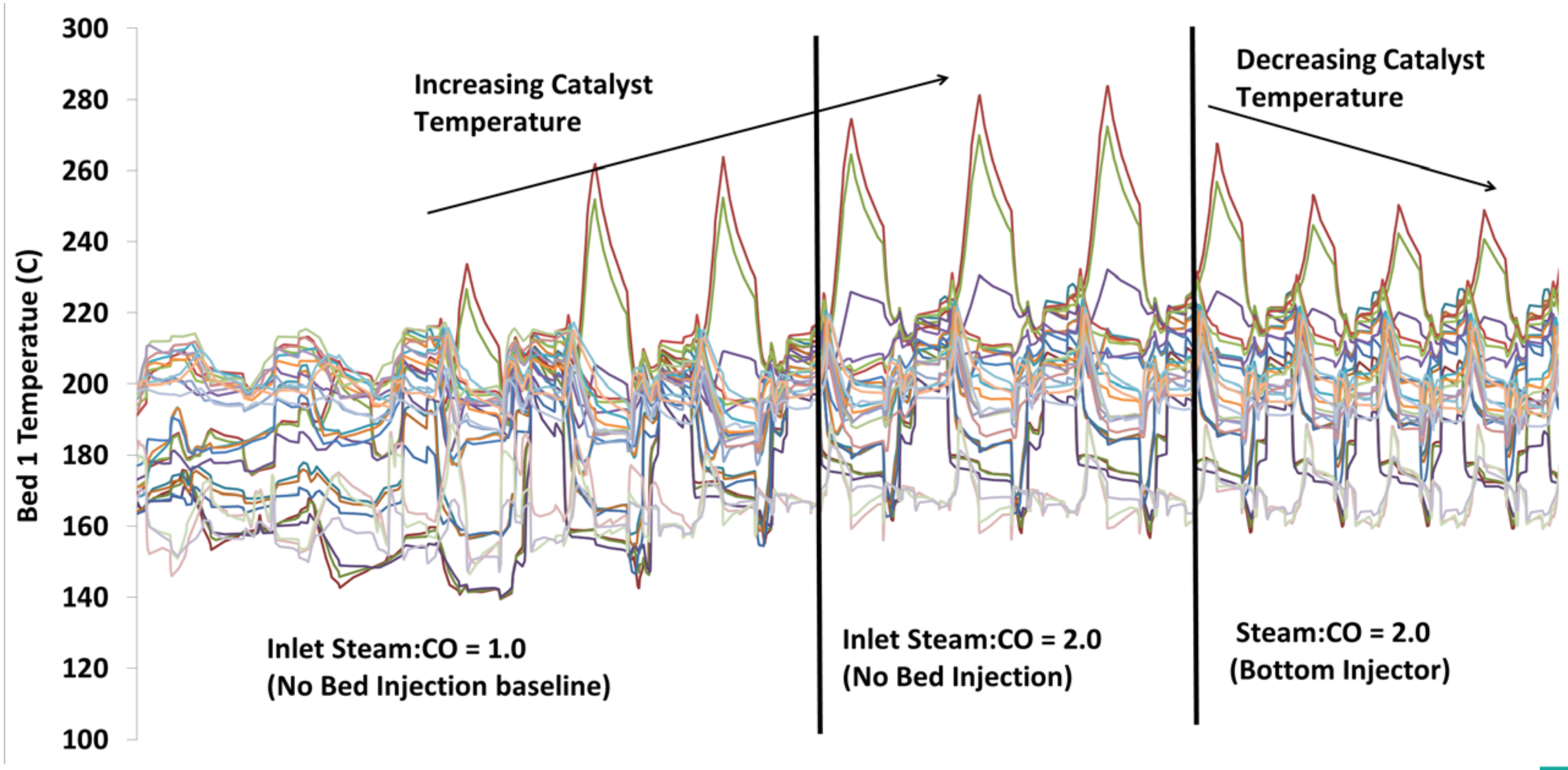
- We demonstrated that precise amounts of water can be injected and their individual flow rates can be controlled within tolerances of less than 0.5 g/min between injectors





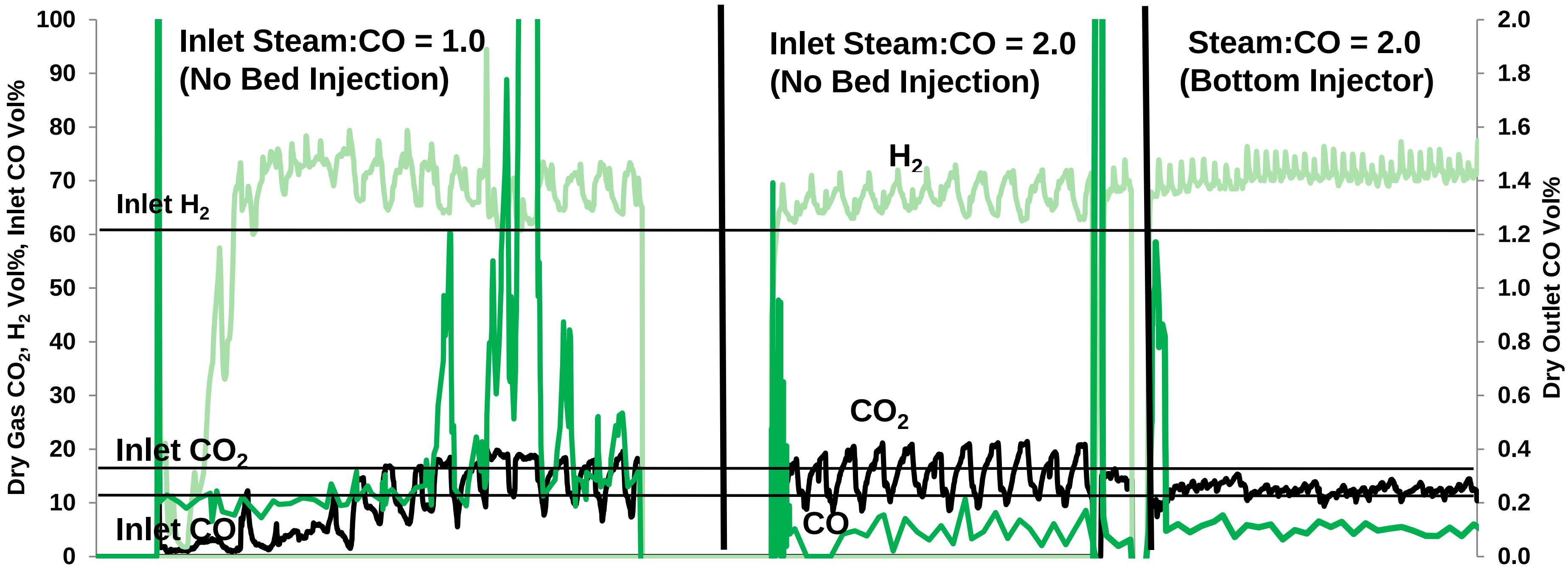
Temperature Management via Water Injection

- We observed an increase in bed temperature by increasing the inlet steam:CO from 1 to 2
- The bed temperature was maintained at ~40ºC lower when injecting the same amount water directly into the beds



Impact of Water Injection

- An overall CO conversion >98% was achieved
- The cycle times were not yet optimized in this run therefore carbon capture was only at 60% (incoming CO_2 + CO_2 from shifted CO_2)
- We will optimize this during our next test period



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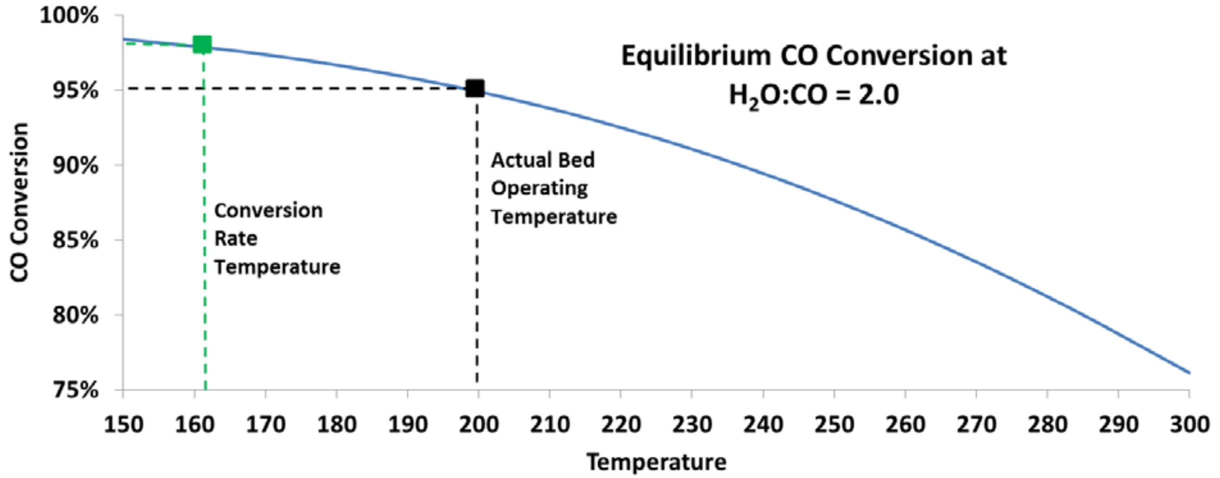
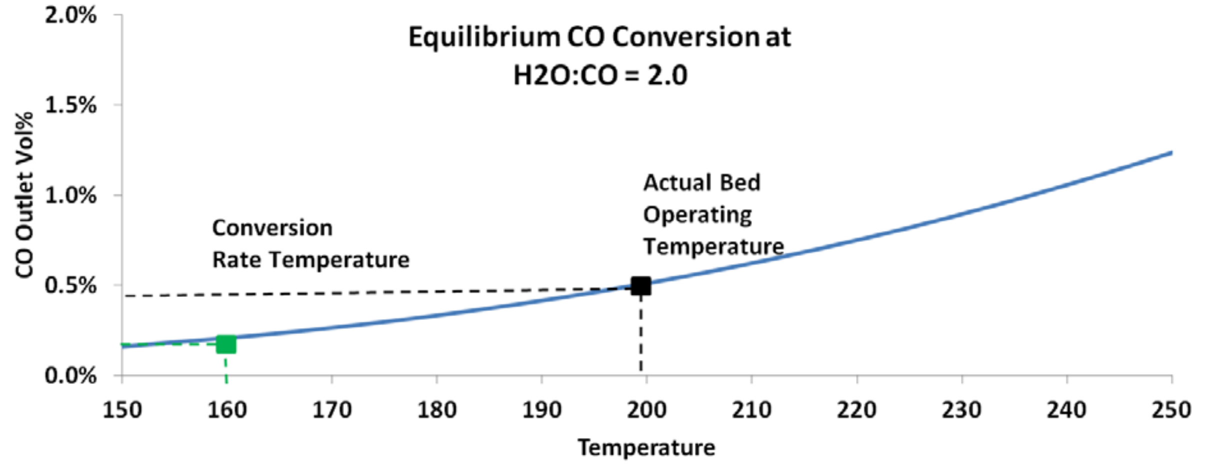
Effect on Equilibrium Conversion

- By coupling the WGS with the CO_2 sorbent and water injection, we were able to operate the beds at 200ºC but achieve the equilibrium CO conversion of a 40ºC cooler bed





Integration with E-Gas™ Gasifier

Gasifier Type/Make	E-Gas		
Case	1	2	2* (WGS/CO_2)
CO_2 Capture Technology	Cold Gas Cleanup Selexol™	Warm Gas Cleanup TDA's CO_2 Sorbent	Warm Gas Cleanup TDA's CO_2 Sorbent
CO_2 Capture, %	90	90	90
Gross Power Generated, kW	710,789	670,056	693,542
Gas Turbine Power	464,000	425,605	427,980
Steam Turbine Power	246,789	244,450	265,562
Syngas Expander Power	-	-	-
Auxiliary Load, kW	194,473	124,138	138,741
Net Power, kW	516,316	545,917	554,801
Net Plant Efficiency, % HHV	31.0	34.1	34.7
Coal Feed Rate, kg/h	220,549	212,265	212,265
Raw Water Usage, GPM/MW	10.9	10.3	10.0
Total Plant Cost, $/kW	3,464	3,042	2,990
COE without CO_2 TS&M, $/MWh	136.8	120.5	118.8
COE with CO_2 TS&M, $/MWh	145.7	128.6	126.7
Cost of CO_2 Captured, $/tonne	**53.2**	**37.4**	**35.8**

- **IGCC plant efficiency is estimated as 34.7% with TDA's WGS/CO_2 system**
- **Cost of CO_2 capture is estimated as less than $26/tonne (including TS&M less than $35.8/tonne)**

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Process Economic Analysis - CTL

Gasifier	Shell	
Coal	Bituminous	
Case	9	10A
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	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

- Testing of the unit at Praxair – Field Test Campaign #2
- Complete CFD Model validation with Praxair Test Data
- Complete a high-fidelity system design/analysis and cost estimate
- Complete an Environmental, Health and Safety (EHS) assessment

Acknowledgement

- NETL, Project Manager, Diane Madden
- Chuck Shistla, GTI
- Sean Kelly, Juan Li, Praxair
- Frank Morton, NCCC
- Ashok Rao, UCI