# Low Cost Air Separation Process for Gasification Applications


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# Project Goals and Objective

- **The project objective is to demonstrate techno-economic viability of a new air separation technology that can be integrated into coal gasification processes**
- **A high temperature chemical absorbent selective for $O_2$ removal is the key component of the air separation process**
  - Early proof-of-concept demonstrations in an SBIR Phase II project and NETL project (DE-FE-0024060) proved high oxygen uptake and stable performance
- **Project Tasks**
  - Sorbent production scale-up
  - Bench-top demonstration of life (minimum 12,500 cycles)
  - Design of a fully-equipped prototype unit to fully demonstrate the concept at the bench-scale (1 kg/hr $O_2$ production rate)
  - Concept demonstration
  - Process design & cost analysis by Aspen Plus™ simulation
    - IGCC power generation and CTL

# Project Partners

**Project Duration**

- Start Date = October 1, 2015
- End Date = November 30, 2018

**Budget**

- Project Cost = $1,600,000
- DOE Share = $1,280,000
- TDA and its partners = $320,000

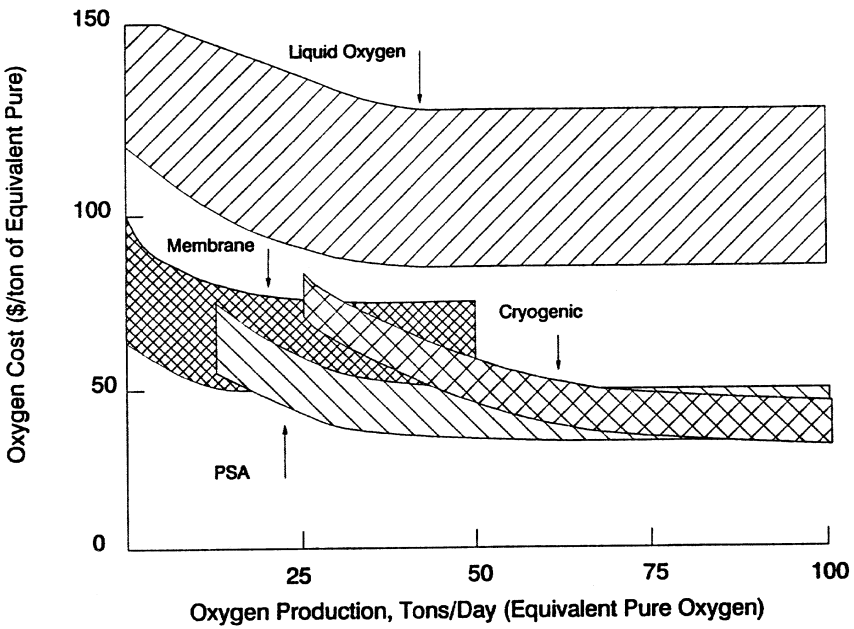
**Expenses as of March 31, 2018**

- DOE Share = $963,417
- Cost Share = $172,531
- Total = $1,135,948

# Background

- **Oxygen-blown gasifiers provide smaller size and higher efficiency**
  - Substantially lower $NO_x$ generation in IGCCs
  - Improved gas purity with the removal of $N_2$ in CTL processes
- **ASU is one of the most expensive components of a gasification plant (constitutes ~15% of plant cost and consumes over 5% of plant power)**
- **Cryogenic air separation is the choice of technology at large-scale**
  - 600 MW IGCC plant requires ~170 ton $O_2$/day
- **Cryo-separation is highly energy intensive due to the thermal inefficiencies inherent in the low operating temperatures**

*Source: Air Products and Chemicals, Inc.*




*Source: Kobayashi, 2002*



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# TDA's Approach

- **TDA's process uses a unique sorbent material for air separation via an oxidation-reduction (redox) process**

$$A_xB_yO_z + nO_{2(g)} \leftrightarrow A_xB_yO_{z+2n}$$

- **Unlike the conventional chemical looping combustion sorbents that also work via a similar redox cycle, the oxygen in our sorbent is released by changing process conditions (the cycle is not driven by the use of fuel)**
- **The oxidized metal oxide phase is "meta-stable" and auto-reduces by changing T, P, oxygen partial pressure**
  - The auto-reduction releases oxygen, which can be recovered as a pure product
  - No use of reducing gases (e.g., $CH_4$, $H_2$, CO, syngas) which will consume oxygen



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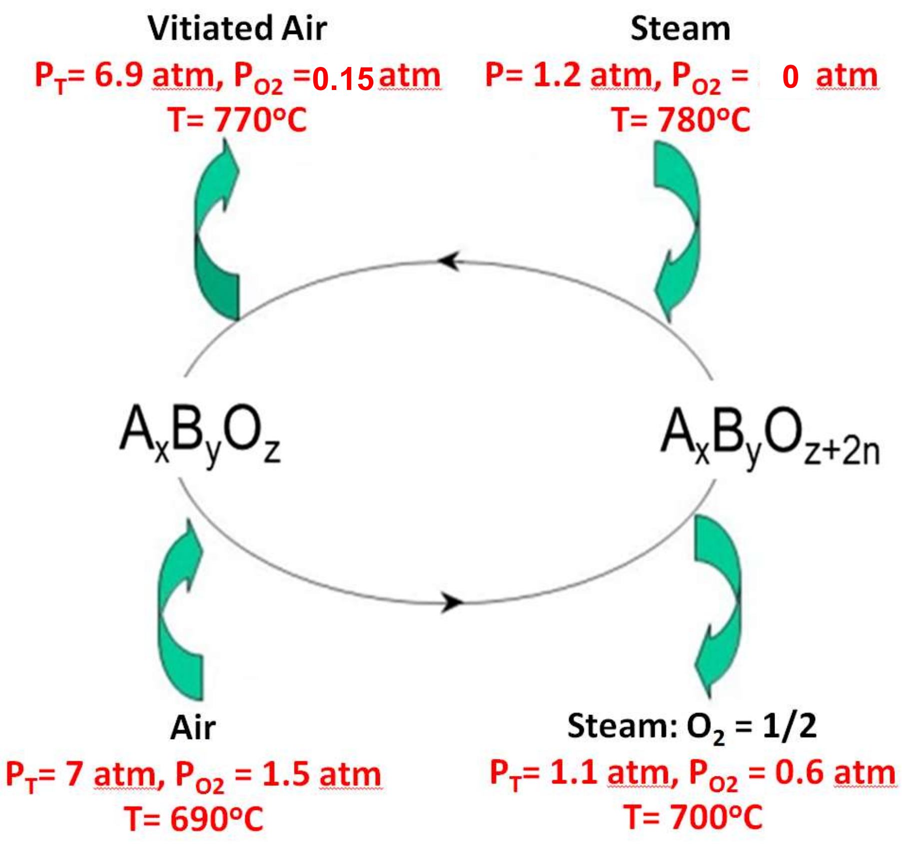
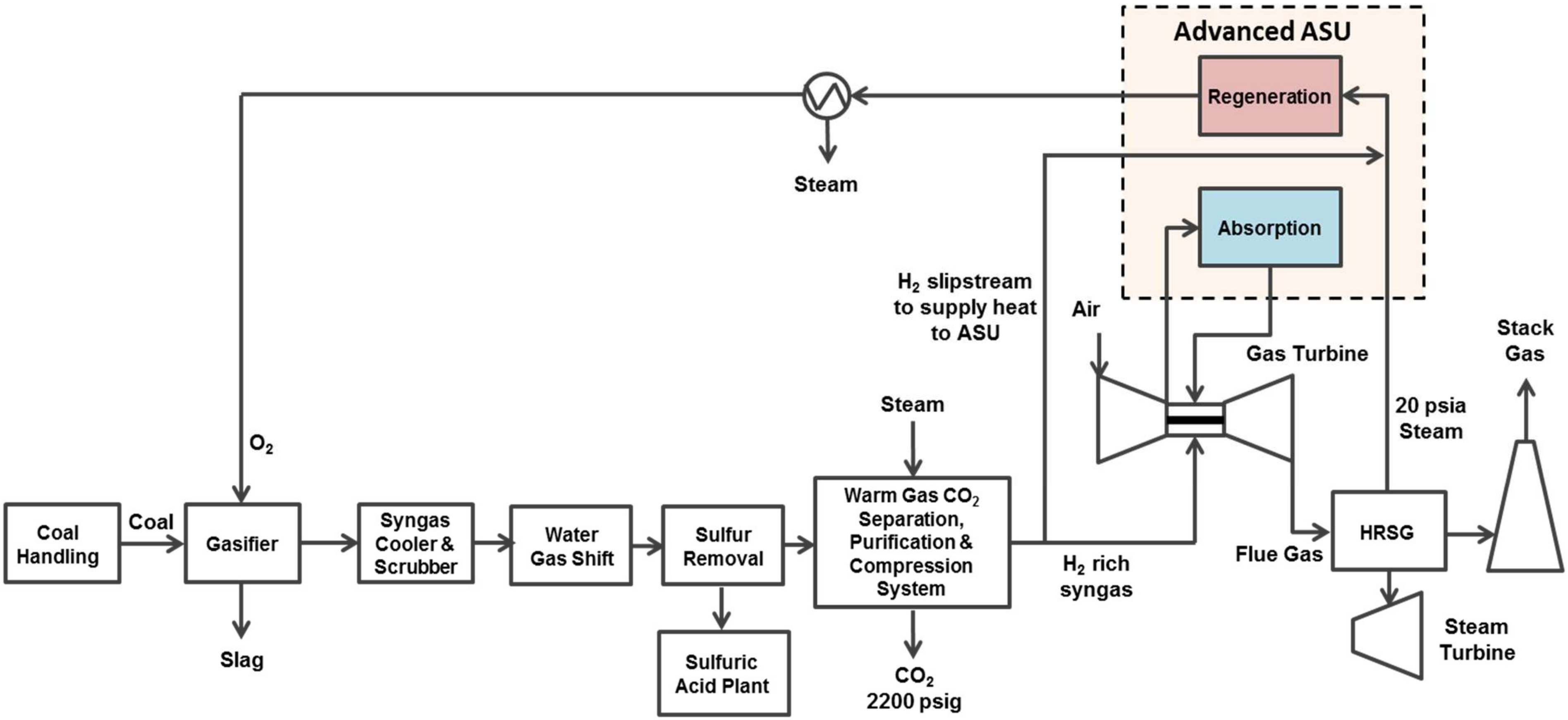
# Separation Process

- **Sorbent removes the oxygen from the high pressure air**
  - 90-95% of the oxygen is selectively removed (if desired)
  - The vitiated high pressure air (now mostly $N_2$) is utilized in a gas turbine after boosting the pressure
- **Regeneration is carried out at low pressure (near ambient pressure) using a warm sweep gas (superheated steam) under near-isothermal conditions**
  - Combined pressure swing and concentration swing (i.e., the partial pressure difference) drives the $O_2$ from the sorbent
- **Temperature or vacuum swing is also feasible but not economical**

## Stand-alone System



# Integrated with IGCC Power Plant



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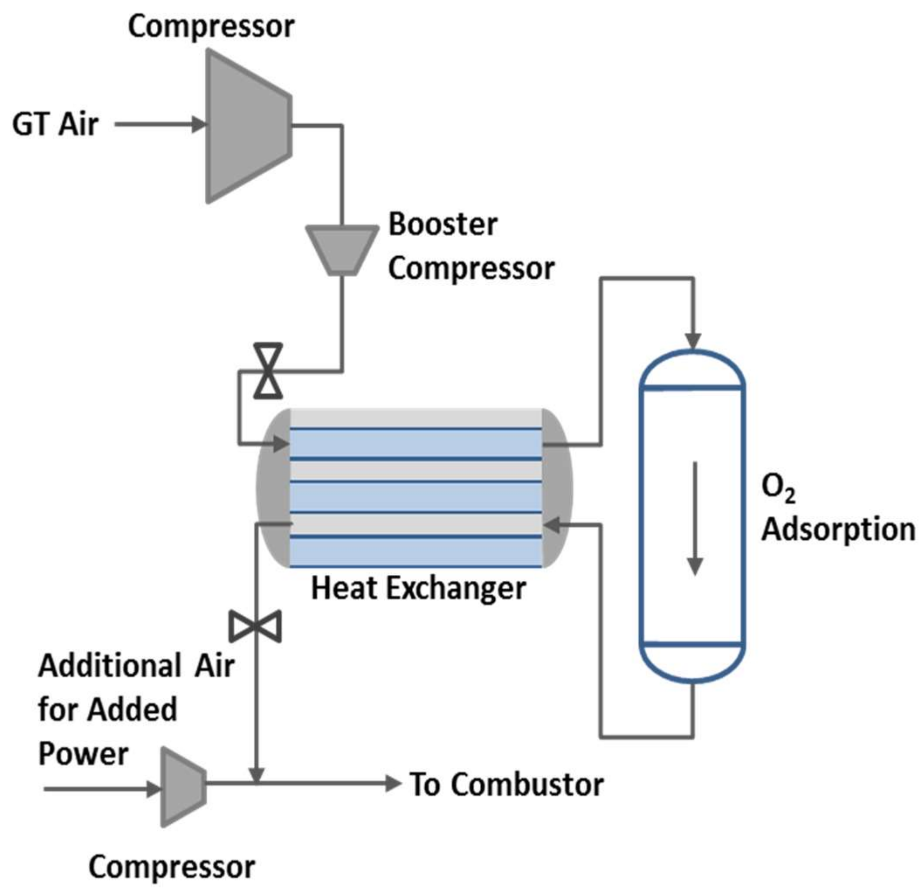
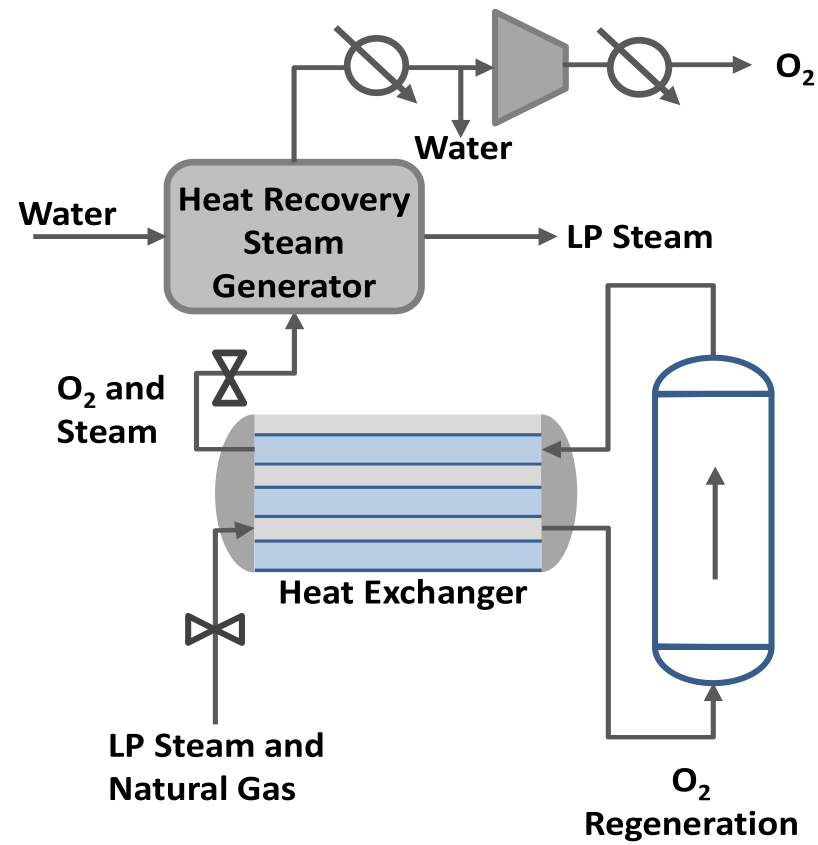
# System Design

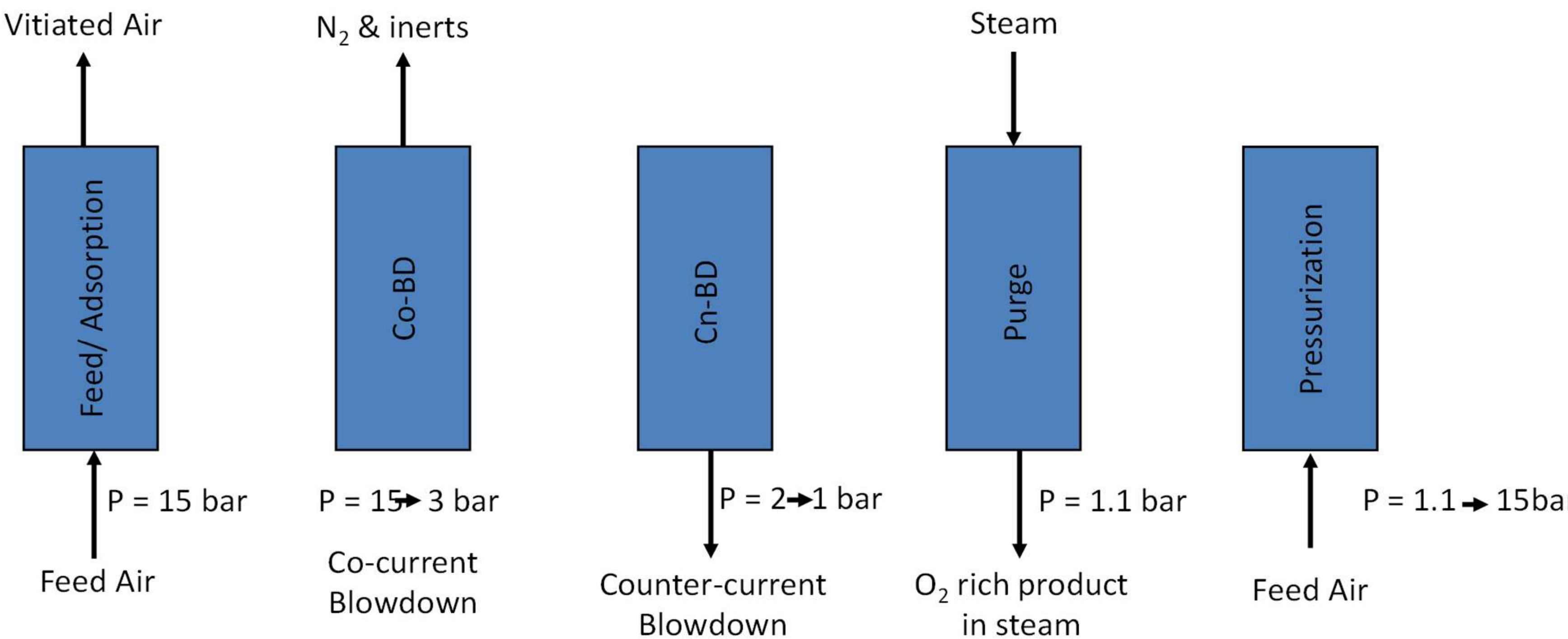


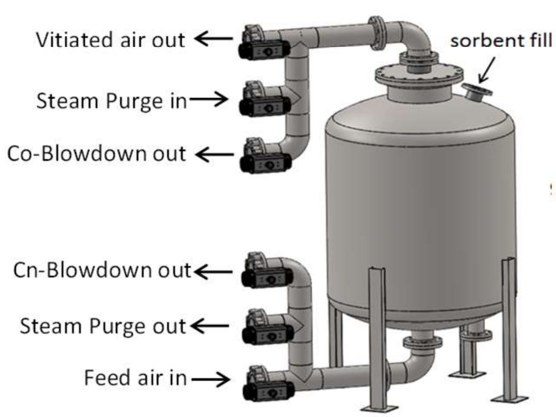

**Absorption Process**




**Regeneration Process**

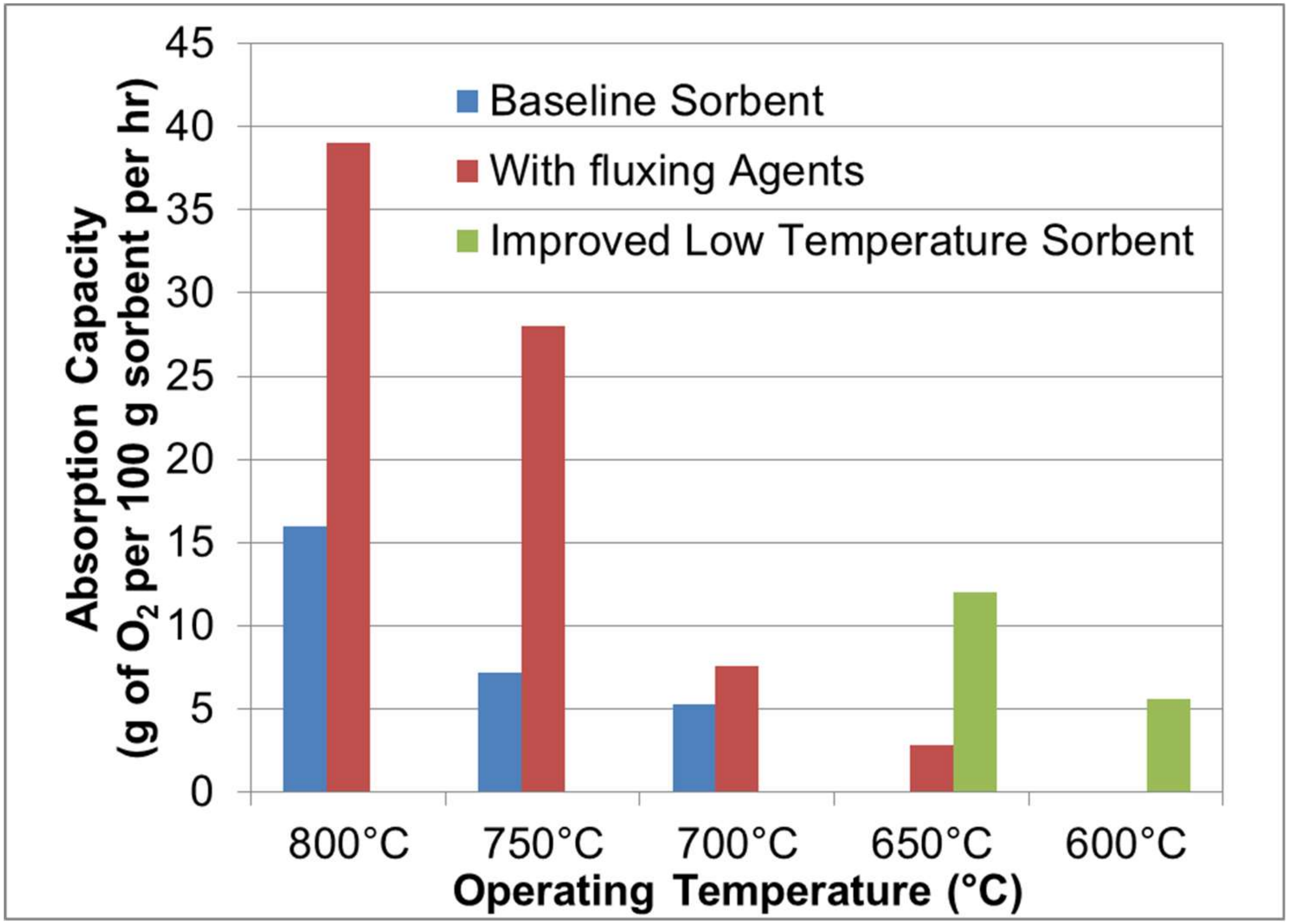
# Cycle Sequence




| | Stage 1 | Stage 2 | | | Stage 3 | | | Stage 4 | | |
|---|---|---|---|---|---|---|---|---|---|---|
| Time (min) | a | b | c | d | b | c | d | b | c | d |
| Bed 1 | ADS | EQ1D | CoBD | CnBD | PURGE | | | EQ1R | PRESS | |
| Bed 2 | EQ1R PRESS | ADS | | | EQ1D | CoBD | CnBD | PURGE | | |
| Bed 3 | PURGE | EQ1R | PRESS | | ADS | | | EQ1D | CoBD | CnBD |
| Bed 4 | EQ1D CoBD CnBD | PURGE | | | EQ1R | PRESS | | ADS | | |

# Sorbent Optimization




- **Oxygen release was documented over a wide range of temperatures**
  - Early work (DE-FE0024060) focused on improving activity at lower temperatures

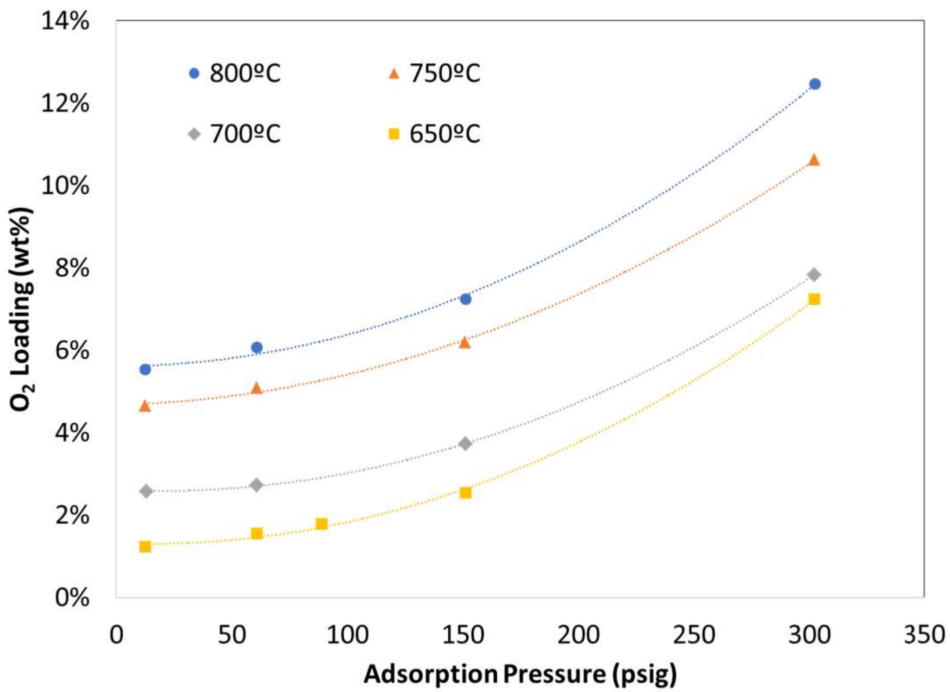
# Sorbent Production Scale-up

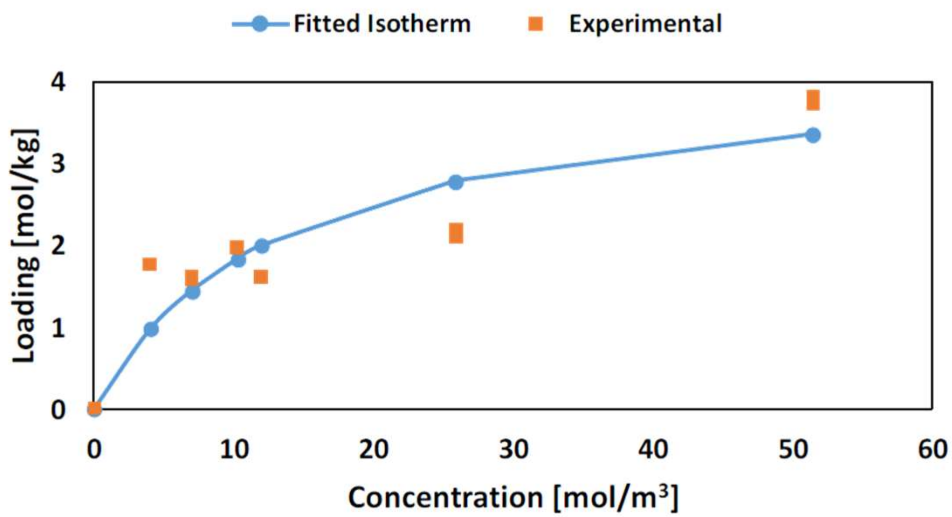
- **Early work batch size 0.1 to 0.5 kg**
- **Current batch size 10 to 100 kg**
  - The scale-up work is carried out at TDA's pilot production facility Golden, CO using high throughput production equipment




- **We completed Manufacturing and Quality Assurance Plans to ensure consistency in the sorbent material within each batch and minimize any batch-to-batch variations**

# Absorption Equilibrium Model



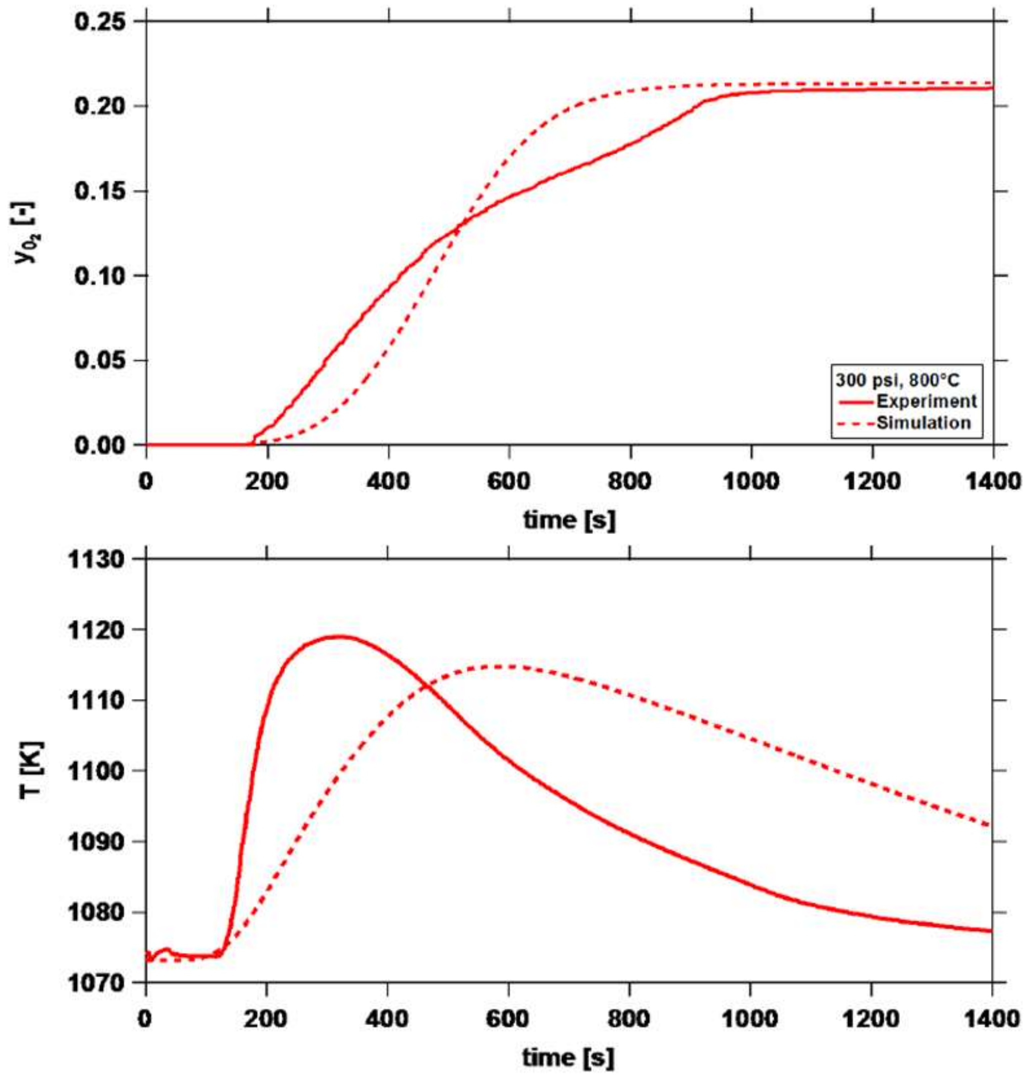




| $q_s$ [mol/kg] | $b_o$ [m³/mol] | -ΔU [J/mol] |
|---|---|---|
| 4.245963 | 0.00453 | 25122.97 |

- **The most recent formulations achieve very high equilibrium capacity above 6% wt. at a low temperature of 650°C**
  - In these tests we ensured complete regenerations between each data point to obtain the maximum possible capacity
- **A predictive model is developed by University of Alberta**

# Breakthrough Simulations

- Equilibrium isotherms were modeled using a simple Langmuir Isotherm
- Isotherm model parameters were used to simulate the breakthrough curves
- These simple models were able to replicate the heat effects and the average breakthrough time
- These models are refined for use in cycle optimization



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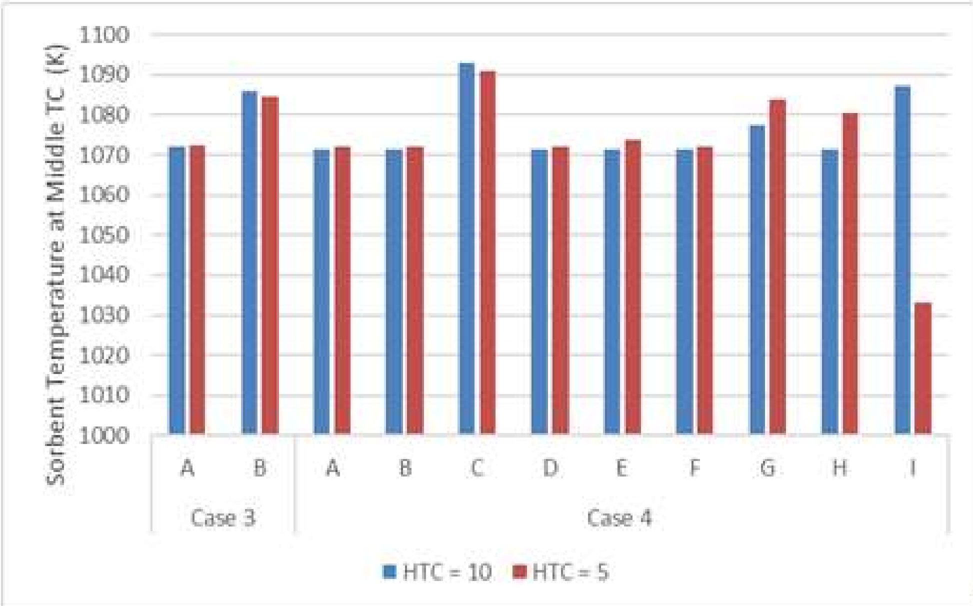
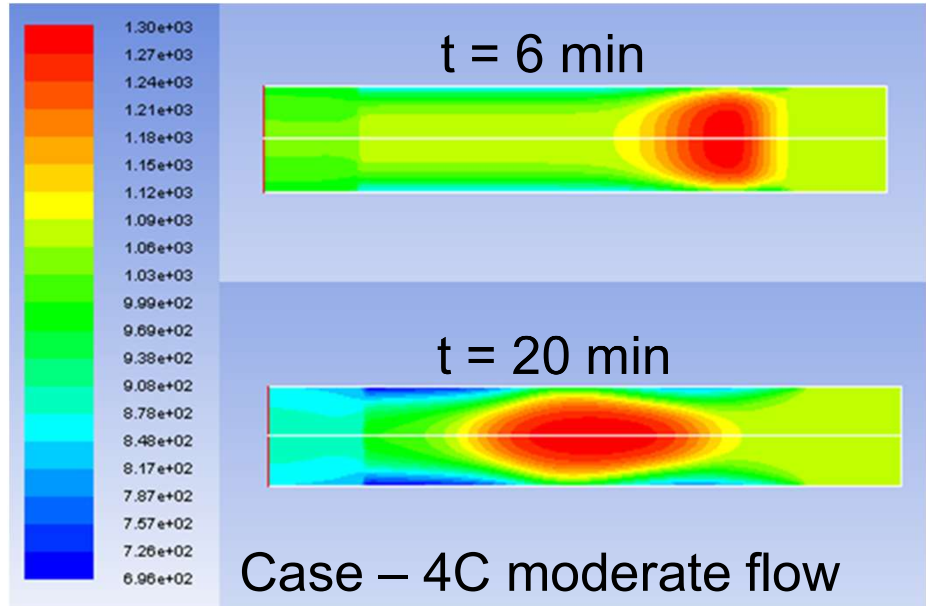
# CFD Modeling




- **To assist with the reactor design, GTI is carrying out CFD modeling work**
  - Model calibrations based on bench-scale test results are completed
  - The lab measurements and model predictions indicate modest temperature increase due to the reaction exotherm (the temperature rise between 60-110°C is predicted based on operating conditions)
- **Model results are used in the design of the 1 kg/hr prototype**
  - It is now being used for full-scale system design



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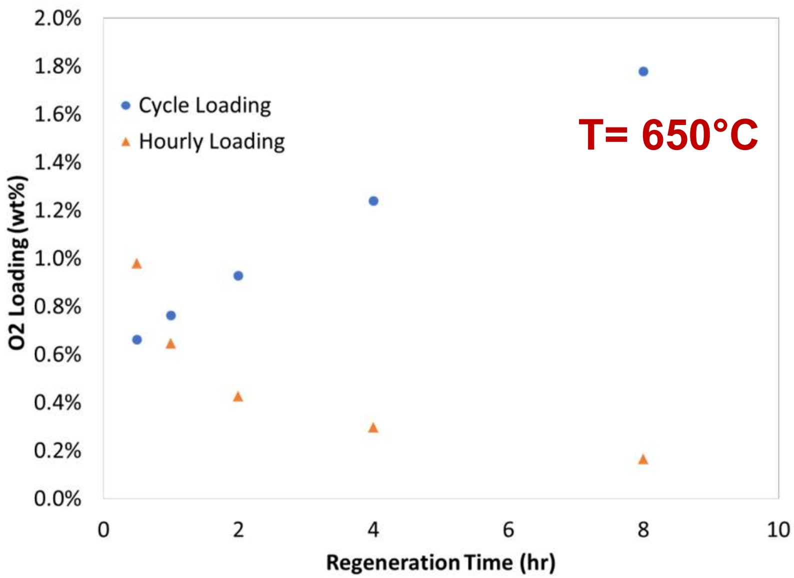
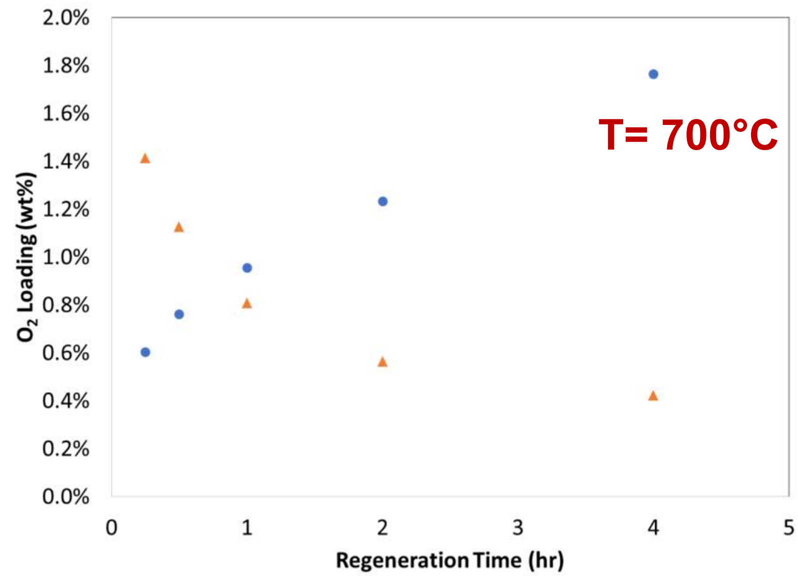
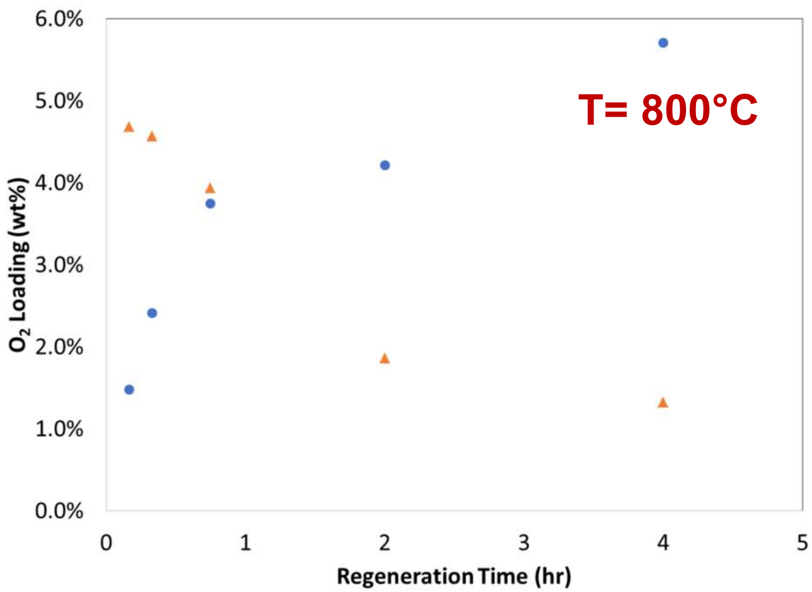
# Working Capacity, Low Absorption P



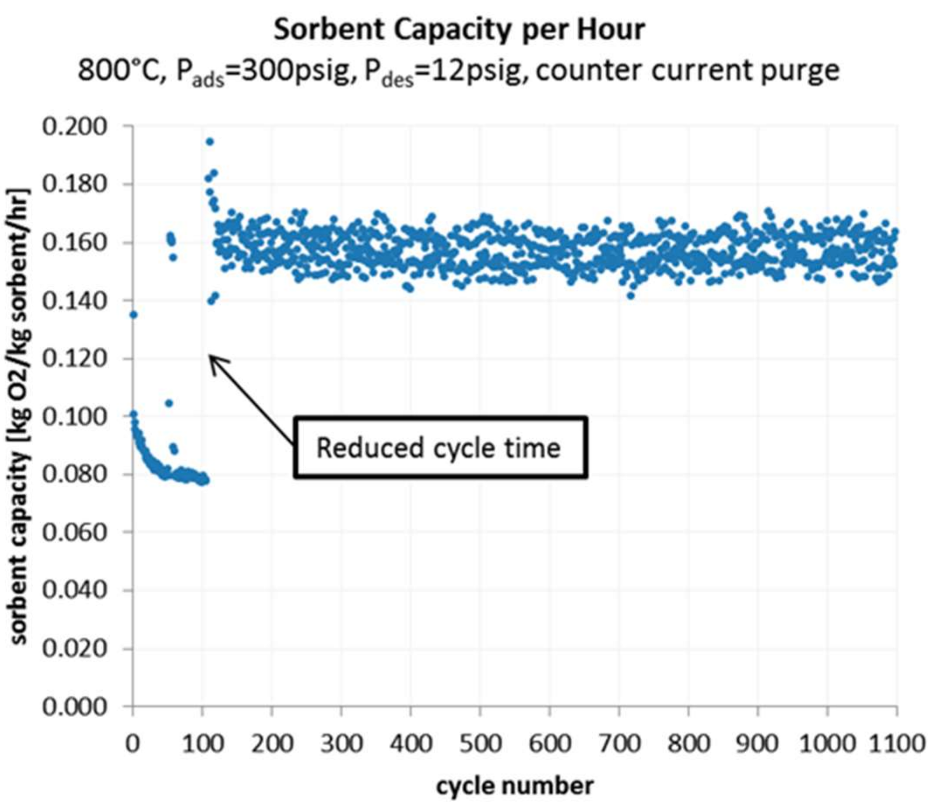



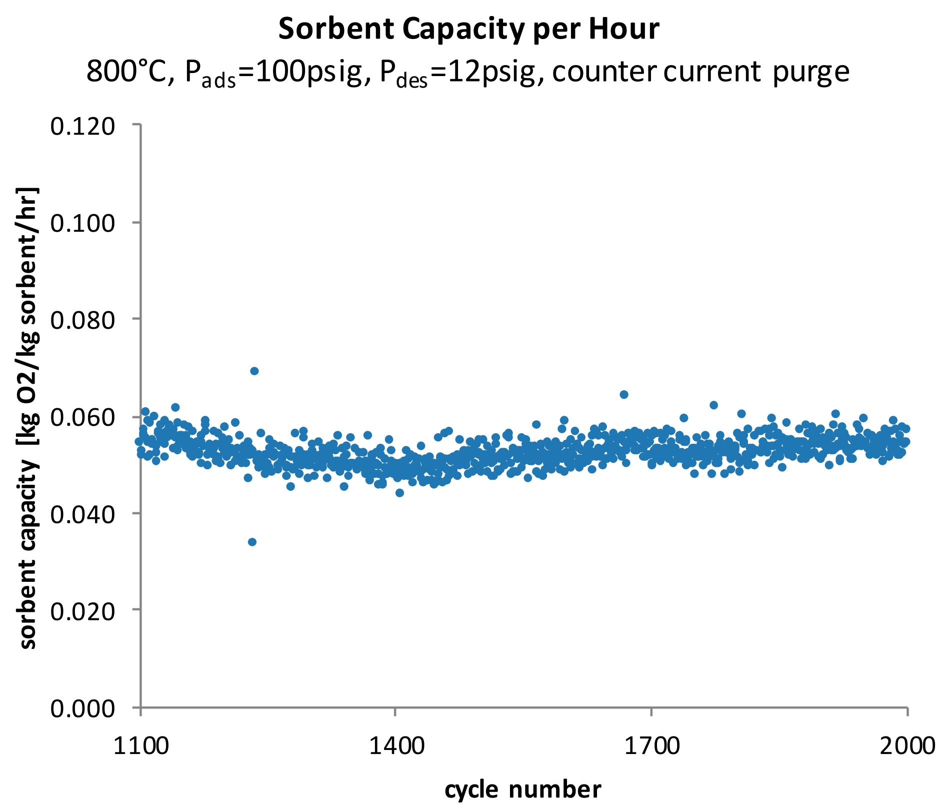




- **Sorbent achieves a high hourly working capacity at short cycle times**
  - Less than 20 min
- **Hourly working capacity**
  - 4.6% wt. $O_2$ at 800°C
  - 1.4% wt. $O_2$ at 700°C
  - 1% wt. at 650°C

# Sorbent Working Capacity

**GHSV = 500 $h^{-1}$, T = 800°C, $P_{abs}$ = 300 or 150 psig, $P_{des}$ = 12 psig**




| Adsorption pressure [psig] | Sorbent Capacity | | Cycles completed |
|---|---|---|---|
| | Per cycle [kg O2/kg sorbent/cycle] | Per hour [kg O2/kg sorbent/hr] | |
| 300 | 2.54% | 0.157 | 1000 |
| 100 | 0.52% | 0.052 | 500 |

- **High pressures in IGCC applications provides three times higher working capacity**



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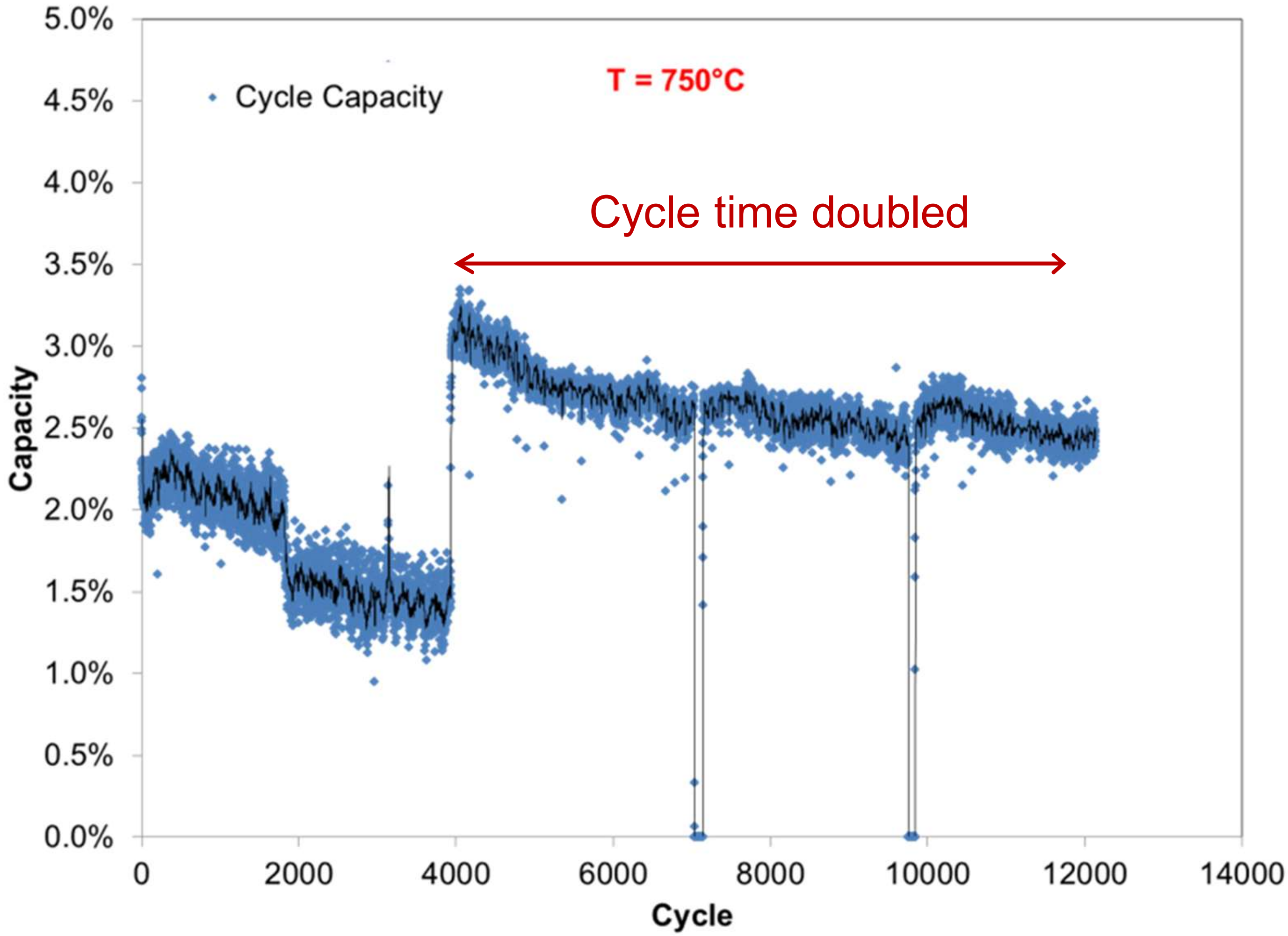
# Multiple Cycle Tests




- **Sorbent showed a stable cyclic capacity of over 2.5% wt. $O_2$ at 750°C**



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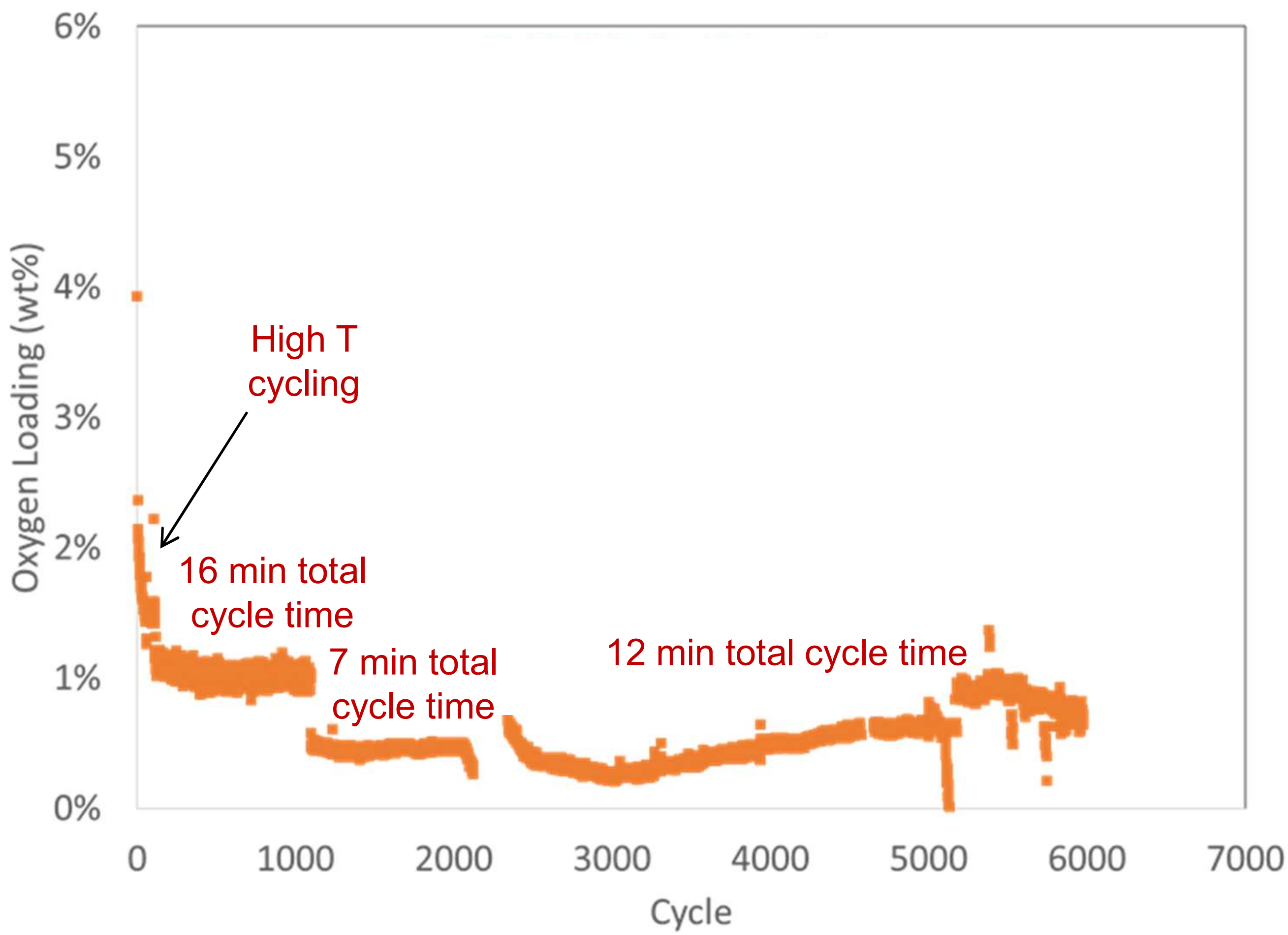
# Sorbent Life Test




- **Sorbent has been cycled more than 6,000 cycles at low temperature**
- **Working capacity of ~ 1% wt. $O_2$ is accomplished**



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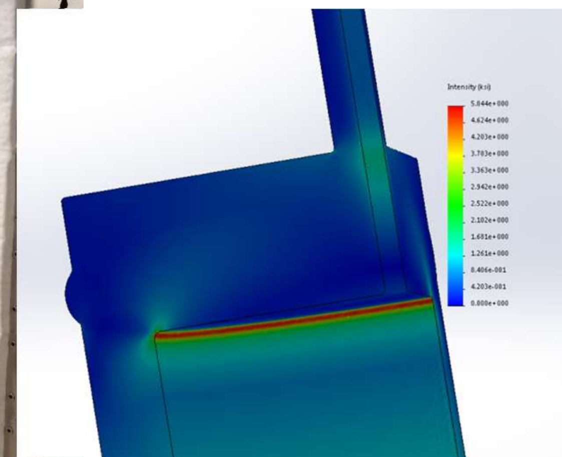
# Prototype Unit


**1 kg/hr $O_2$ Generation System**

# Reactor Design

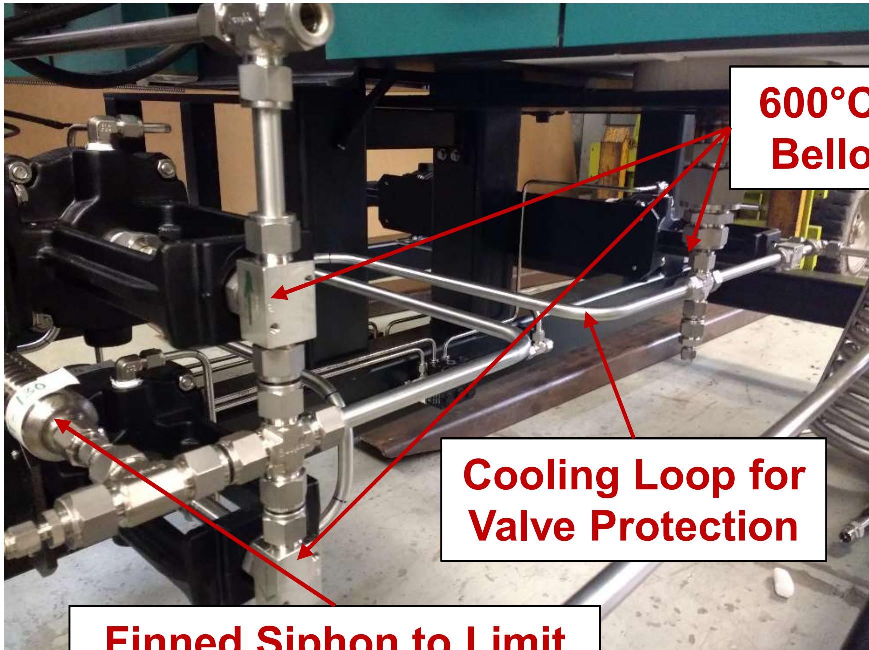



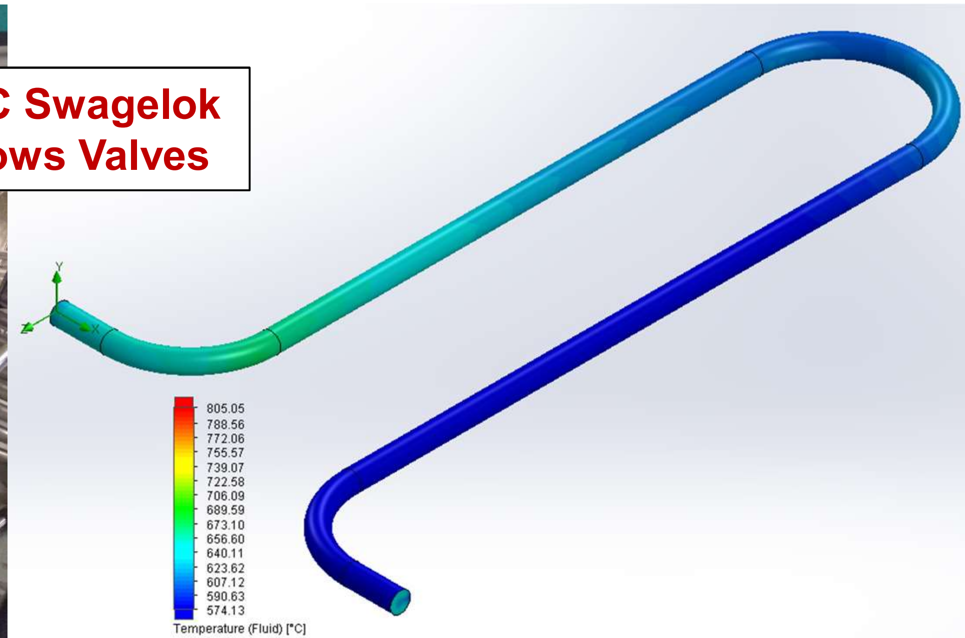
### Vessel Sizing for 1 kg/hr $O_2$

| $O_2$ Product Rate | 1 | kg/h |
|---|---|---|
| $O_2$ Product Rate | 16.7 | g/min |
| Sorbent Capacity | 1.57% | wt. O2 |
| Sorbent density | 0.793 | kg/L |
| Cycle time | 30 | min |
| Sorbent needed | 31.8 | kg |
| Total Sorbent Volume | 40.2 | L |
| Sorbent Volume (1 Bed) | 10 | |

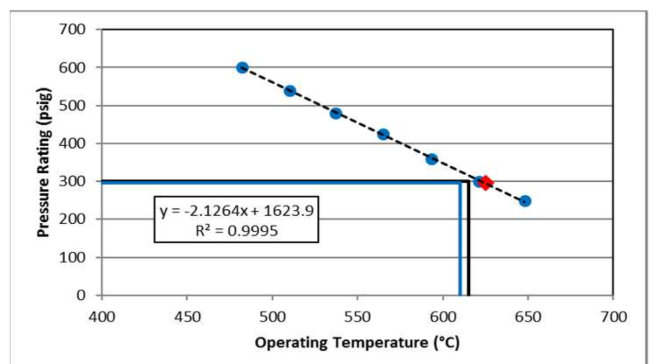
- **6” diameter 36” height vessels to house 10-12L (0.4 CF) sorbent**
  - Incoloy HT is chosen for the material with a design temperature of 805°C and pressure of 295 psig

# Passive Cooling Loops



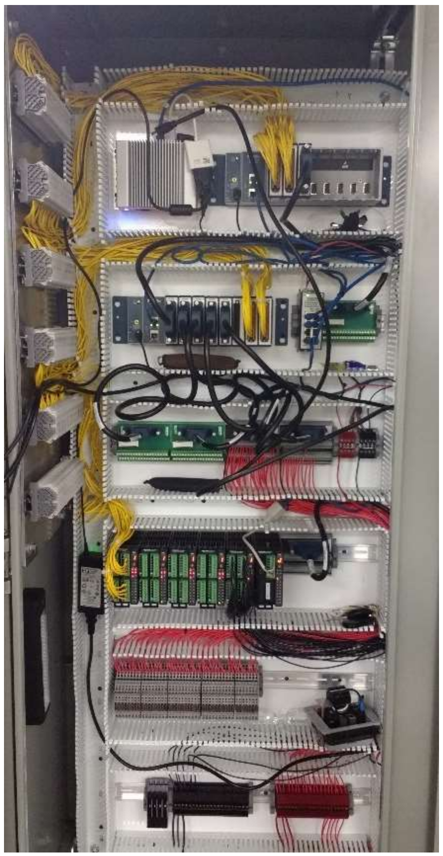

Flow Simulation of Passive Cooling Loops




- Passive Cooling Loops are designed to cool the Steam/$O_2$ stream from 800°C to ≤ 600°C to safeguard the system valves
- Additional passive cooling employed to protect Instrumentation

# Control and Instrumentation Hardware

**Low-Voltage (12–24DC) Signal I/O**




**Skid Electronics and Control Panel with HMI**

**High-Voltage (480V 3-Phase AC) Motor and Heater Control**

# Techno-economic Analysis (TEA)

- **TDA in collaboration with University of California, Irvine is carrying out a high fidelity process design and economic analysis**
- **TDA's ASU provides significant improvements in plant performance**
  - An increase in net plant efficiency from 32% to 34.0% for an IGCC plant equipped with a cold gas cleanup system (compared to a cryogenic ASU)
  - Efficiency also improved for IGCC plant with warm gas cleanup from 35.3% vs 34.5%

| ASU Desorption Temp, C | 650 | 750 | 800 | 650 | 750 | 800 |
|---|---|---|---|---|---|---|
| Gas Cleanup | Cold | Cold | Cold | Warm | Warm | Warm |
| Net Efficiency, HHV | 34.46 | 33.79 | 33.54 | 35.25 | 34.92 | 34.90 |

- **There is a significant efficiency gain by lowering the operating temperature of the ASU since it reduces the steam temperature used in the desorption process**
- **From equipment design standpoint, the lower temperature is highly advantageous:**
  - Allow us to use lower cost alloys
  - Reduce the wall thickness for the pressure vessels

# ASU Operating Temperature

| ASU Desorption Temp, C | 650 | 750 | 800 | 650 | 750 | 800 |
|---|---|---|---|---|---|---|
| Gas Cleanup | Cold | Cold | Cold | Warm | Warm | Warm |
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- **There is a significant efficiency gain by lowering the operating temperature of the ASU since it reduces the steam temperature used in the desorption process**
- **From equipment design standpoint, the lower temperature is highly advantageous:**
  - Allow us to use lower cost alloys
  - Reduce the wall thickness for the pressure vessels
- **However, the working capacity will be lower at the lower operating temperature increasing the bed size**
  - Trade off between high cost of construction materials against the reactor size
- **After optimization of the desorption temperature, preliminary TEA analysis was completed and a Topical Report was submitted to DOE**



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# Process Techno-economic Analysis

| Case | | Case 1A | | Case 1B |
|---|---|---|---|---|
| Type Plant | IGCC – Cold Gas Cleanup -Selexol$^{TM}$ GE Gasifier | | IGCC – Warm Gas Cleanup –TDA Sorbent - GE gasifier | |
| ASU Technology | Cryogenic | TDA Sorbent | Cryogenic | TDA Sorbent |
| $CO_2$ Capture, % | 90 | 90 | 90 | 90 |
| Gross Power Generated, kWe | 727,370 | 733,394 | 674,331 | 736,952 |
| Gas Turbine Power | 464,000 | 464,000 | 417,554 | 464,000 |
| Steam Turbine Power | 257,403 | 260,589 | 246,746 | 262,405 |
| Syngas/Air Expander | 5,968 | 8,806 | 10,031 | 10,547 |
| Auxiliary Load, kWe | 192,927 | 163,827 | 120,661 | 140,536 |
| Net Power, kWe | 534,443 | 569,567 | 553,671 | 596,416 |
| Net Plant Efficiency, % HHV | 32.00 | 34.0 | 34.46 | 35.25 |
| Coal Feed Rate, kg/h | 221,584 | 222,095 | 213,013 | 224,318 |
| Raw Water Usage, GPM/MWe | 10.92 | 9.36 | 10.55 | 10.86 |
| Total Plant Cost, $/kWe | 3,359 | 3,208 | 3,212 | 3,161 |
| COE without $CO_2$ TS&M, $/MWh | 133 | 126.5 | 126 | 123 |
| COE with $CO_2$ TS&M, $MWH | 142 | 134.5 | 134 | 130.7 |
| Cost of $CO_2$ Capture, $/tonne | 37 | 31.6 | 31 | 28.4 |



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# Future Work

- We will complete the sorbent life tests (12,500 cycles) at low temperature
- TDA will start the testing of the 1 kg/hr prototype unit demonstrating the high temperature air separation process
- The results from the prototype tests will be used to validate the CFD and absorption cycle models
- The performance results will also be used to revise the process design models being developed by UCI
- Revise our estimates for the cost of $CO_2$ capture for GE and E-Gas gasifier based IGCC power plants and oxy-combustion coal fired power plant

# Acknowledgements


- Dianne Madden, NETL (Project Manager)
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- Ashok Rao, UCI