Evaluation of Dry Sorbent Technology for Pre-Combustion CO_2 Capture

NETL DE-PS26-08NT00699-03

DE-PS26-08NT00699-03
Project Overview

Investigate/develop a dry sorbent process that combines CO_2 capture with the water-gas shift reaction by developing and optimizing sorbents to perform in syn-gas at high pressure and high temperature

Dry Sorbent CO_2 Capture Test Program Presentation Overview

- **Project Organization**
- **Technology Background**
- **Technical Approach**
- **Schedule**
- **Milestones/Deliverables**

Project Organization

Project Team

- **DOE-NETL**
  - [COR-Susan Maley]
- **Illinois Clean Coal Institute, ICCI**
  - [co-funder]
- **University of Illinois at Urbana-Champaign/ Illinois State Geological Survey, UIUC-ISGS**
  - [modeling, sorbent synthesis and screening; co-funder]
- **URS Group**
  - [prime contractor; sorbent evaluation testing]

Project Team – Key Personnel

- **NETL** – Susan Maley (COR)
- **ICCI** – Francois Botha (ICCI Lead)
- **UIUC/ ISGS** – Massoud Rostam-Abadi (ISGS P.I.)
  - Yongqi Lu (Modeling, Laboratory Lead)
- **URS** – Carl Richardson (Project Manager)
  - Gary Blythe (Technical Advisor)
  - Katherine Dombrowski (Task Leader)
  - Jennifer Paradis (Laboratory Director)
  - William Steen (Reactor Design)

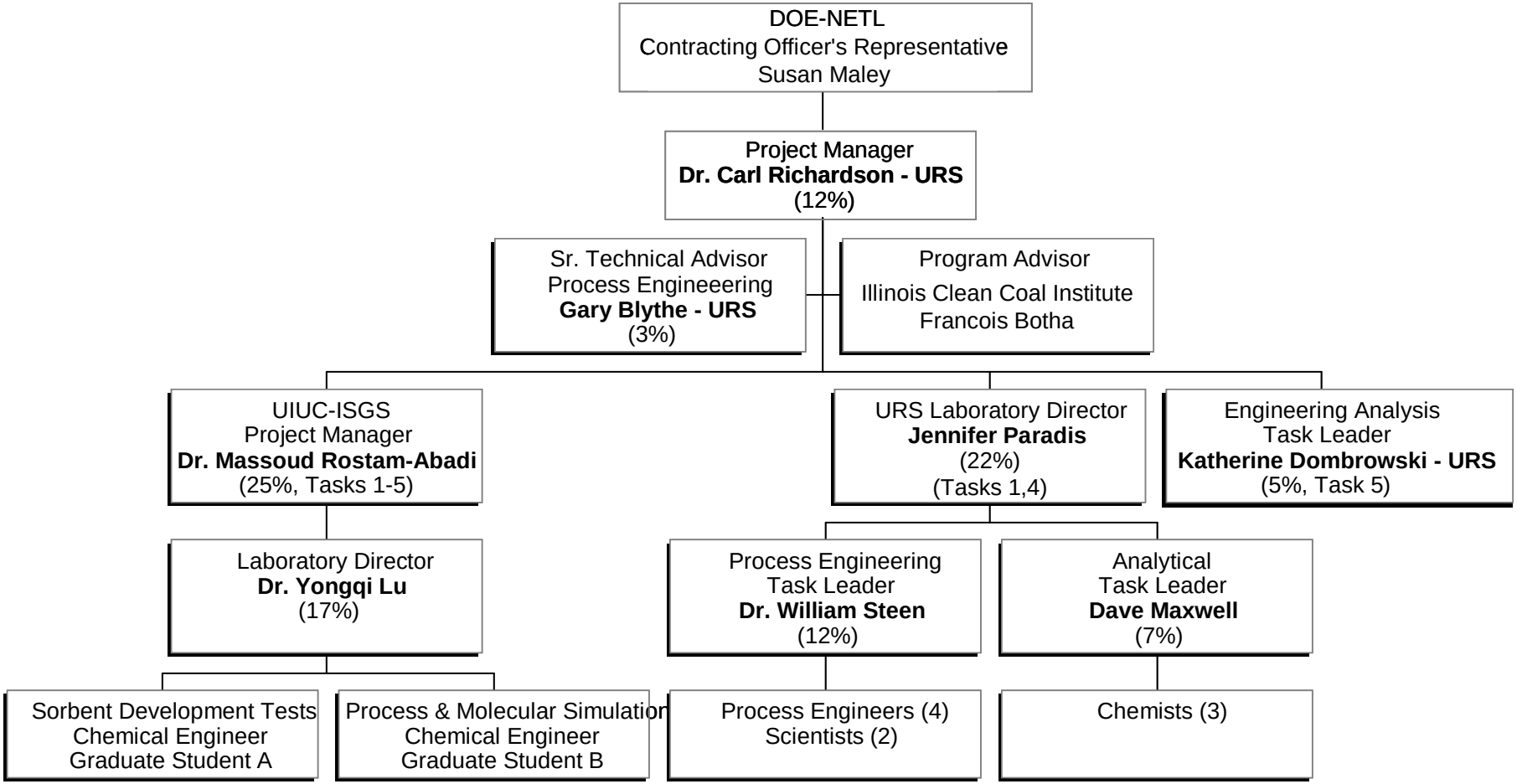
Project Tasks

- **Task 1: Project Management & Planning**
  - *1.1 Project management plan*
  - *1.2 Program management*
  - *1.3 Kick-off meeting*
  - *1.4 Test plan/QA-QC plan*
  - *1.5 Laboratory mobilization activities*
- **Task 2: Sorbent Engineering Analysis & Selection**
  - *2.1 Sorbent thermodynamic analysis*
  - *2.2 Process simulation analysis*
  - *2.3 Molecular simulation*
  - *2.4 Sorbent identification*

Project Tasks

- **Task 3: Sorbent Preparation**
  - *3.1 Sorbent synthesis*
  - *3.2 Analytical characterization*
- **Task 4: Sorbent Evaluation Testing**
  - *4.1 HTPR parametric testing*
  - *4.2 Syngas impurity testing*
  - *4.3 Sorbent regeneration testing*
  - *4.4 Analytical characterization*
  - *4.5 Sorbent model development*
- **Task 5: Engineering Feasibility Study**

Project Organization



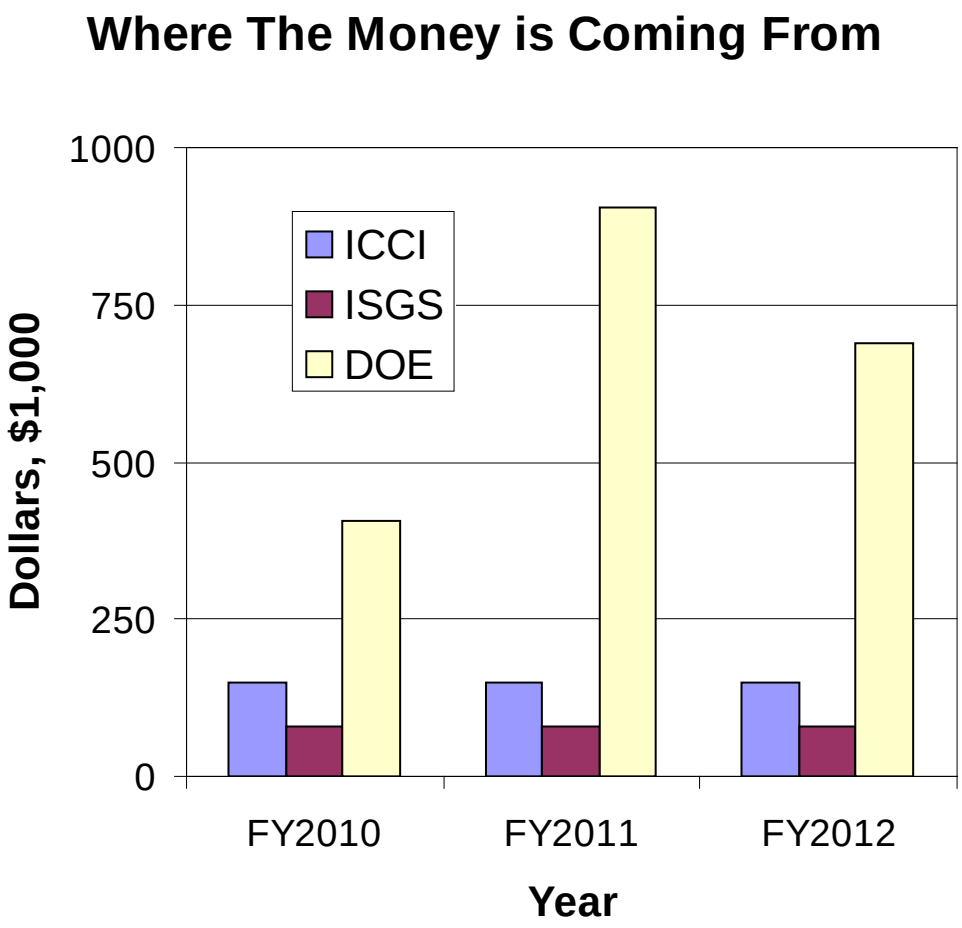
Project Budget

FY10: $ 633,669

FY11: $1,134,602

FY12: $ 916,123

Total: $2,684,394

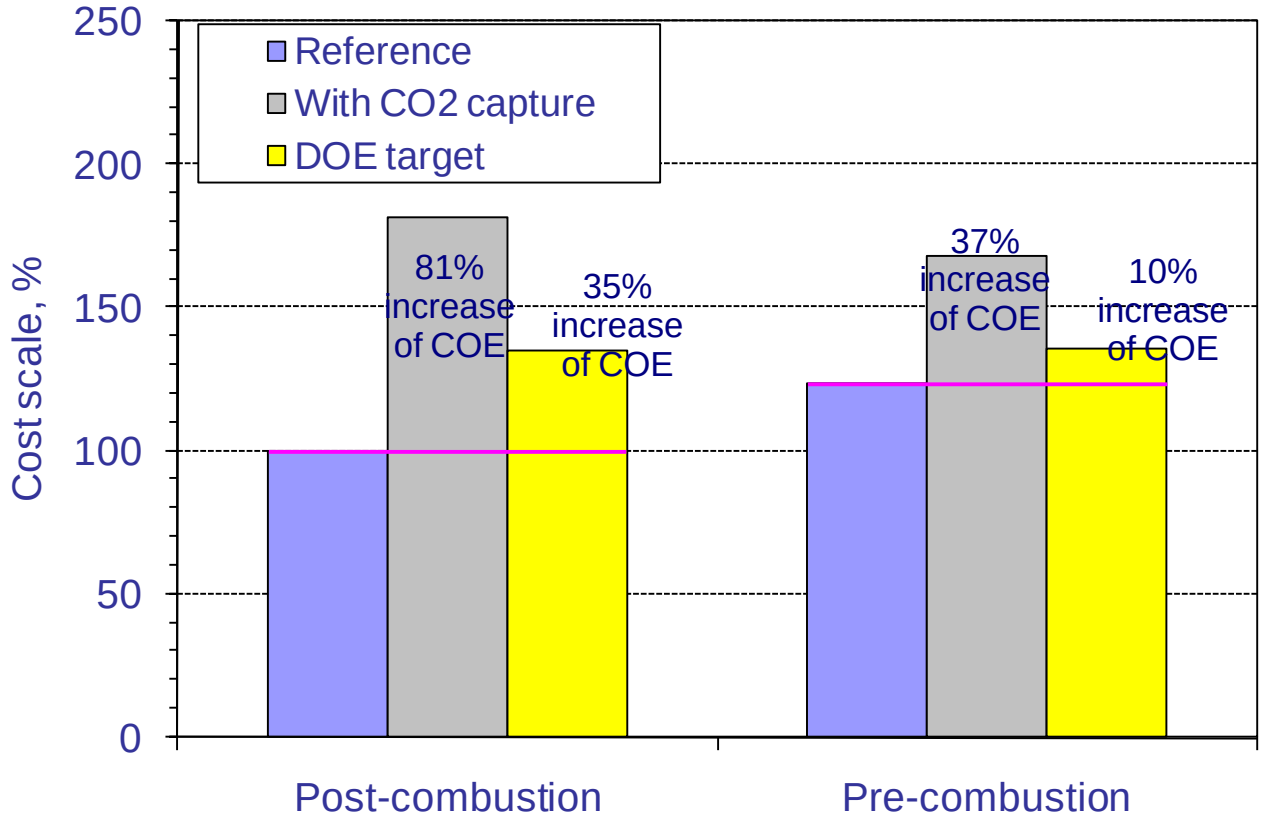


Cost Share is 25%

Background

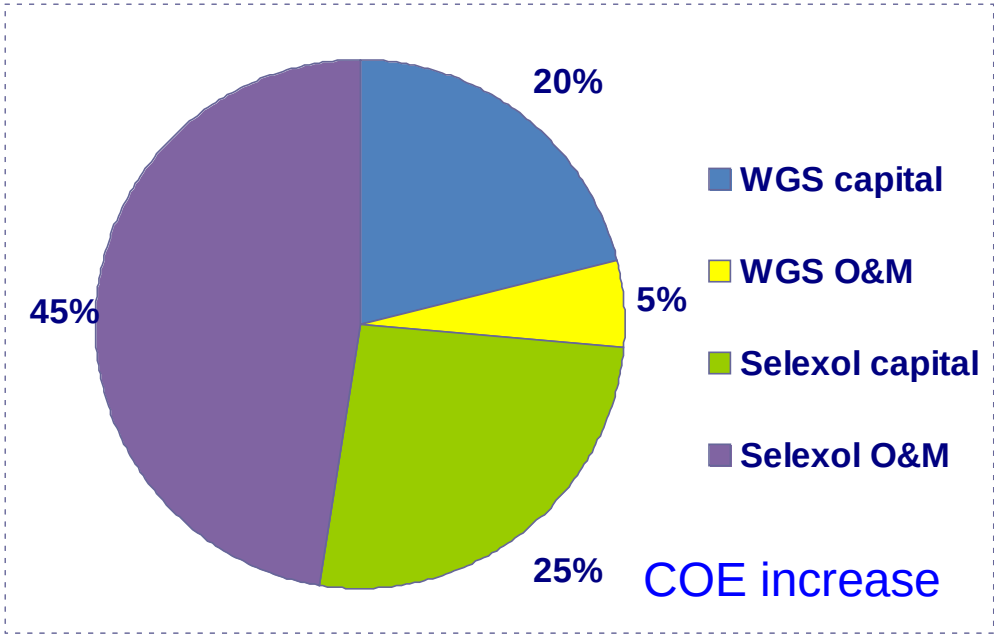
U.S. DOE's Cost Target for CO_2 Capture

- 90% capture efficiency
- 10% increase in COE for pre-combustion
- 35% increase in COE for post-combustion



Selexol Process for CO_2 Capture in IGCC

- Generation efficiency
  - 32% for IGCC + Selexol
  - 38% for IGCC w/o CO_2 capture
- Electricity use for 492 MWe IGCC + Selexol
  - 27 MWe for CO_2 compression
  - 17 MWe for Selexol process
- COE increases by 30-40% compared to IGCC w/o CO_2 capture

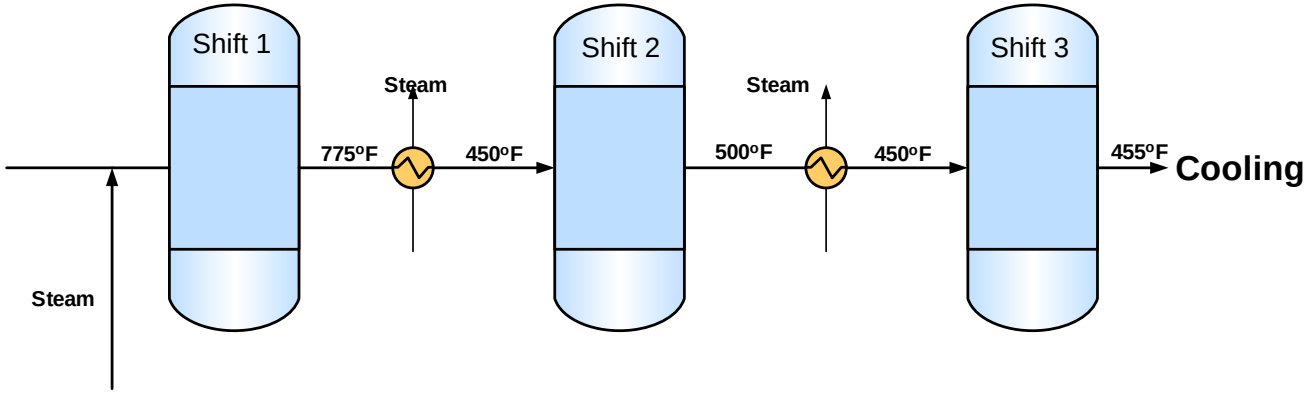


Water-Gas-Shift (WGS) Reaction

- WGS reaction in IGCC with CO_2 capture

$$CO + H_2O = CO_2 + H_2 \ (\Delta\Delta = -41 \text{kJ/mol})$$

  - Exothermic
  - Equilibrium limited at high temperature
- Conventional WGS reactor
  - Multiple stages required
  - CO conversion at high temperature (300–500°C) with no catalyst
  - Complete CO conversion at low temperature (180-300°C) with catalyst

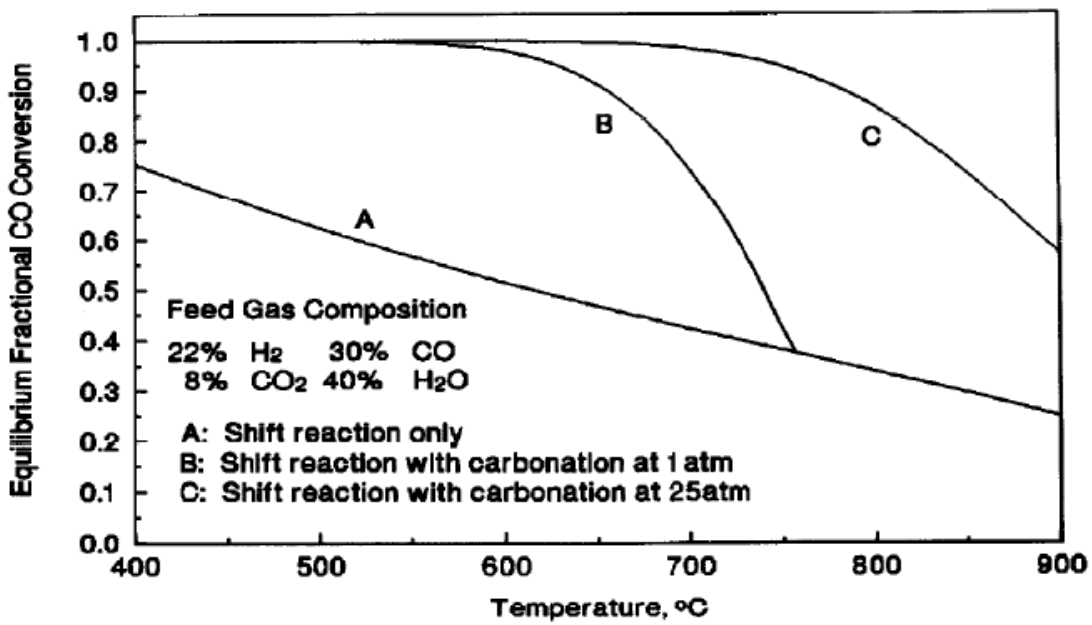


Sorption-Enhanced Water-Gas-Shift (SEWGS)

- Simultaneous WGS + CO_2 Capture
- Complete conversion of CO to CO_2 at ≥500 °C
  - CaO sorbent as an example

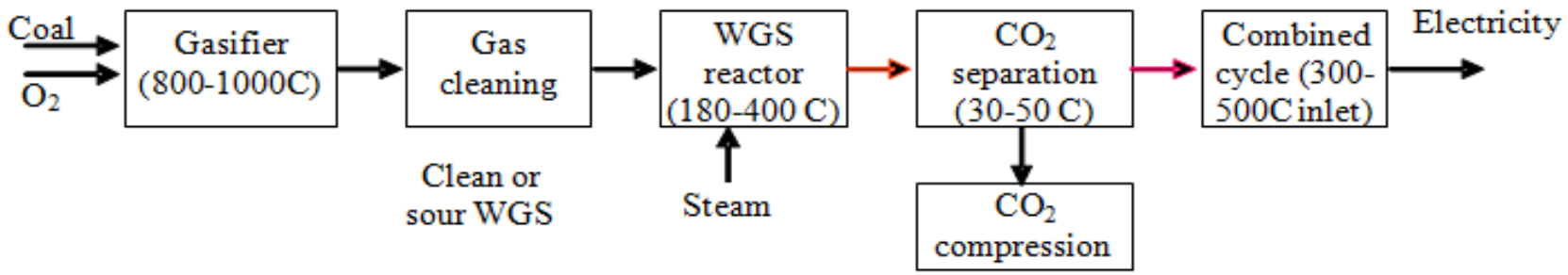
$$CO + H_2O = CO_2 + H_2 \ (\Delta H = -41\ kJ/mol)$$

$$\downarrow \ + CaO = CaCO_3 \ \ (\Delta H = -183\ kJ/mol)$$

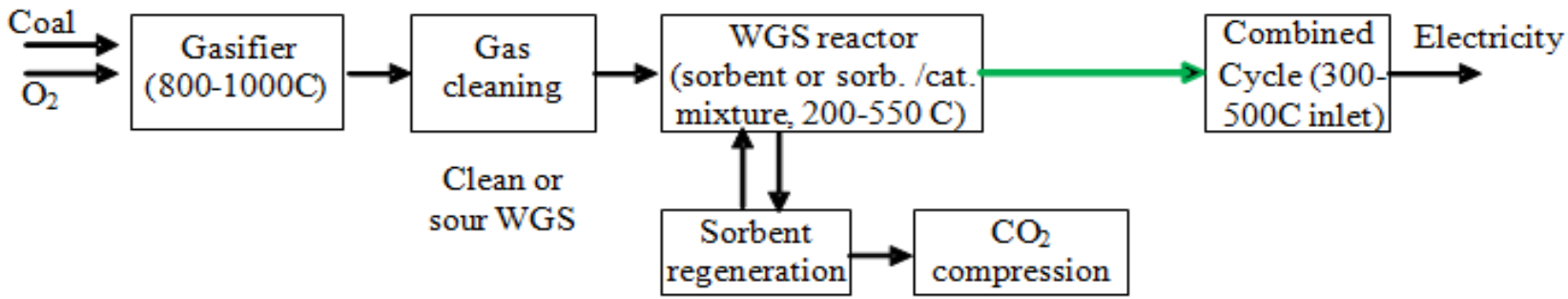


Source: Han & Harrison, *Chem. Eng. Sci.* 1994, 49(248):5875.

IGCC with SEWGS vs. Conventional IGCC



Conventional IGCC plant with CO_2 capture

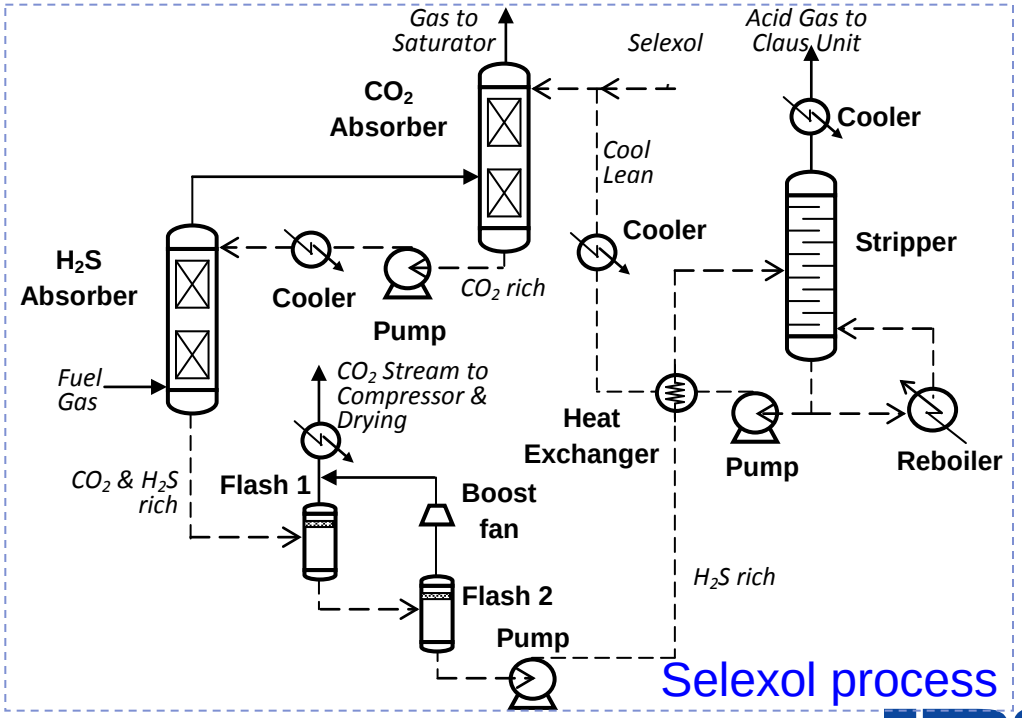


IGCC Plant with sorption-enhanced WGS

- **No or limited WGS catalyst use**
- **No gas cooling/reheating**
- **No separate CO_2 capture unit required**

Engineered Adsorbents for SEWGS

- Lower cost
  - No or limited WGS catalyst use
  - Increased efficiency with no gas cooling/reheating
- High regeneration pressure reduces CO_2 compression work
  - Selexol: 3 → 80 atm
  - SEWGS: 30 → 80 atm (75% lower compression)



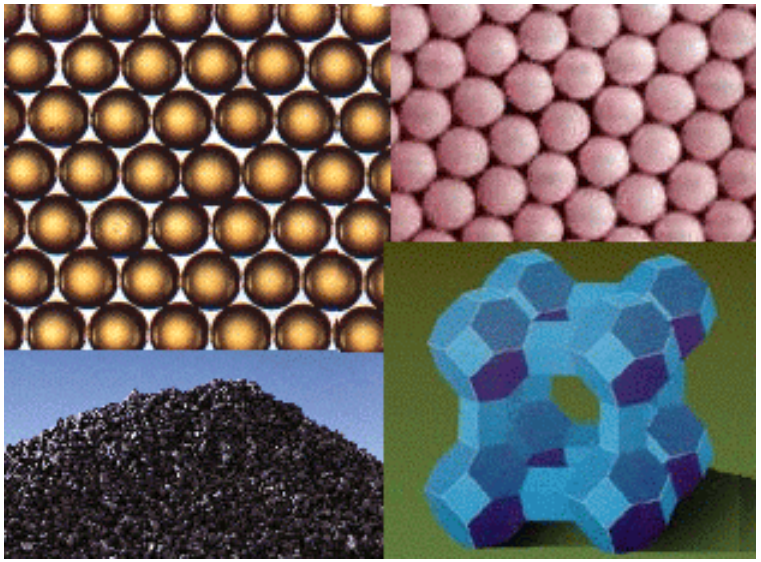
Selexol process

Existing SEWGS Sorbents

- Sorbents
  - Calcium-based (calcite, dolomite, huntite, etc.), silicates, zirconates, alumina, hydrotalcites, and their promoted forms
- Technical issues
  - Capacity and activity loss due to considerable sintering after multiple cycles
  - Low regeneration pressure or very high regeneration temperature
  - Low CO_2 capture level (<90%)

SEWGS Sorbents

- Desired properties of sorbents
  - Ability to recover high-quality heat during CO_2 adsorption
  - Regenerate sorbent at elevated pressure
  - Minimal deactivation over multiple cycles
  - High selectivity at high temperatures
  - High adsorption capacity
  - Acceptable thermal stability
  - Acceptable mechanical integrity



Technical Approach

Program Objectives

- Combine modeling and bench scale experiments to develop and characterize SEWGS sorbents and the SEWGS process
  - **UIUC/ISGS**
    - Thermodynamic and molecular modeling
    - Sorbent characterization, development, and screening with clean syn-gas
  - **URS**
    - Development of a bench scale sorbent testing facility
    - Sorbents will be tested in a synthetic syn-gas including impurities (e.g., H_2S)
    - Regeneration parameters and sorbent cycle-ability will be determined
  - **A techno-economic study will compare SEWGS to other CO_2 capture approaches**

Decision Tree

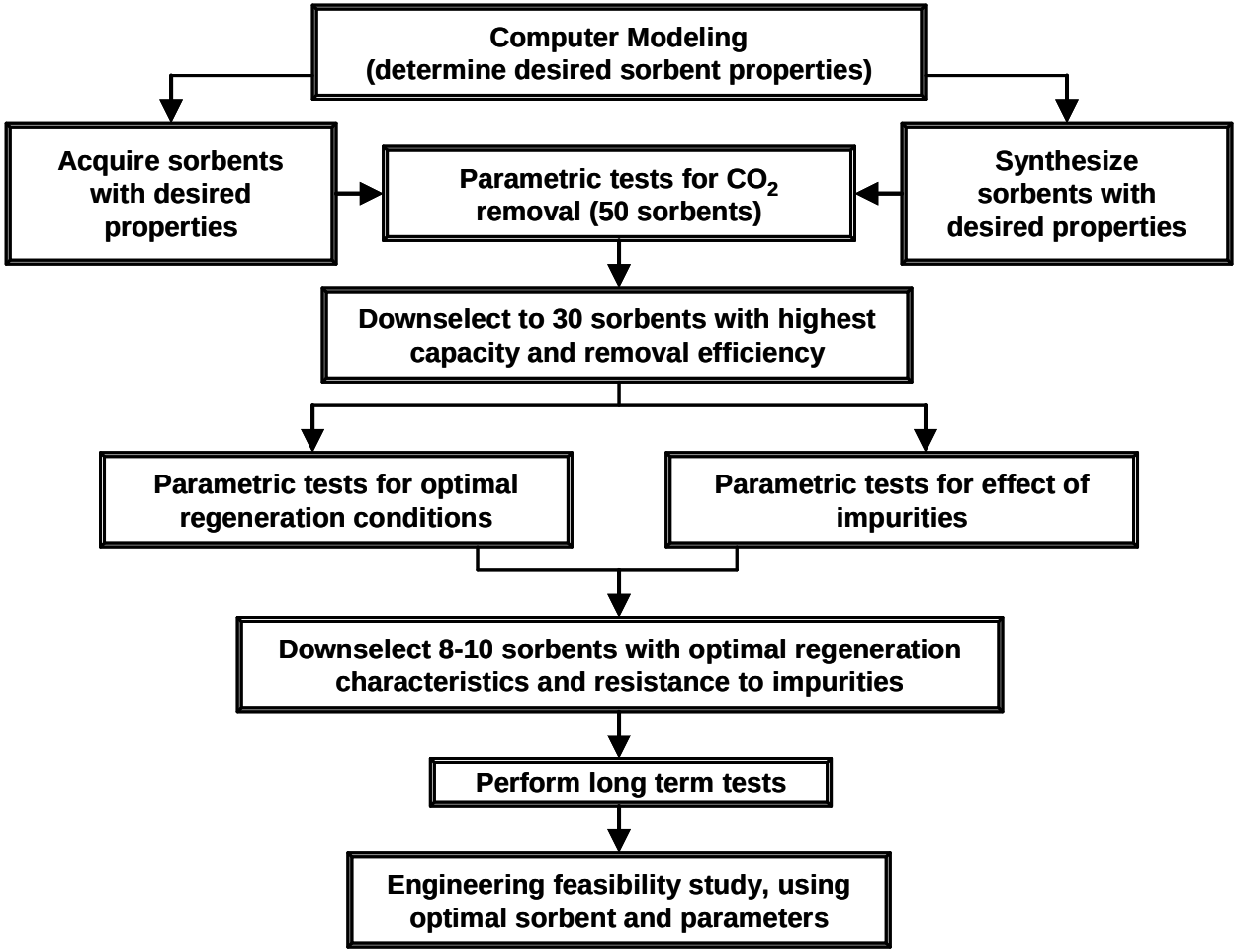
Modeling

Parametric Testing Phase I

Parametric Testing Phase II

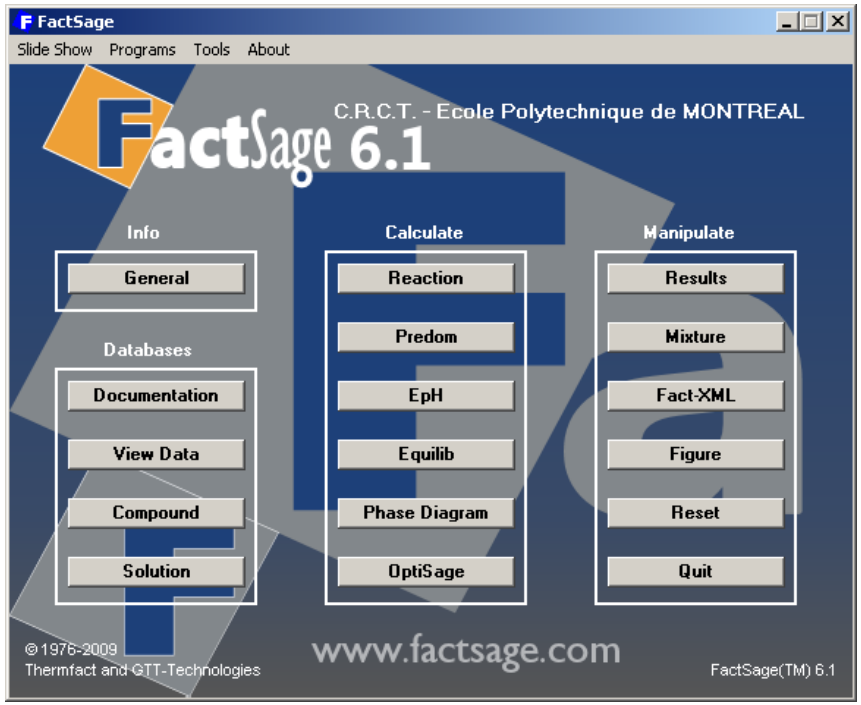
Long Term Test

Engineering Study



Sorbent Engineering Analysis and Selection (Task 2)

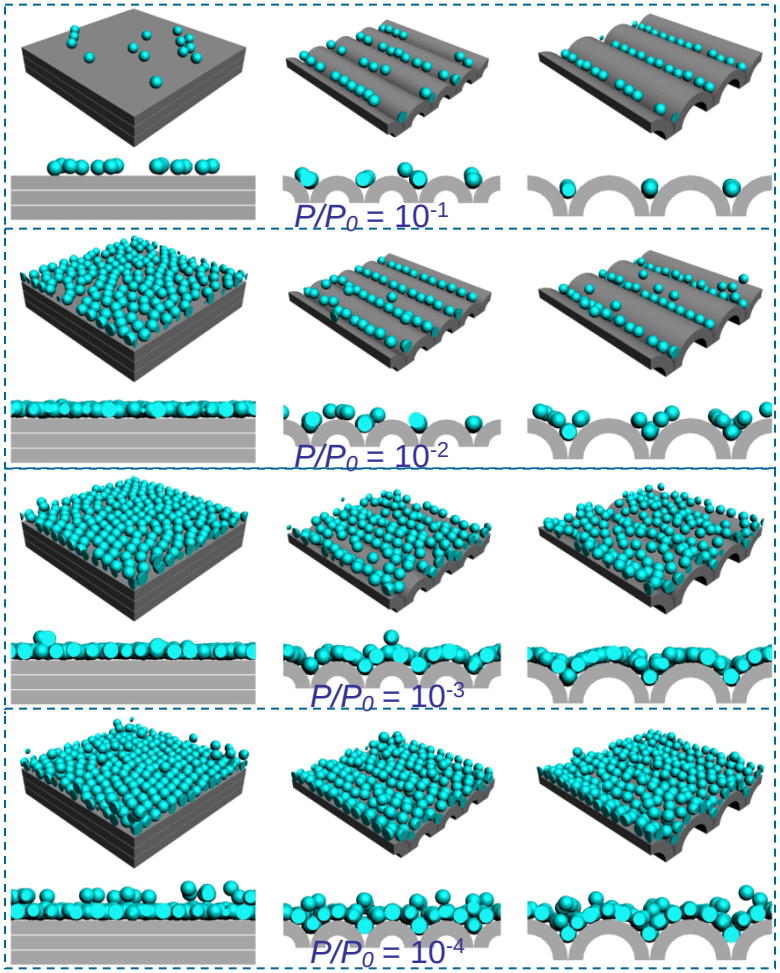
- Thermodynamic study
  - Develop phase equilibrium diagrams for potential sorbents (e.g. metal oxides/salts)
  - Identify optimum operating conditions for CO_2 capture
  - Impacts of syn-gas impurities
  - Identify promising sorbents



- Software
  - Fact-Sage software package
  - Databases of pure substances (~4,500) & solutions (150)

Sorbent Engineering Analysis and Selection (Task 2)

- **Molecular simulation**
  - Predict isotherms and properties
  - Predict kinetics/dynamics
  - Identify sorbents with desired properties
- **Approach**
  - Grand canonical Monte Carlo (GCMC) simulation
  - Integrated Kinetic Monte Carlo (KMC) and Molecular Dynamics (MD) simulation

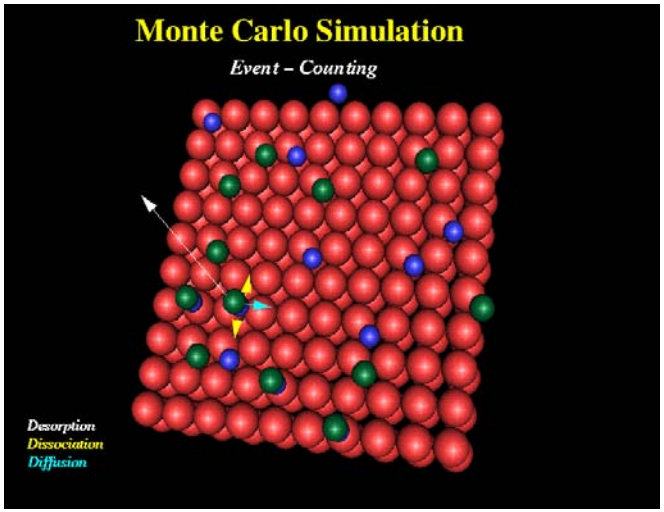


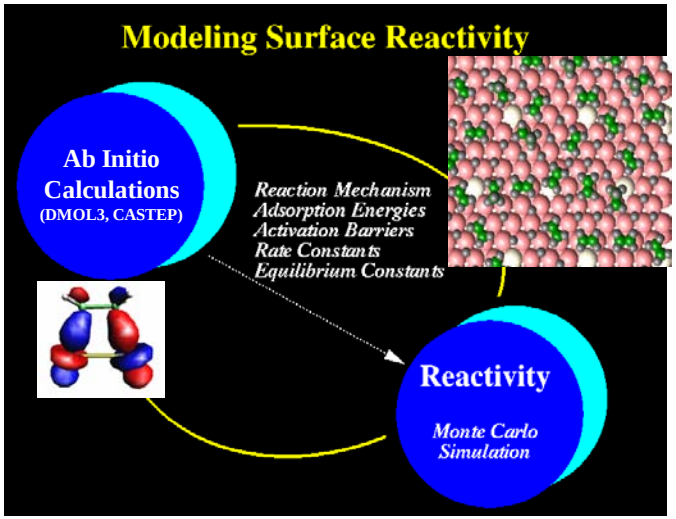
An example: GCMC simulation for adsorption on a carbon material

Rostam-Abadi et al., *LANGMUIR 2005, 21(3):896*

Sorbent Engineering Analysis and Selection (Task 2)

- **Software: Materials Studio**
  - Sorption, Adsorption Locator
    - Force field based Monte-Carlo approaches
    - Binding sites and energies in porous materials or on surfaces
    - Thermodynamic quantities
  - DMol^3, CASTEP, VAMP
    - Homogenous and heterogeneous reactions
    - Thermodynamics
    - Kinetics
  - Potential collaboration with Accelrys

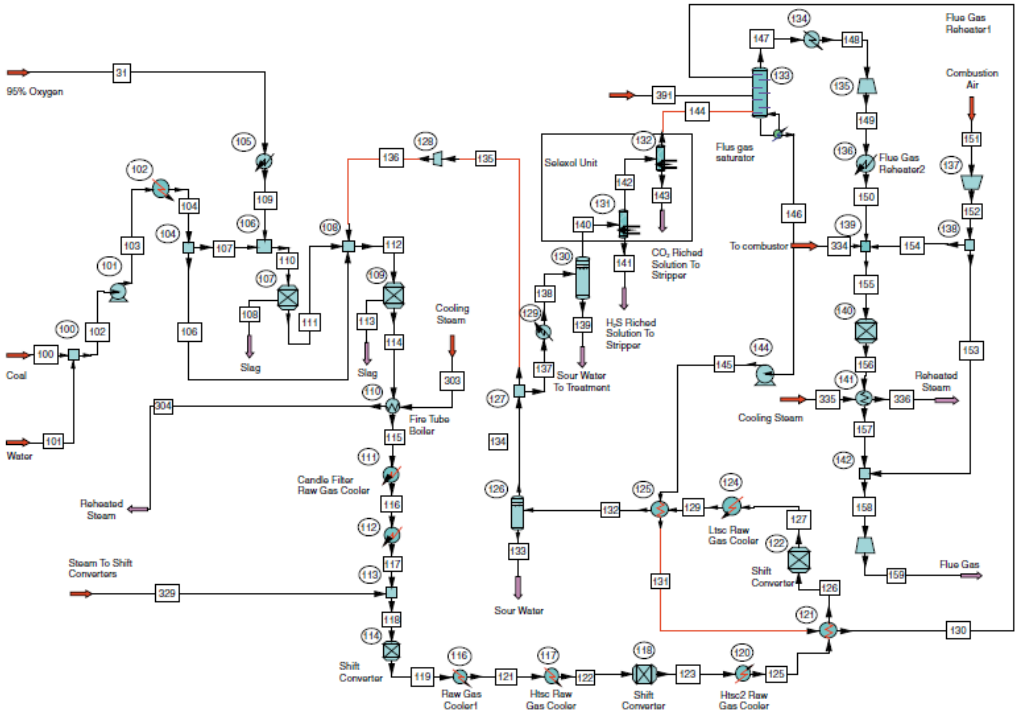




accelrys®

Sorbent Engineering Analysis and Selection (Task 2)

- **Process Simulation Analysis**
  - –Various process scenarios for heat integration between SEWGS and IGCC
  - –Process energy performance for individual sorbents
  - –high-performance, low-energy sorbents
- **Software**
  - –Chemcad or AspenPlus



IGCC process simulation using Chemcad

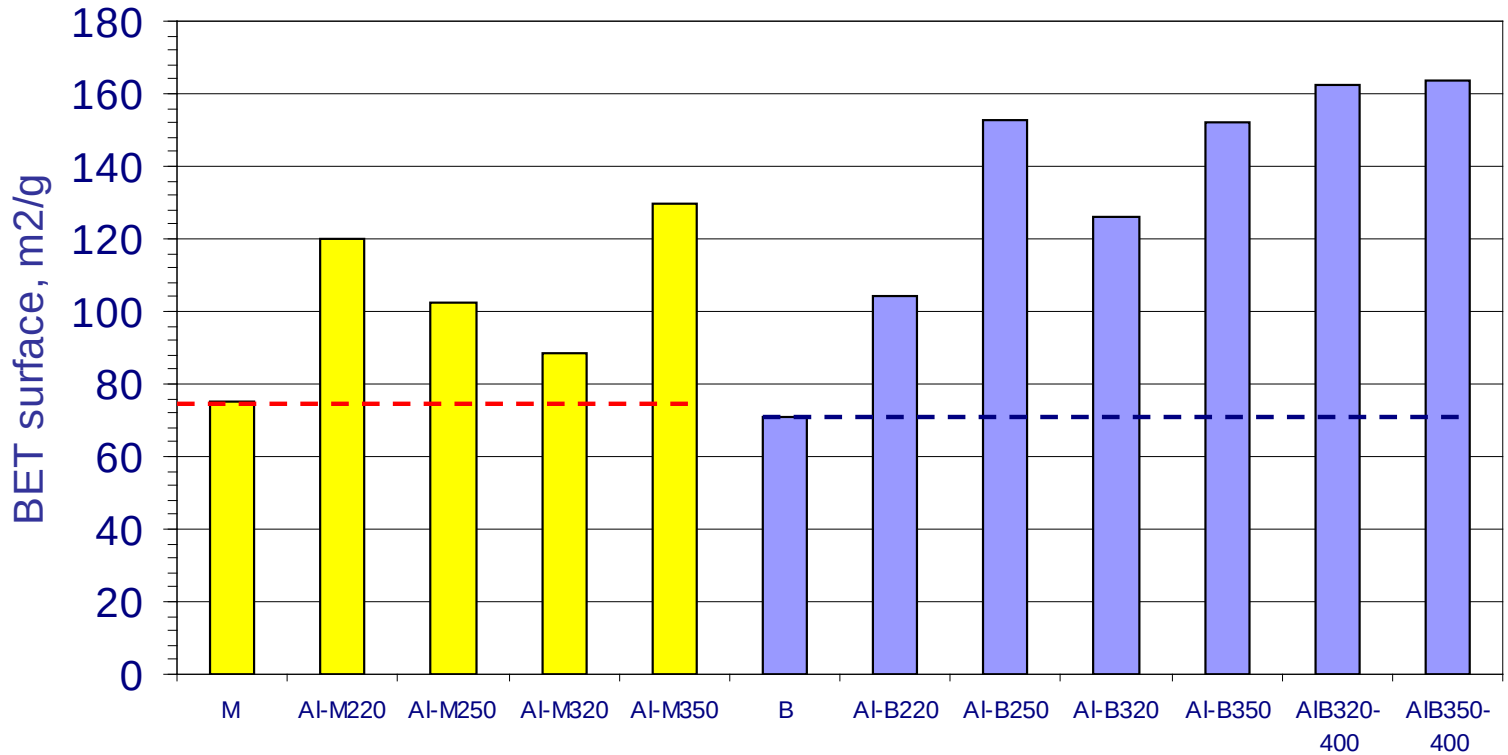
Lu et al, Topical report , Contract No: DE-FC26-03NT41994, 2005

Sorbent Procurement, Preparation and Characterization (Task 3)

- **Sorbent synthesis**
  - **Properties and chemical compositions guided by Task 2**
  - **Standard and proprietary procedures to prepare "smart" sorbents with desired pore structure, surface functionality, and composition**
  - **Various precursors**
    - ✓ **Calcium and magnesium aluminates**
    - ✓ **Clay-based materials**
    - ✓ **Metal oxides and salts**
    - ✓ **Adsorbent-shift catalyst hybrid**

Sorbent Procurement, Preparation and Characterization (Task 3)

- **Sorbent synthesis (clay-based materials)**
  - **Pillaring with various additives to increase SA**
  - **Depositing functionalities to increase CO_2 capacity**



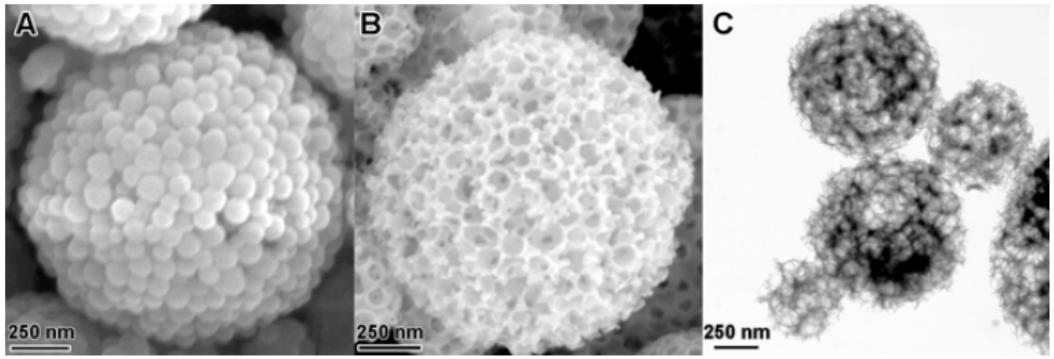
BET surface areas of bentonite and montmorillonite pillared with Al

Rostam-Abadi et al, EPRI report , 2005

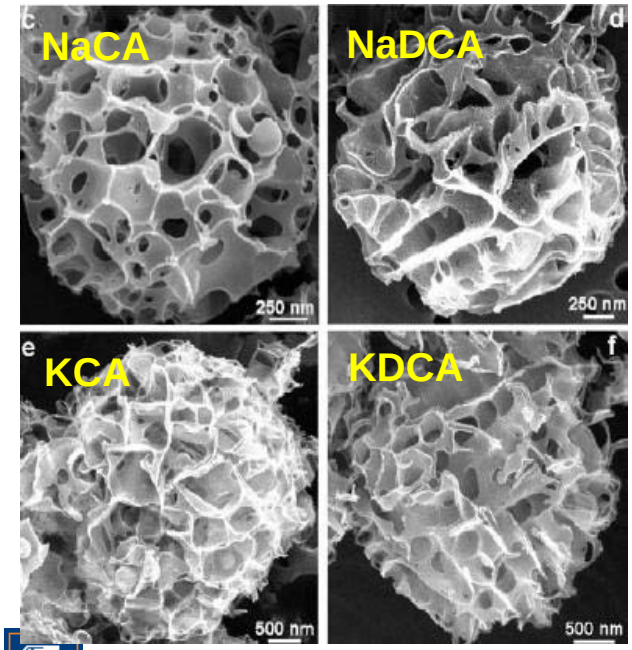
Sorbent Procurement, Preparation and Characterization (Task 3)

- **Sorbent synthesis**

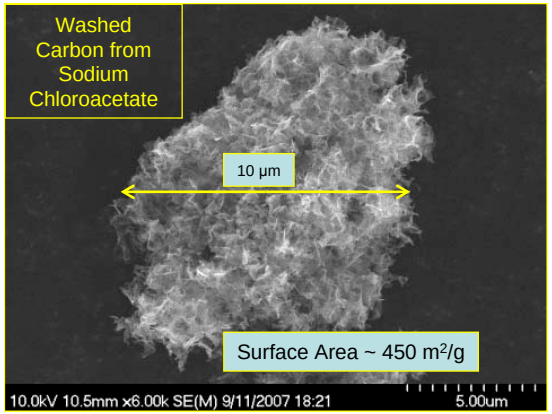
  (CO_2 sorbent-shift catalyst hybrid)
  - Novel sorbents prepared by Ultrasonic Spray Pyrolysis (USP)
  - Carbon and silica materials developed at INRS/UIUC



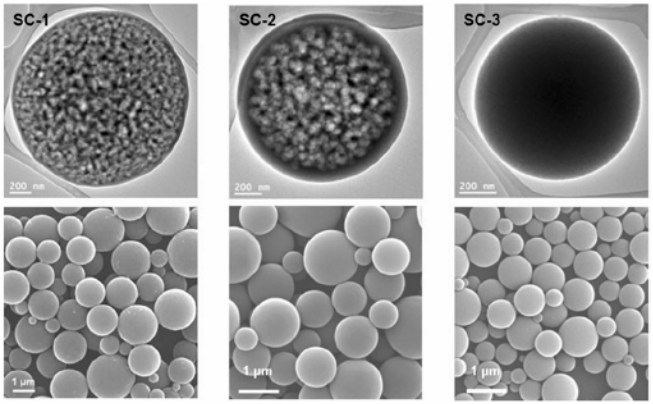
(a) MoS_2/SiO_2 composite. (b) SiO_2 leached (c) TEM of USP product with SiO_2 leached



Carbon from DCA/CA aerosol precursor



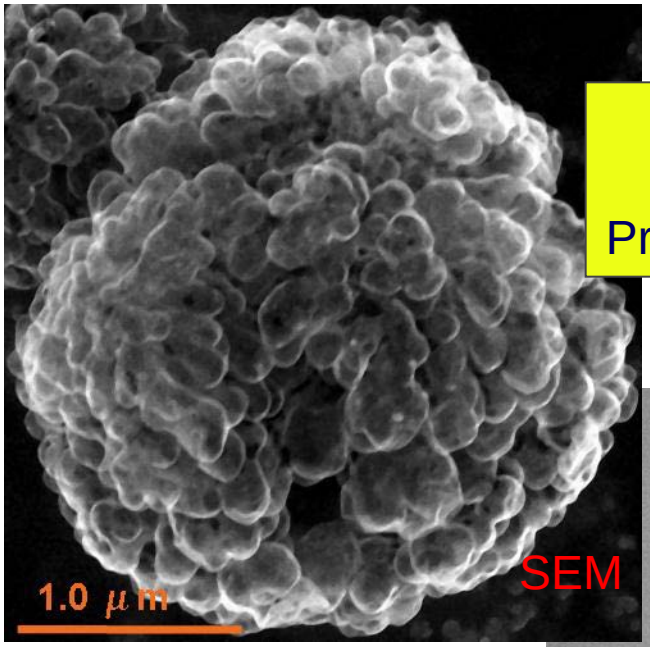
DCA powder precursor



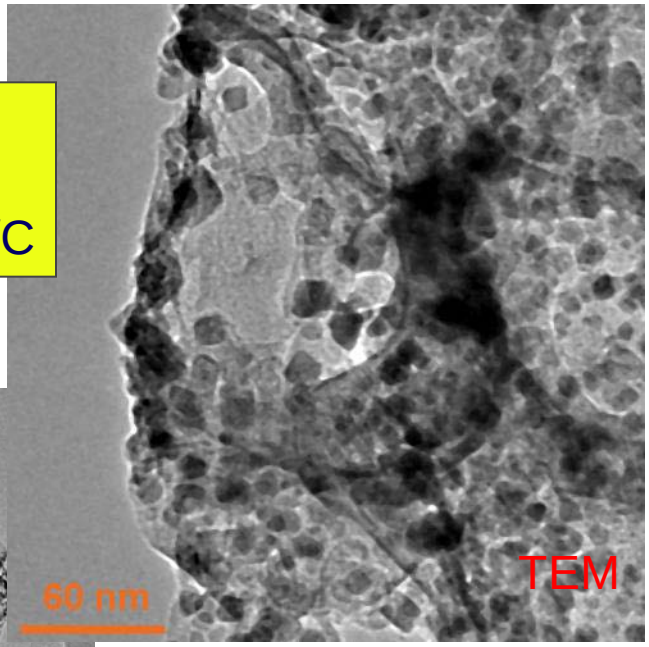
S/C aerosol precursor

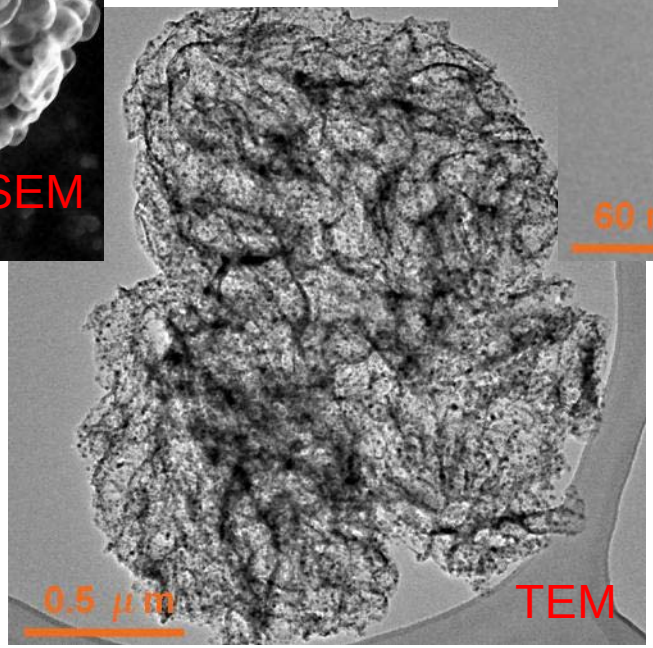
Sorbent Procurement, Preparation and Characterization (Task 3)

- Fe-Carbon Supported Catalyst developed at INRS/UIUC



T = 600 °C
Q = 0.5 SLPM
Precursor Fe = 8% Fe/C





Support's sphericity caused by aerosolizing precursor

1 μm < d_p < 3 μm

Overall iron content varies from 2 – 35% depending on processing conditions

Sorbent Procurement, Preparation and Characterization (Task 3)

- **Characterization**
  - Particle size, pore size distribution, surface area, active functional groups, chemical composition, etc.
  - SEM, TEM, XPS, XFS, Chemi-Physisorption, etc. at UIUC

RHK Ultrahigh Vacuum AFM

Kratos Axis ULTRA XPS

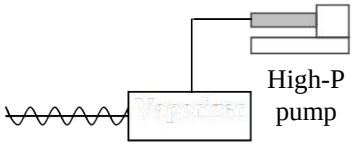
JEOL 2200 FS(S) TEM

Hitachi S 4800 SEM

Rigaku D-Max

Sorbent Screening (Task 4)

- **High temperature & pressure reactor (HTPR) system at INRS/UIUC**
  - **Double shell reactor**
  - **Maximum 300 psig and 950 °C**
  - **1’’ by 30’’ reactor tube**



Sorbent Screening (Task 4)

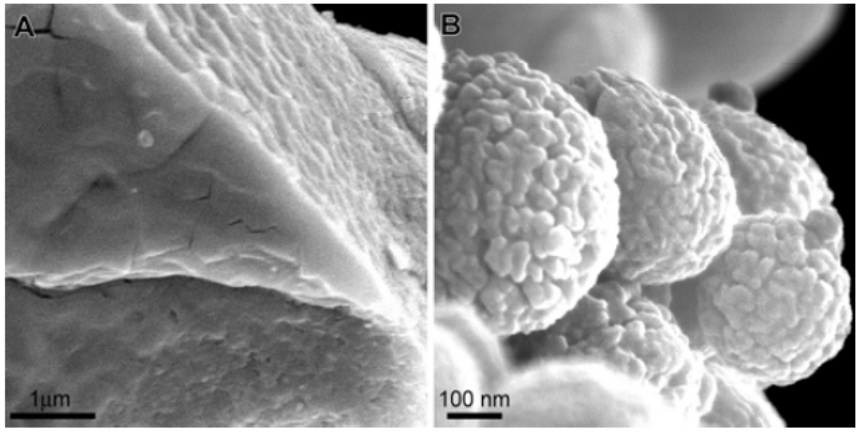
- **HTPR parametric testing (1)**
  - 200°-550 °C and P_{CO2}= 0.15-15 bar
  - Adsorption isotherms and breakthrough curves under CO_2/N_2
  - Sorbent tests using simulated syn-gas mixtures (CO,H_2O,CO_2,H_2)

Typical gas compositions at WGS inlet

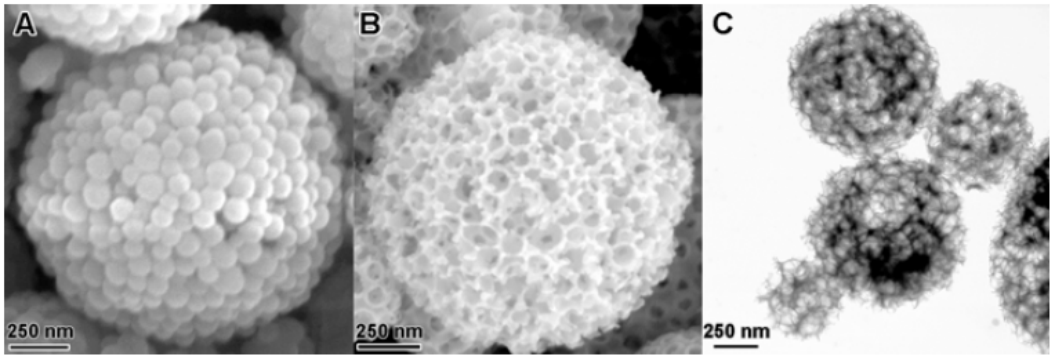
Gas Composition [mol%]	Dry-fed Gasification after Gas Cleaning (clean shift)	Dry-fed Gasification after Venturi scrubber (sour shift)	Slurry-fed Gasification after Venturi Scrubber (sour shift)
H_2	31.3	28.2	27.5
CO	60.5	54.5	38.4
H_2O	0.3	9.1	20.0
CO_2	2.9	3.8	12.0
CH_4	0.0	0.0	0.1
N_2	3.8	3.4	1.5
Ar	1.1	1.0	0.1
H_2S	0.001– 0.002	0.13	0.11
Temperature	40 ºC	180 ºC	210 ºC
Pressure [bar]	28	28	40

Sorbent Screening (Task 4)

- **HTPR parametric testing (2)**
  - **Sorbents mixed with commercial WGS catalysts**
  - **Sorbent-catalyst hybrid materials**
  - **Optimal operating conditions**



(a) conventional MoS_2;
(b) USP generated MoS_2-Silica spheres



USP generated MoS_2-Silica spheres

Suslick et al., In Material Syntheses: A Practical Guide, 2008, 83-88.

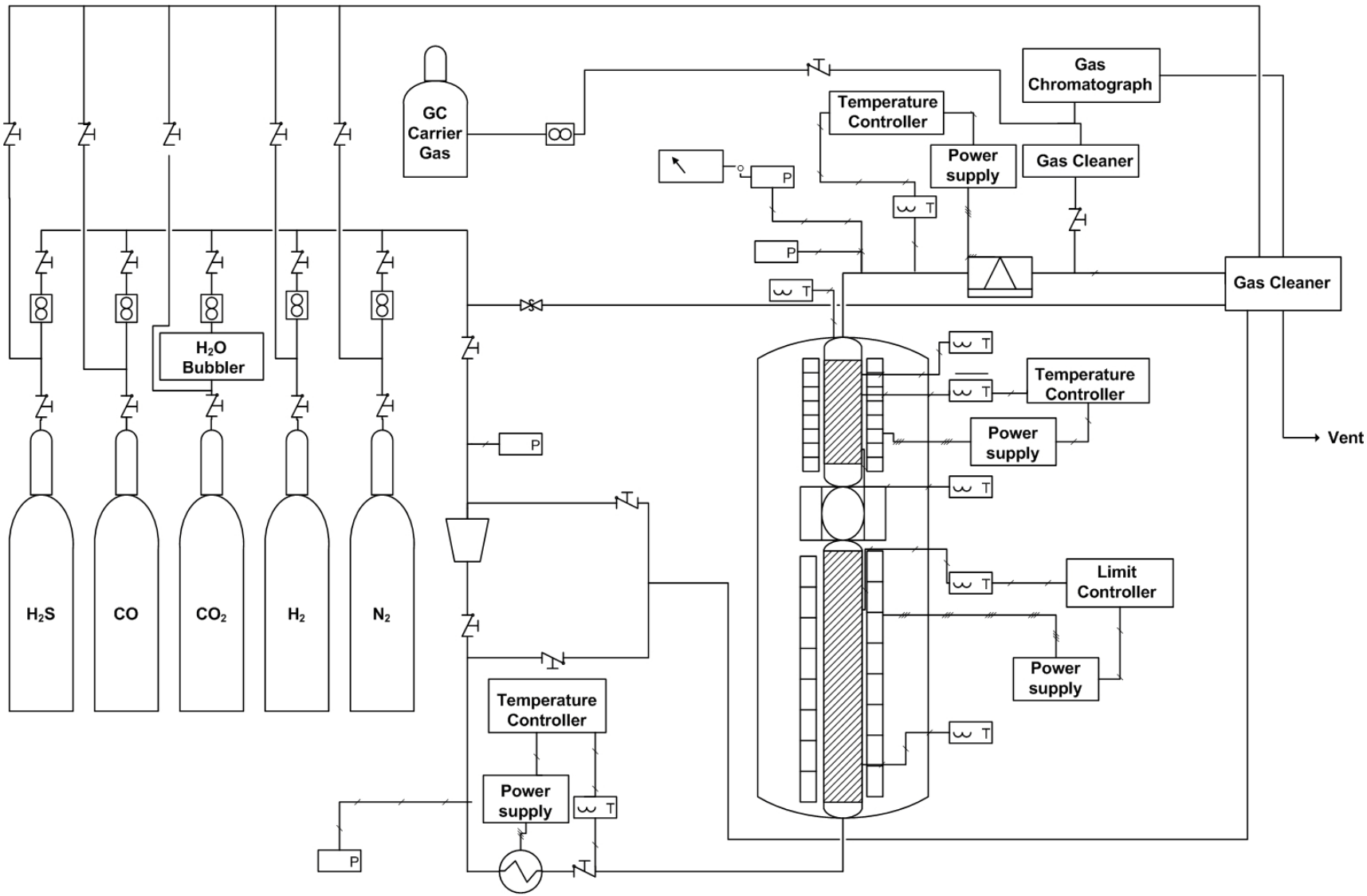
Sorbent Screening (Task 4)

- **High pressure TGA testing**
  - **Isotherm and kinetics data**
  - **Selected sorbents**
  - **TA TGA-HP 50 (725 psig and 800 °C)**

Impurities and Regeneration Testing (Task 4)

- URS will construct a high-pressure, high temperature reactor
  - **Designed to evaluate sorbent adsorption and regeneration performance**
    - **Adsorption in presence of syngas impurities**
  - **In-line GC will determine effluent CO_2 concentration to determine desorption kinetics and amount of CO_2 remaining**
  - **Laboratory space modified to be H&S compliant**
- 30 down-selected sorbents will be tested for:
  - **Evaluate sorbent resistance to syngas impurities**
  - **Determine optimal regeneration parameters**
- 8-10 further down-selected sorbents will be tested on a longer-term basis

URS Reactor and Testing System with Integrated Sorbent Regeneration Capabilities (Task 4)



Impurity Sorbent Testing (Task 4)

- Determine the effect of syngas impurities on sorbent CO_2 removal and capacity
  - **Series of parametric tests**
  - **CO_2 breakthrough curves**
- Impact of single impurities as well as multiple impurities added to the baseline syngas will be determined

Impurity Concentration Ranges for Parametric Tests

Impurity	Concentration Range (mol %)
H_2S	0.1 – 0.6
COS	0 – 0.1
CH_4	0 – 0.6
NH_3	0 – 0.1
HCl	0 – 0.1

Regeneration Sorbent Testing (Task 4)

- Tests conducted on sorbents resistant to impurities
- Regeneration conditions primary variables:
  - **100°-200ºC above CO_2 adsorption conditions, and**
  - **1-5 bars below CO_2 adsorption conditions**
- Parametric tests to determine optimal conditions for selected sorbents
  - **Target: >75% CO_2 desorbed**
- 8-10 sorbents will be subjected to longer term tests
  - **Continuous operation over 1-2 week period (500 – 1000 cycles)**
  - **Multiple adsorption/regeneration cycles**
  - **Target: maintain >90% removal, >75% desorption of CO_2**
  - **Characterize physical integrity of sorbents**

Engineering Feasibility Study (Task 5)

- Lab results will be used to perform techno-economic study
- Included parameters
  - **Cost of >90% removal (COE, O&M)**
  - **Sorbent costs**
    - **Anticipated lifetime (i.e., replacement rate)**
    - **Estimated future market costs of precursor materials**
    - **Handling equipment**
  - **Sorbent regeneration costs**
  - **Heat/energy integration**
  - **Compression costs with SEWGS**
  - **Unit footprint and capital costs**
  - **Scalability**

Engineering Feasibility Study (Task 5)

- Comparison made to base WGS operation and other CO_2 removal strategies
- If feasible, an addendum study will prepare a preliminary design for a pilot system that can be tested at a future IGCC site

Project Schedule

Project Schedule

Month	N	D	J	F	M	A	M	J	J	A	S	O	N	D	J	F	M	A	M	J	J	A	S	O	N	D	J	F	M	A	M	J	J
Year	09	09	10	10	10	10	10	10	10	10	10	10	10	10	11	11	11	11	11	11	11	11	11	11	11	11	12	12	12	12	12	12	12
Months After Contract Award			1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30	31
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4.4 Analytical Characterization																																	
4.5 Sorbent Model Development																																	
Task 5: Engineering Feasibility Study																																	
5.1 Techno-economic Analysis of Technology																																	
5.2 Scale-up Test Design																																	

Period of Performance

Jan 1, 2010 to Dec 31, 2012

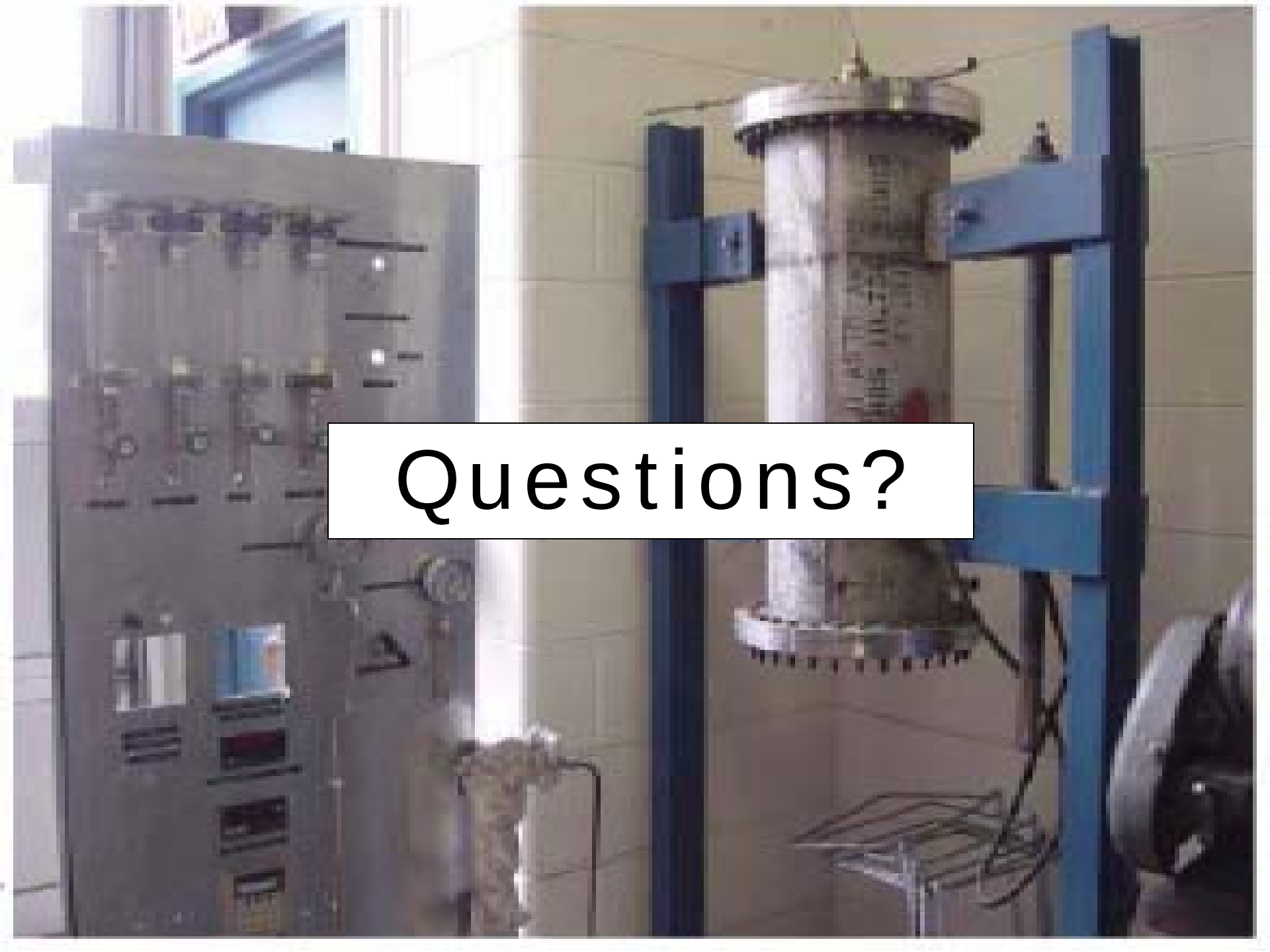
Project Milestones and Deliverables

Project Milestones

Milestones	Quarter Due Date
DOE Project Kickoff Meeting	Q1 FY2010
Project Test Plan Submittal	Q2 FY2010
Begin Sorbent Synthesis	Q3 FY 2010
DOE Contractor's Meeting	Q3 FY 2010
Process Simulation Complete	Q4 FY 2010
Begin HTPR Parametric Tests	Q4 FY 2010
Begin Syngas Impurity Tests	Q3 FY 2011
Begin Sorbent Regeneration Parametric Tests	Q3 FY 2011
DOE Contractor's Meeting	Q3 FY 2011
Begin Long-term Sorbent Regeneration Tests	Q4 FY 2011
Complete Techno-economic Analysis	Q2 FY 2012
DOE Contractor's Meeting	Q3 FY 2012
Final Report	Q3 FY 2012

Project Deliverables

- **Project Management Plan**
- **Test Plan**
  - **Includes Health and Safety Procedures**
- **QA/QC Plan**
- **Quarterly progress reports**
- **Final technical report**
  - **Summary of all development, analysis, testing, design and economic analysis**
- **Other reports**
  - **Financial, property, annual renewal, and close-out reporting, as defined in contract**


Questions?