# Development Novel Carbon Sorbents for Carbon Dioxide Capture

2012 NETL $CO_2$ Capture Technology Meeting
July 9-12, 2012 in Pittsburgh, PA.

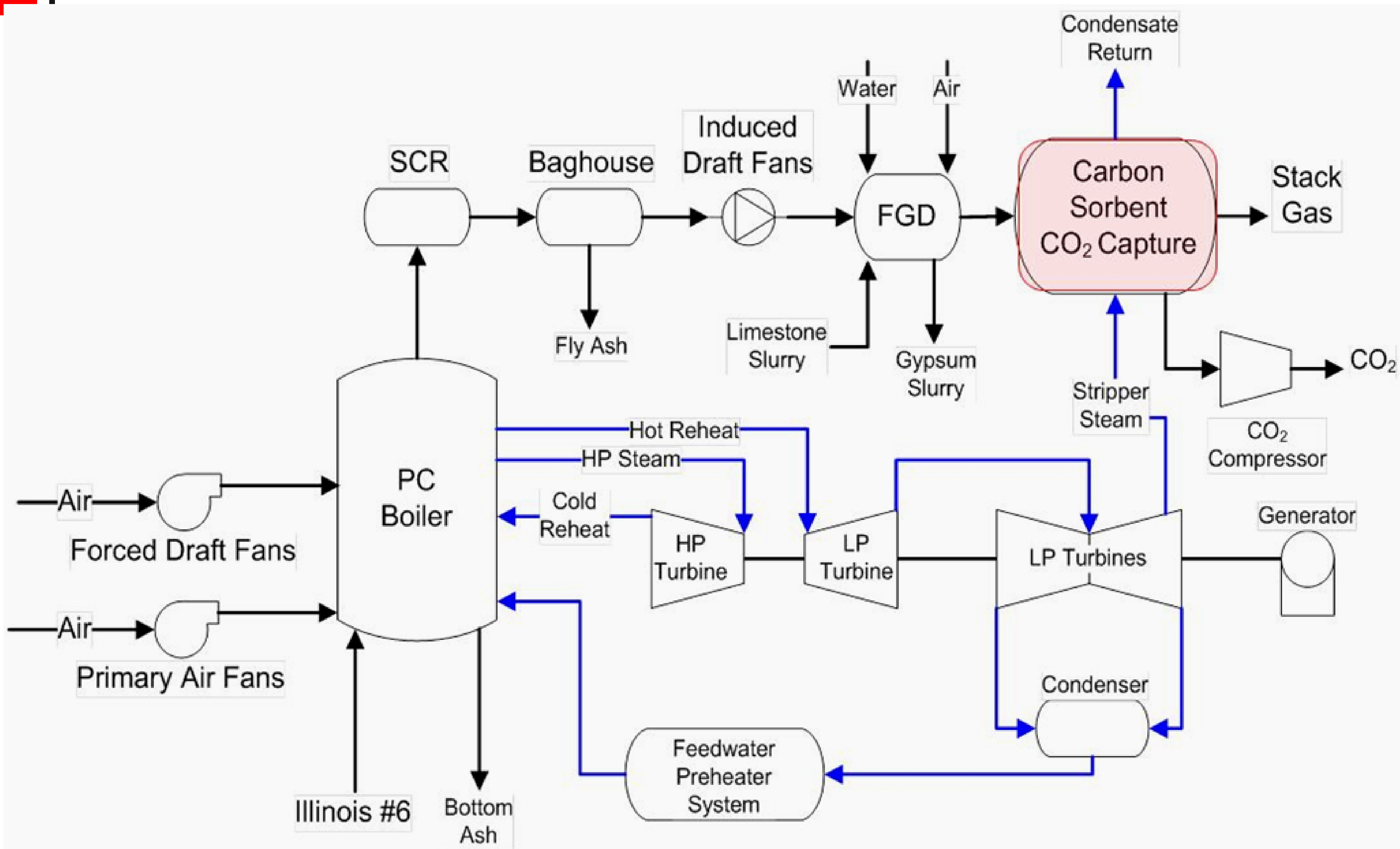
# Project Overview

- Participants:
  - SRI International, Menlo Park, CA
  - ATMI, Inc., Danbury, CT
  - University of Toledo, OH
  - DOE-National Energy Technology Center
- Period of Performance:
  - 10-1-2008 through 9-30-2012
- Funding:
  - U.S.: Department of Energy: $1.35 million
  - Cost share: $0.45 million
  - Total: $1.8 million

# Project Objectives

- Validate the performance of novel carbon sorbents for $CO_2$ capture on a bench-scale system for post-combustion applications.
- Perform parametric experiments to determine the optimum operating conditions.
- Evaluate the technical and economic viability of the technology.
- Field test at the bench-scale level with an actual flue gas.
- Pilot-scale testing in a future phase.

# Block Flow Diagram



# Basic Principles

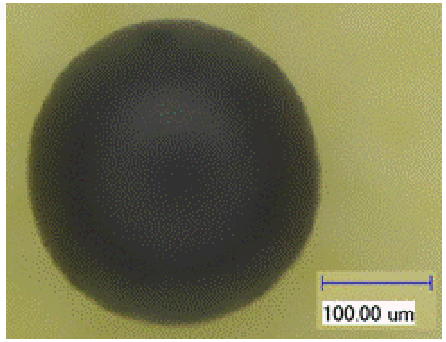
- Adsorption of $CO_2$ from flue gas on a selective and high capacity carbon sorbent.
- Ability to achieve rapid adsorption and desorption rates (no solid state diffusion limit).
- Minimize thermal energy requirements
- Ability to desorb as pure $CO_2$.
- A falling micro-bead sorbent reactor geometry integrates the adsorber and stripper in a single vertical column:
  - Provides a low pressure drop for gas flow and minimize physical handling of the sorbent.

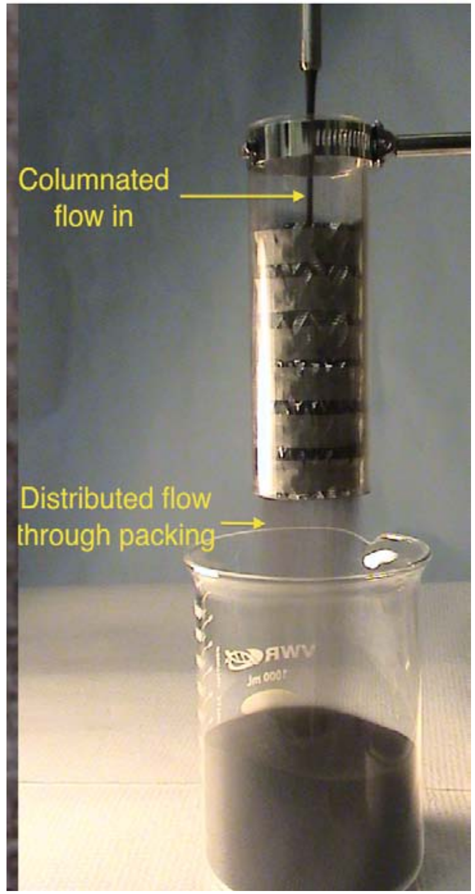
# Sorbent Attributes: Chemical Properties

- High $CO_2$ capacity:
  - The sorbent has a high capacity for $CO_2$ adsorption (20 wt% at 1 atm $CO_2$) and good selectivity for $CO_2$ over other flue gas components.
- Rapid adsorption and desorption rates:
  - The adsorption of $CO_2$ occurs on the micropores of the sorbent with very low activation energy (<5kJ/mole), allowing rapid cycling of the sorbent.
- Low heat of adsorption and desorption:
  - The relatively low heats (<28 kJ/mole) indicate that this process has a low heat demand for regeneration and low cooling requirements.
- High hydrothermal stability:
  - Direct heating with steam can be used for $CO_2$ desorption.

# Sorbent Attributes: Physical Properties

- Mechanical robustness for long lifetime:
  - Hard and attrition resistant; Unusually tough for a high surface area (1600 $m^2/g$) porous solid
  - ASTM Test D-5757: Attrition resistance very high: Weight loss <0.01%/hour
- Spherical morphology of the sorbent granules:
  - Sorbent spheres (100 to 300 μm) allows a smooth flow
  - This free-flowing, liquid-like characteristic allows the use of commercially available structural packing
- Low heat capacity:
  - The low heat capacity of the sorbent (1 J/g/K) and low density (1 $kg/m^3$) minimizes the thermal energy needed to heat the sorbent to the regeneration temperature
- High thermal conductivity:
  - The thermal conductivity of 0.8 w/m-K enables rapid thermal equilibrium between the sorbent surface and interior



# Summary of Previous Reported Results

- Determined several physical and chemical properties of the advanced carbon sorbent in the context of flue gas $CO_2$ capture.
- Demonstrated an unique sorbent and a reactor geometry for $CO_2$ capture under simulated flue gas conditions in a 1000-cycle test:
  - Achieved ~99% $CO_2$ capture from air-$CO_2$ gas mixture
  - Achieved >98% pure $CO_2$ during regeneration
  - Capable of rapid adsorption and regeneration
  - Fluid-like flow properties
  - High attrition resistance
  - Integrated absorber-desorber geometry
  - Minimize solids handling
  - Minimize heat exchanger requirements
  - Stable operation over 1000 cycles

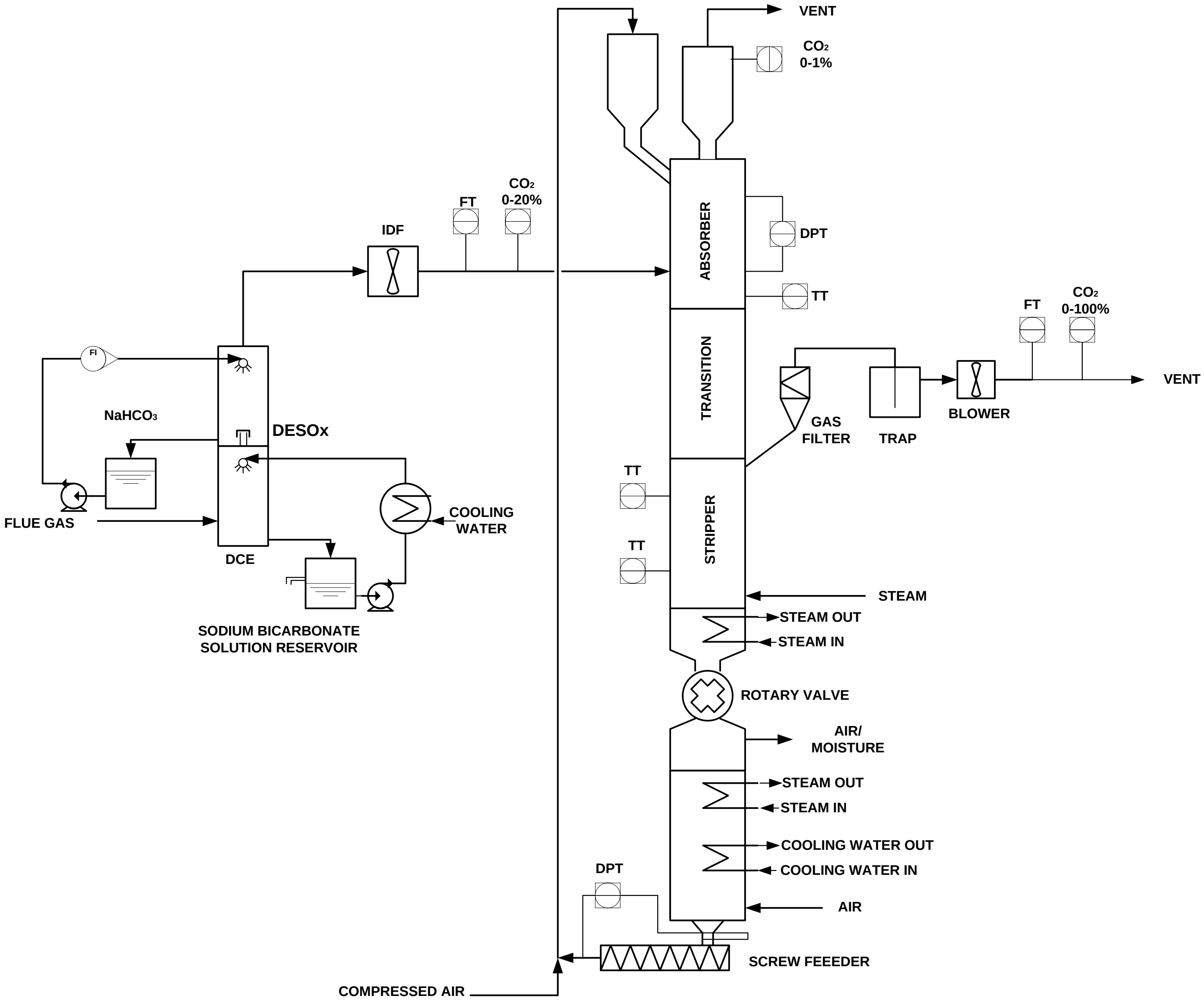
# Comparison of $CO_2$ Capture Costs

| | Base Case | Econamine FG+ | Carbon Sorbent |
|---|---|---|---|
| Carbon Capture | No | Yes | Yes |
| Gross Power Output (kW) | 580,400 | 662,800 | 642,113 |
| Auxilary Power Requirement (kW) | 30,410 | 112,830 | 98,751 |
| **Net Power Output (kW)** | **549,990** | **549,970** | **543,363** |
| Net Plant HHV Efficiency (%) | 39.30 | 28.40 | 36.00 |
| Net Plant HHV Heat Rate Btu/kWh) | 8.69 | 12.00 | 9.47 |
| Coal Flow Rate(lb/h) | 409,528 | 565,820 | 441,178 |
| CO2 Emissions (lb/MWh) | 972,382 | 134,193 | 102,924 |
| Power Plant Capital (¢/kWh) | 3.17 | 5.96 | 4.40 |
| Power Plant Fuel (¢/kWh) | 1.42 | 1.96 | 1.55 |
| Variable Plant O &M (¢/kWh) | 0.10 | 0.70 | 0.66 |
| Fixed Plant (¢/kWh) | 0.80 | 1.30 | 0.96 |
| **Power Plant Total (¢/kWh)** | **5.89** | **10.10** | **7.56** |
| CO2 T, S, and M (¢/kWh) | 0.00 | 0.56 | 0.54 |
| **Total Cost (¢/kWh)** | **5.89** | **10.66** | **8.10** |
| **Increase in COE (%)** | **0.00** | **80.20** | **37.20** |

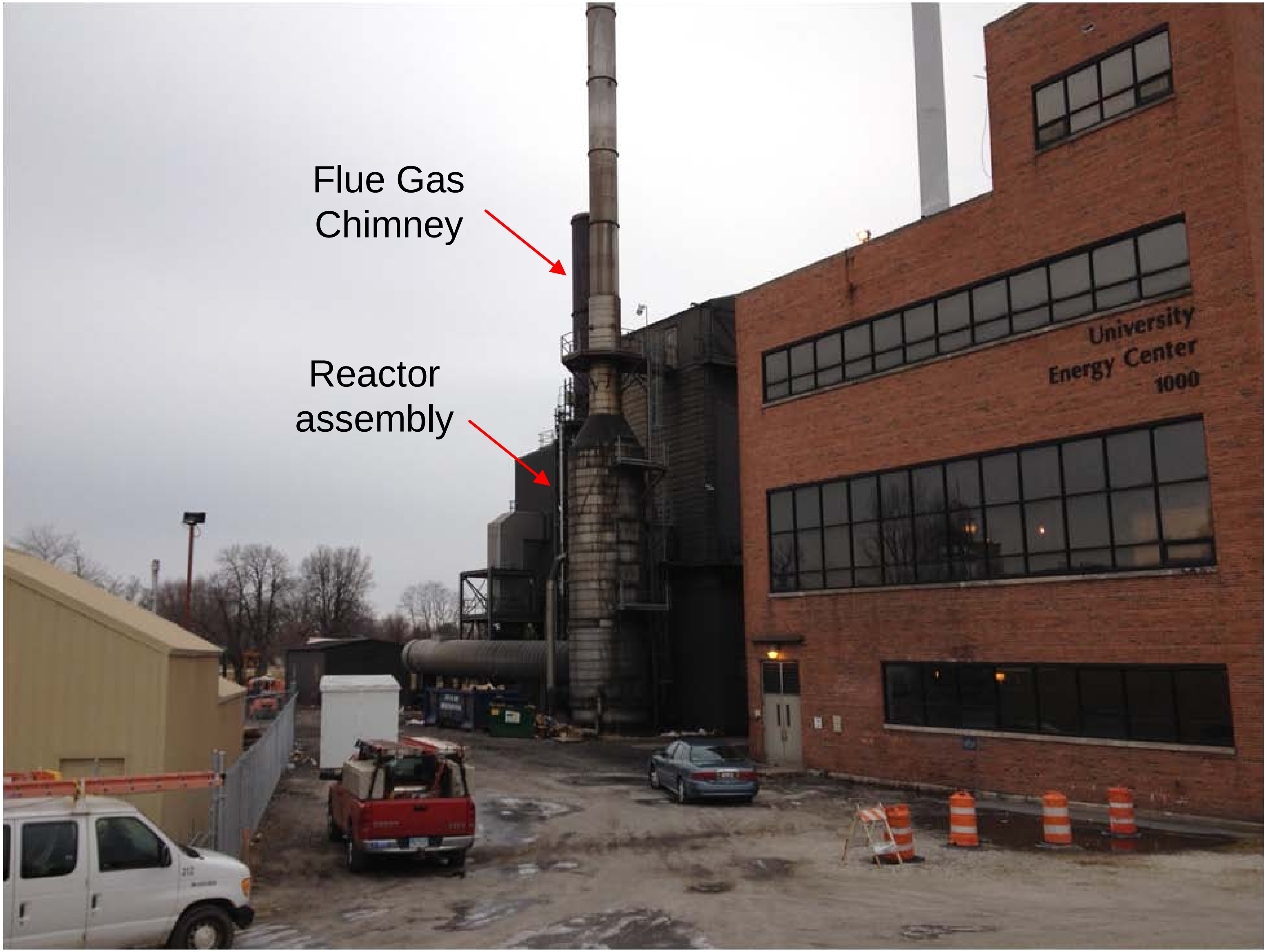
# Field Tests at the University of Toledo

- Coal-fired steam boilers provide steam for its Health Science campus.
- A stoker boiler operated with a low-sulfur coal to generate 15,0000 lb/h steam.
- The flue gas from the boiler is sent to an electrostatic precipitator and then to a chimney.
- No flue gas desulfurization or nitrogen oxide control was practiced at the plant ($SO_2$ level ~60 ppm measured; $NO_x$ level: 60 ppm estimated).

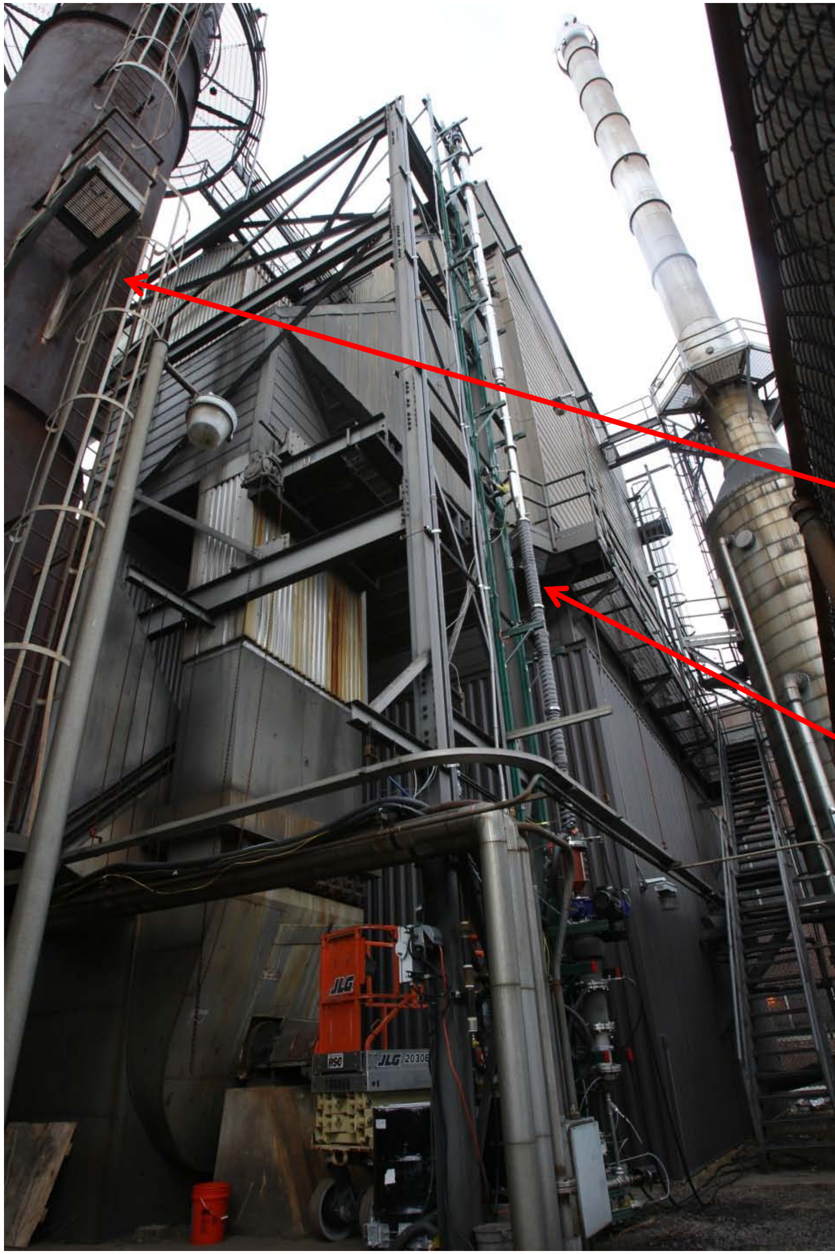
# Schematic Diagram of the System



# Coal-Fired Boiler Facility at UT



# The $CO_2$ Capture System Installed at UT



Flue Gas Chimney

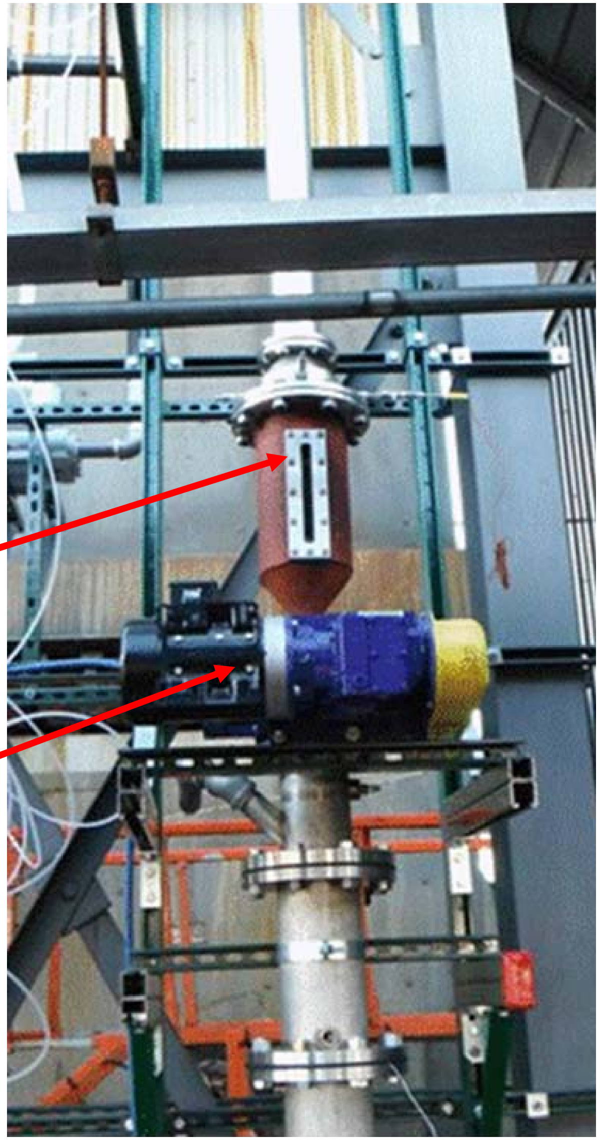
Integrated Reactor

# Absorber Section

# Stripper Section

Stripper

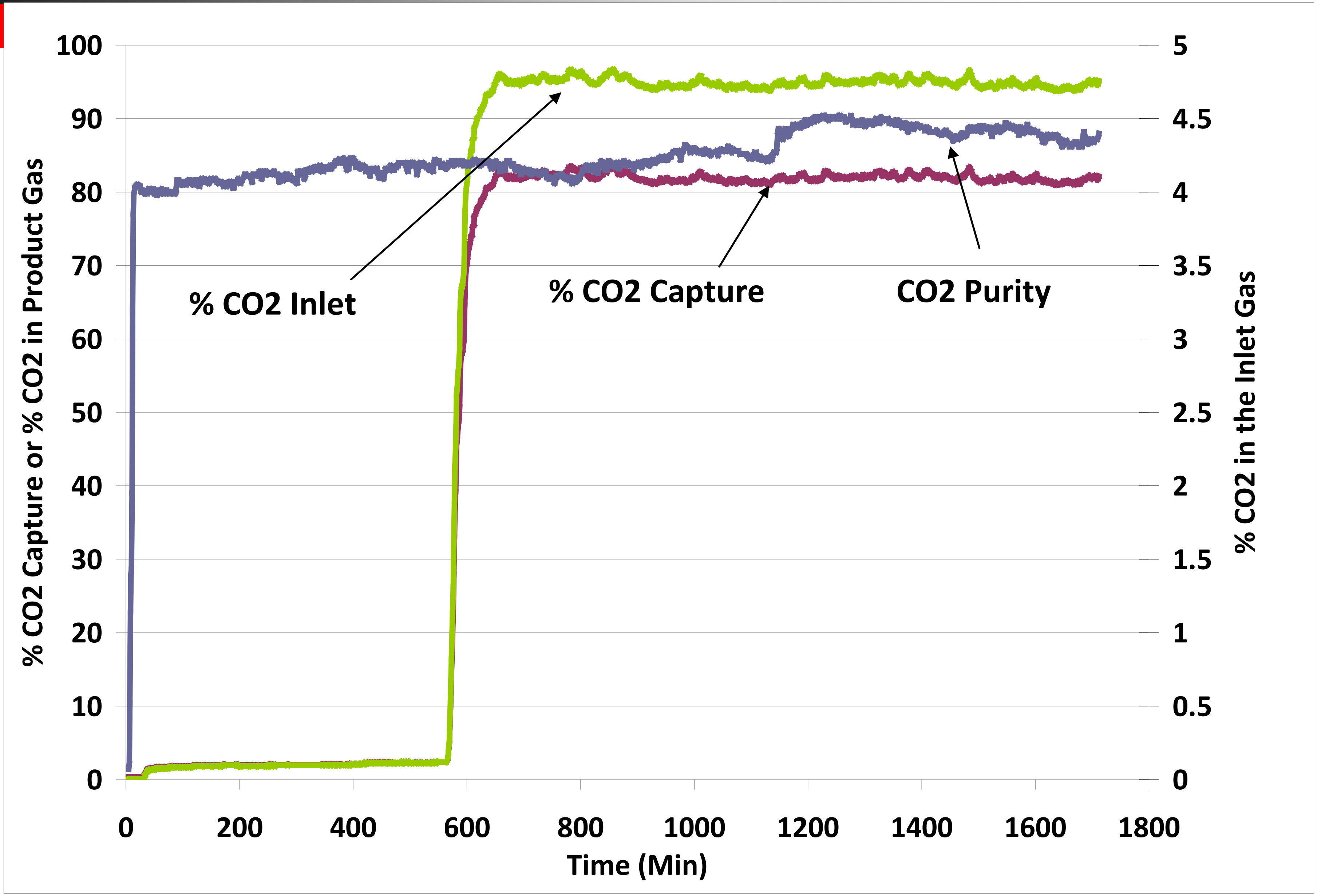
Rotary Valve



# Operation at UT

- The system was operated during the day time from 8 AM to 7 PM, about 6 days a week for one month (including shake-down runs).
- The flue gas flow rate was about 200 standard liters/min.
- $CO_2$ concentration: 4.5% v/v.
- $SO_2$ concentration: 60 ppm reduced to ~1 ppm with the use of a FGD with sodium bicarbonate.
- NOx control was not practiced.
- Pressure drop across the adsorber: 0.4 in WC.
- Total hours of operation: 130 hours (7,000 cycles).

# CO2 Capture Efficiency and Product Gas Purity



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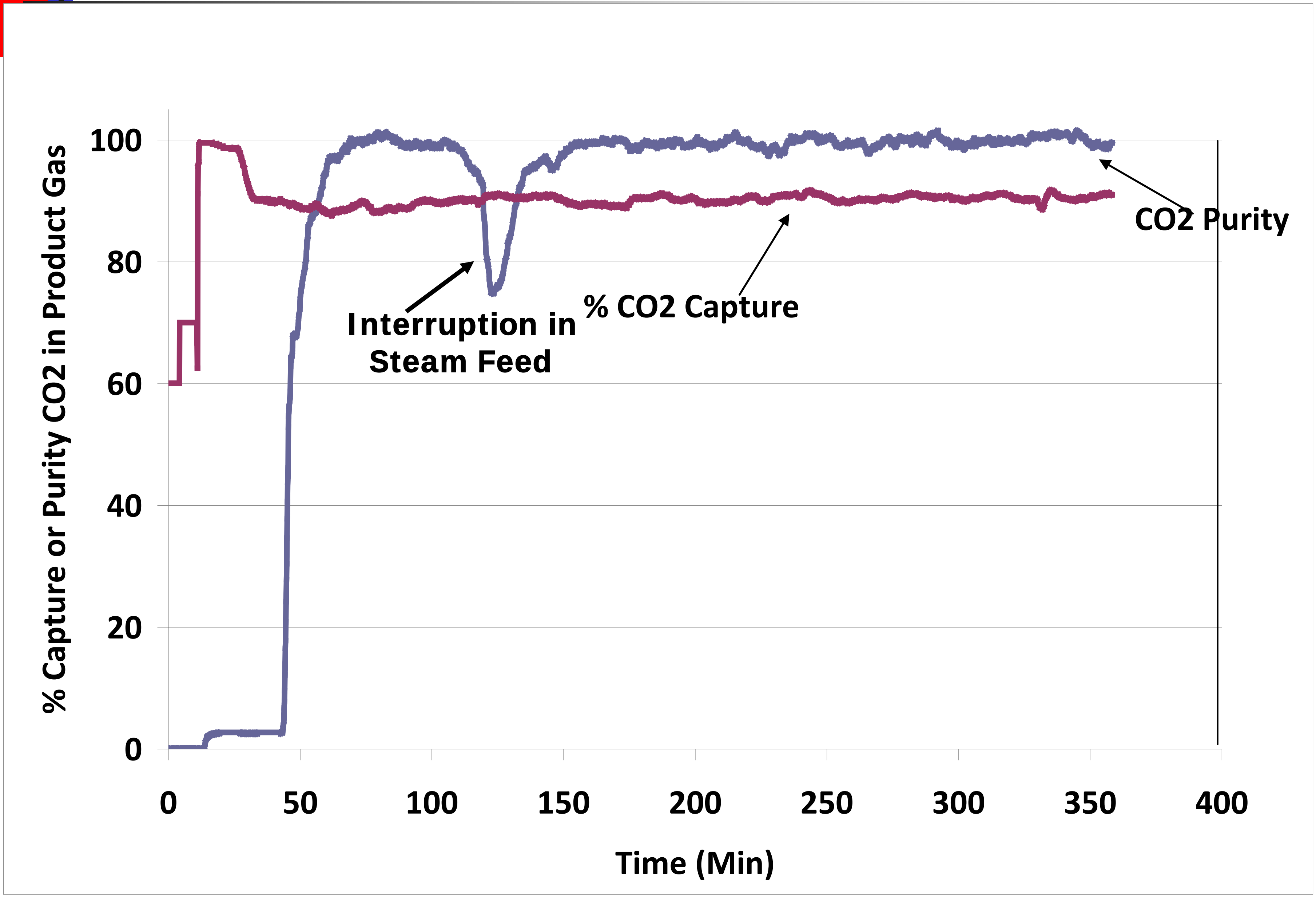


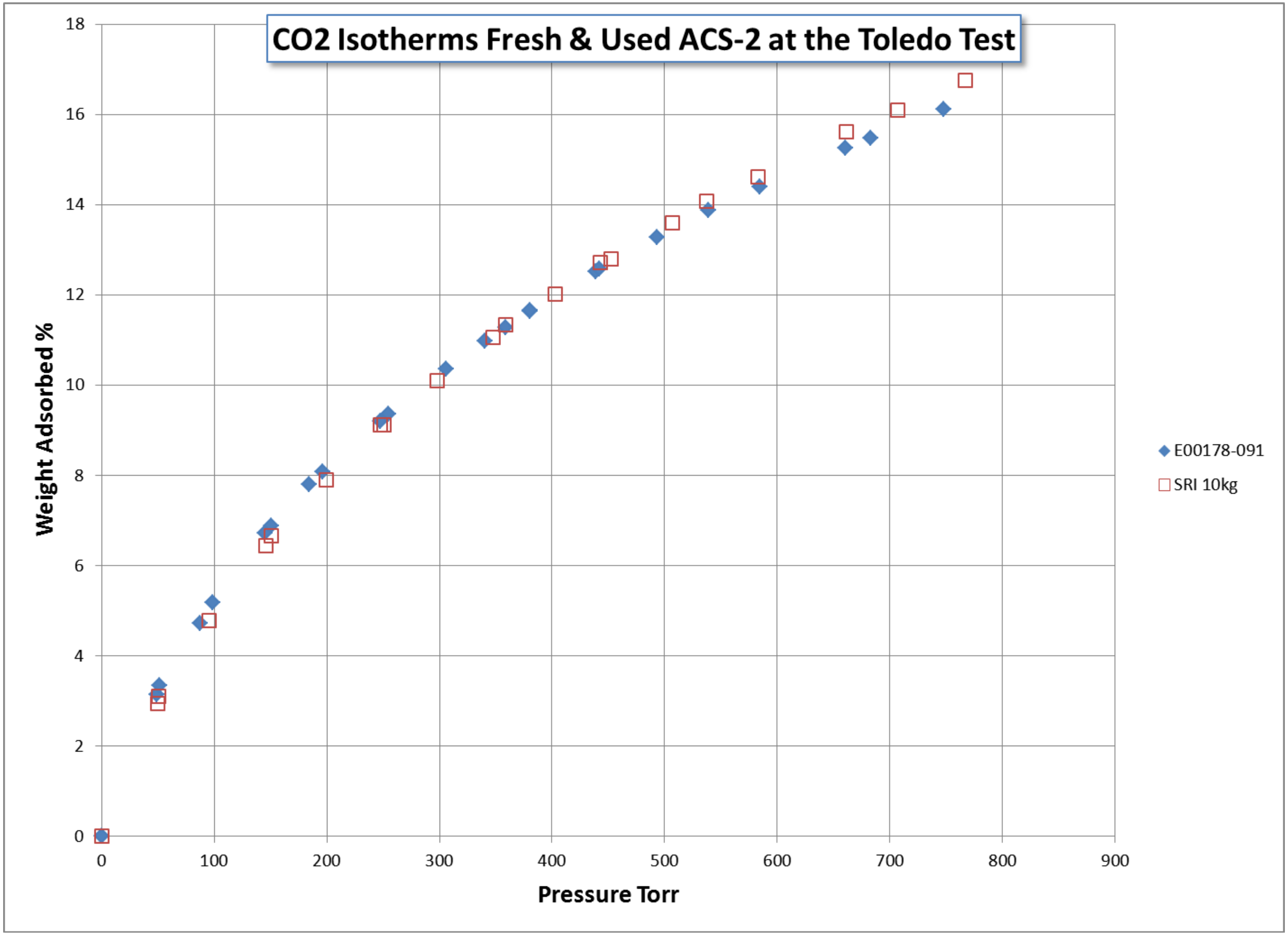
# General Observations During the Operation at UT

- The system was able to reduce the $CO_2$ level from 4.5% to <0.05% (full regen).
- We achieved steady-state operation with 90% capture efficiency with >98% $CO_2$ purity in the product gas.
- Sorbent flow: Smooth
  - sorbent inventory:1.2 kg.
  - Typical cycle time: ~1 min.
- No significant operational issues were observed.

# Post Analysis

- The sorbent was analyzed after the test:
  - $N_2$ porosimetry
  - Thermo-gravimetric analysis in vacuum
  - $CO_2$ adsorption isotherms
  - Trace metals analyses plus S, Cl, Hg

# CO2 Isotherm at 298 K



# Porosity Changes

| N2 porosity properties | | | |
| --- | --- | --- | --- |
| | | Used Toledo ACS-2 | Fresh Toledo ACS-2 |
| | Units | E00178-091 | ATMI-1174 |
| BET SA | m2/g | 982 | 1036 |
| t-MPV | cc/g | 0.353 | 0.372 |
| H-K | nm | 0.533 | 0.537 |
| D-R Eo | J/mol | 30.7708 | 30.6193 |
| D-R-MPV | cc/g | 0.391 | 0.413 |
| D-A-MPV | cc/g | 0.393 | 0.414 |
| D-A Integer | | 1.9214 | 1.9437 |
| D-Stoeckli | nm | 0.558 | 0.562 |

# Trace Elements in the Sorbent

| Used Toledo ACS-2 | | Fresh Toledo ACS-2 | |
|---|---|---|---|
| Na | 95 | Na | 102 |
| P | 66 | P | 80 |
| K | 6 | K | 74 |
| Ca | 41 | Ca | 41 |
| Mn | 24 | Mn | < 2 |
| Fe | 1234 | Fe | < 2 |
| Zn | 15 | Zn | < 2 |
| Cl | 611 | Cl | 468 |
| S | 132 | S | 19 |
| Hg | 0.31 | Hg | < 0.06 |

# Future Plans

- Field Testing:
  - Field test the process using a flue gas from an operating pulverized coal-fired boiler.
    - 1000 h of operation
    - Effect of flue gas contaminants
    - Thermal management
- Technology Transfer
  - SRI and ATMI are in touch with several utility and chemical companies for further development.

# Team

- SRI International
  - Dr. Gopala Krishnan – Associate Director (MRL) and PI
  - Dr. Marc Hornbostel, Senior Materials Scientist
  - Dr. Jianer Bao, Materials Scientist
  - Dr. Angel Sanjurjo – Materials Research Laboratory Director and Project Supervisor
- ATMI Inc.
  - Sorbent developer, Industry perspective
  - Dr. Joshua B. Sweeney, Director, Business Development
  - Dr. Melissa Petruska, Materials Scientist
  - Dr. Donald Carruthers; Senior Research Scientist
- University of Toledo
  - Dr. Glenn Lipscomb, Professor and Chairman, Chem. Eng.
  - Mr. Terry Yuecun, Graduate student, Chemical Engineering
- DOE-NETL
  - Andrew O'Palko