Evaluation of Dry Sorbent Technology for Pre-Combustion CO_2 Capture

(FE-0000465)

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URS Group

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Project Objectives and Scope of Work

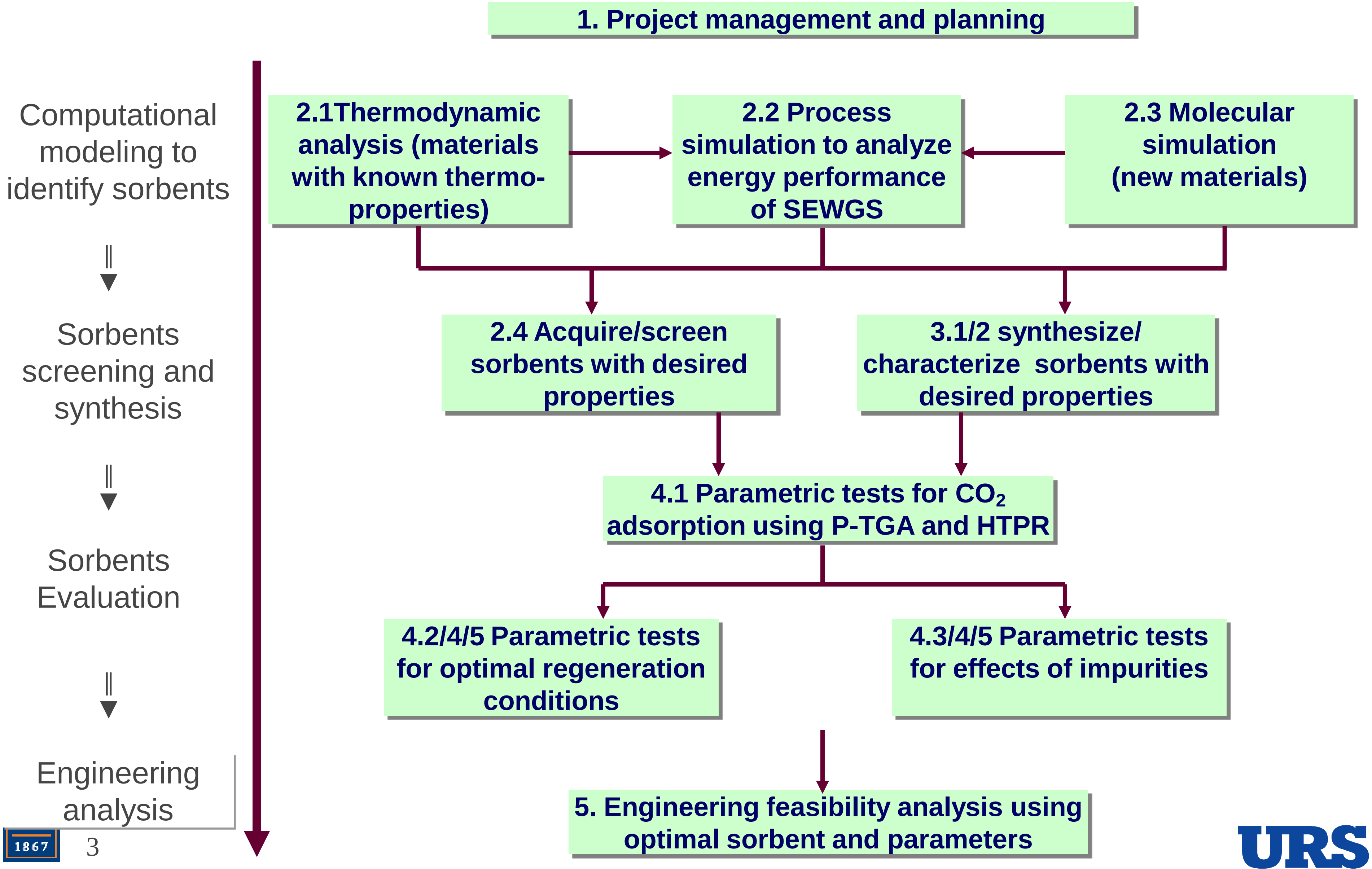
Objective

- **Identify, develop, and optimize engineered sorbents for a process that combines CO_2 capture with the water gas-shift (WGS) reaction**

Scope of Work

- **Thermodynamic, molecular and process simulation modeling to identify/predict optimal sorbent properties and process operating conditions**
- **Synthesis and characterization of sorbents**
- **Experimental evaluation of sorbents for CO_2 adsorption and regeneration**
- **Techno-economic analysis**

Research Tasks



Computational modeling to identify sorbents

Sorbents screening and synthesis

Sorbents Evaluation

Engineering analysis

1. Project management and planning

2.1Thermodynamic analysis (materials with known thermo-properties)

2.2 Process simulation to analyze energy performance of SEWGS

2.3 Molecular simulation (new materials)

2.4 Acquire/screen sorbents with desired properties

3.1/2 synthesize/ characterize sorbents with desired properties

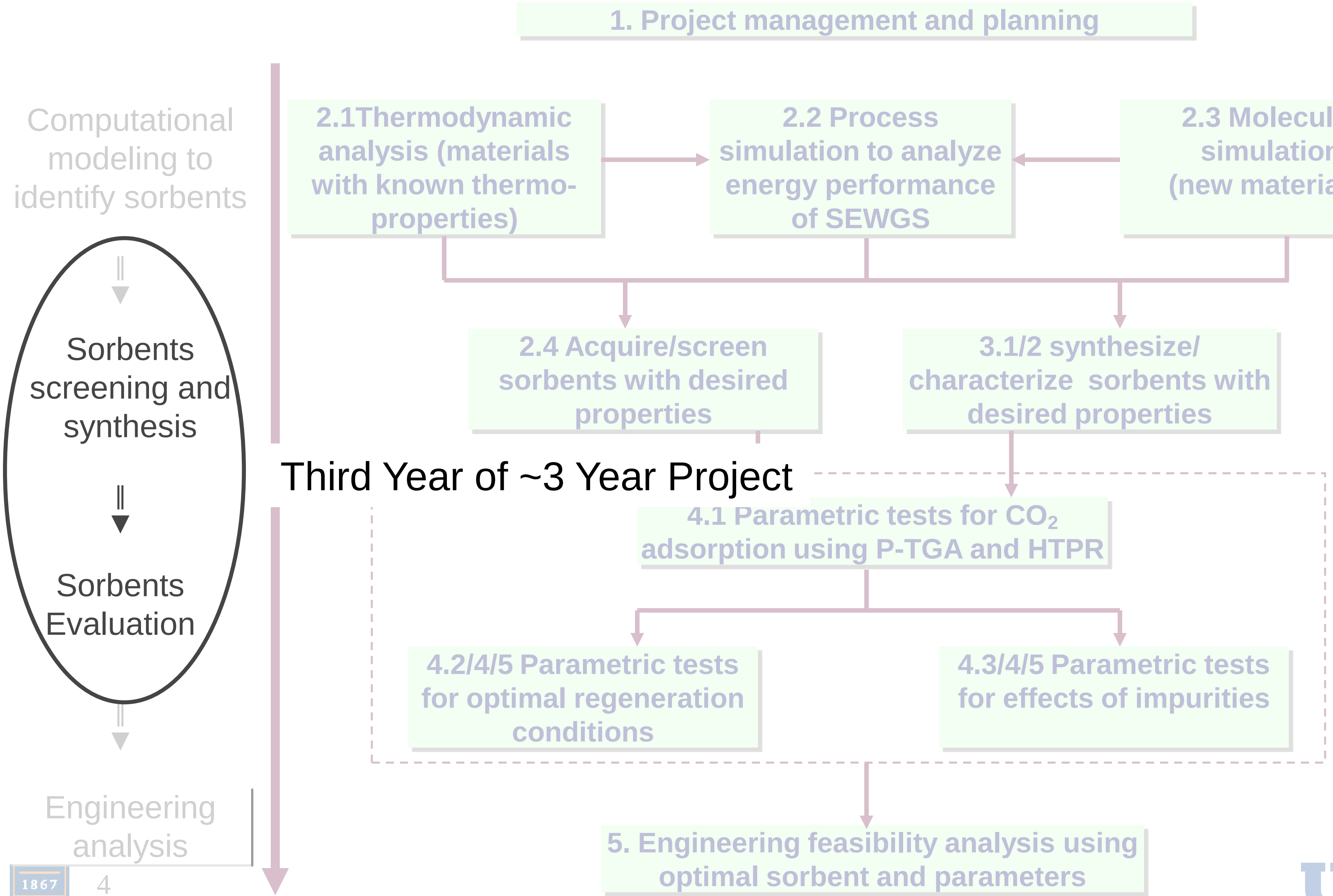
4.1 Parametric tests for CO_2 adsorption using P-TGA and HTPR

4.2/4/5 Parametric tests for optimal regeneration conditions

4.3/4/5 Parametric tests for effects of impurities

5. Engineering feasibility analysis using optimal sorbent and parameters

Research Tasks



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Third Year of ~3 Year Project

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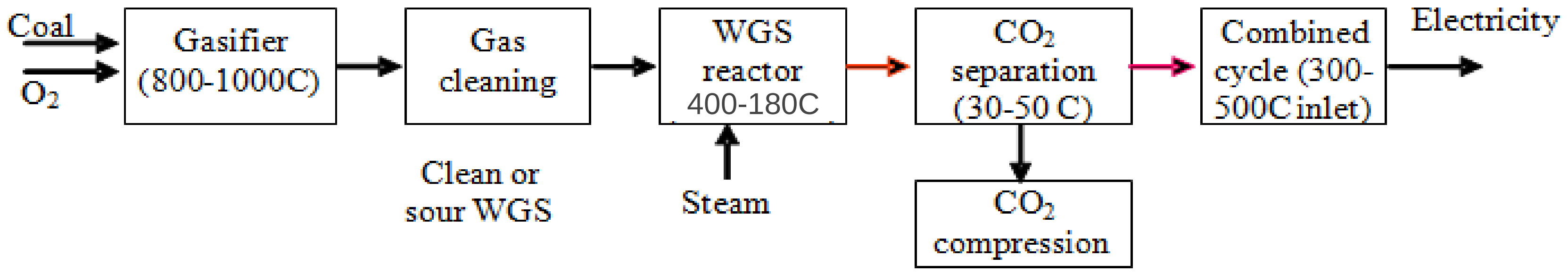
Technology Fundamentals/Background

IGCC + SEWGS vs. Conventional IGCC

$CO + H_2O = CO_2 + H_2$

- Exothermic reaction
- Kinetically limited at low temperatures, multiple stages / temperatures required
- SEWGS can achieve high CO conversion at high temperature



Coal

O_2

Gasifier (800-1000C)

Gas cleaning

Clean or sour WGS

WGS reactor 400-180C

Steam

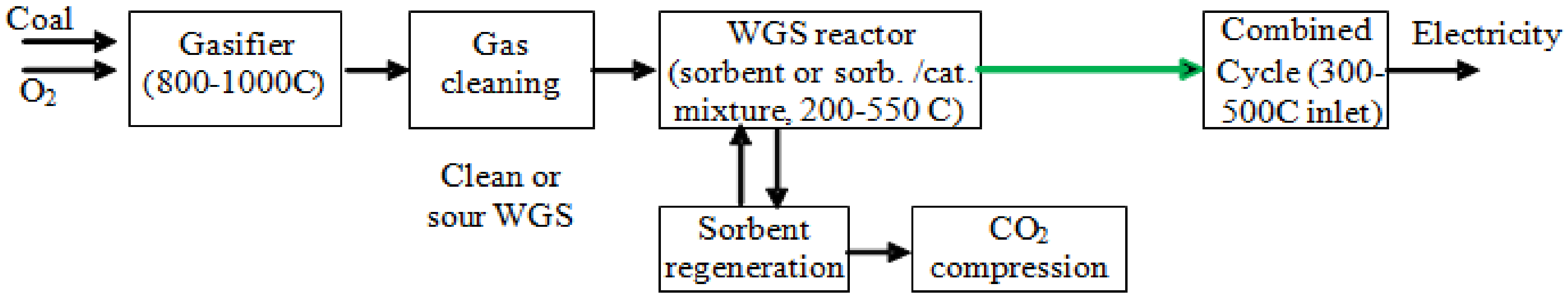
CO_2 separation (30-50 C)

CO_2 compression

Combined cycle (300-500C inlet)

Electricity

Conventional CO_2 capture



Coal

O_2

Gasifier (800-1000C)

Gas cleaning

Clean or sour WGS

WGS reactor (sorbent or sorb. /cat. mixture, 200-550 C)

Sorbent regeneration

CO_2 compression

Combined Cycle (300-500C inlet)

Electricity

SEWGS

IGCC-SEWGS Advantages

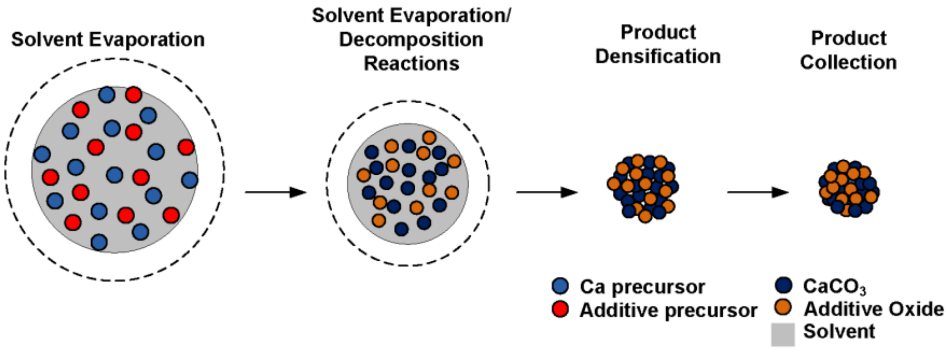
- High CO conversion with reduced steam addition
- No or limited WGS catalyst use
- High quality heat usable for generating high quality steam
- Limited gas cooling/reheating requirement downstream
- No separate CO_2 capture unit required
- Sorbents are key, an ideal sorbent:
    - High capacity, selective
    - Adsorb at T > 300 C
    - Regenerate at P > 1 bar
    - Minimal deactivation
    - Thermally and mechanically stable

Progress and Current Status

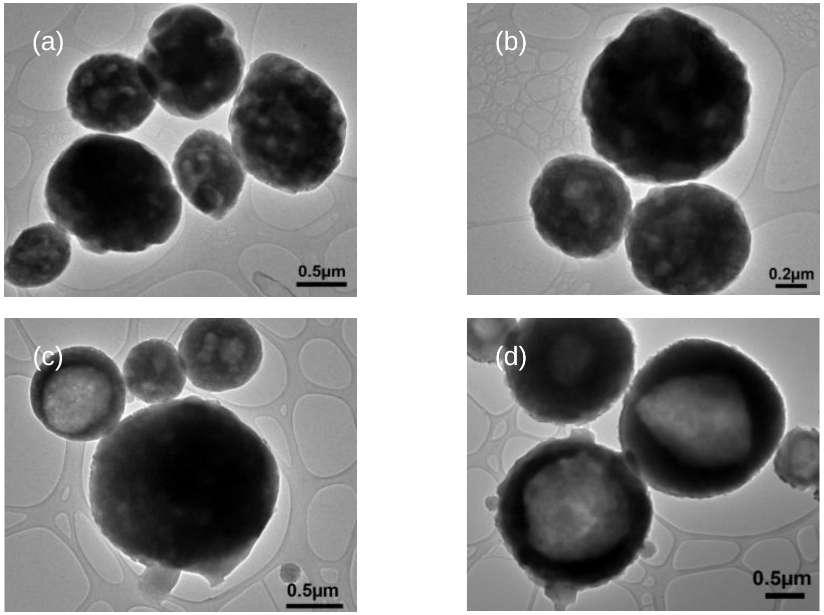
Current Status Overview

- Computational Modeling
  - Thermodynamic Modeling: down-selected from 40+ to 7 ‘optimal’ sorbents
  - Process Simulations: mass and energy balance comparison for SEWGS vs conventional WGS / CO_2 capture, focused on 7 ‘optimal’ sorbents
  - Molecular Simulations: investigated morphology, sintering, dopants, impurities
- Sorbent Preparation
  - Ultrasonic Spray Pyrolysis: added ESP for capture, hollow structures
  - Flame Spray Pyrolysis: high surface area, scalable
  - Molecular Alloying: energetic synthesis process
- Sorbent Evaluation
  - Analytical Characterization: SEM, TEM, etc
  - TGA: workhorse screening technique, studies at relevant P_{CO2}
  - High Temperature, High Pressure Reactor Studies: laboratory simulated, closest to real world conditions short of pilot studies
- Techno-Economic Study

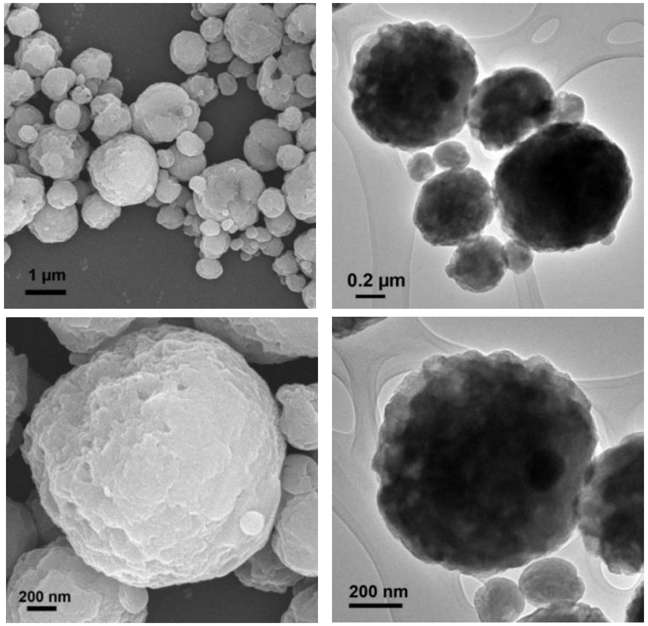
Task 3: USP Sorbents



Mechanism of formation of USP sorbents



Zirconia (ZrO_2)-doped $CaCO_3$ (a) with (wt)= 95:5 wt% CaO: $CaZrO_3$; (b) 90:10, (c) 80:20, (d) 66:34



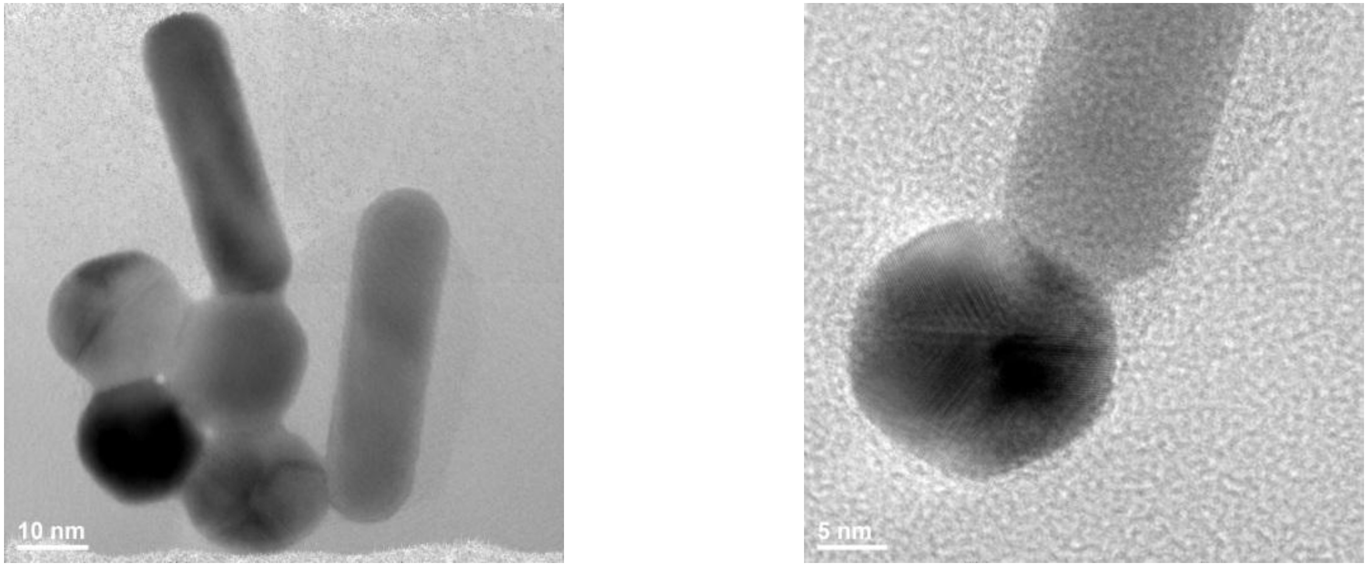
Yttrium oxide (Y_2O_3)-doped $CaCO_3$

(20:80 wt% Y_2O_3:CaO)

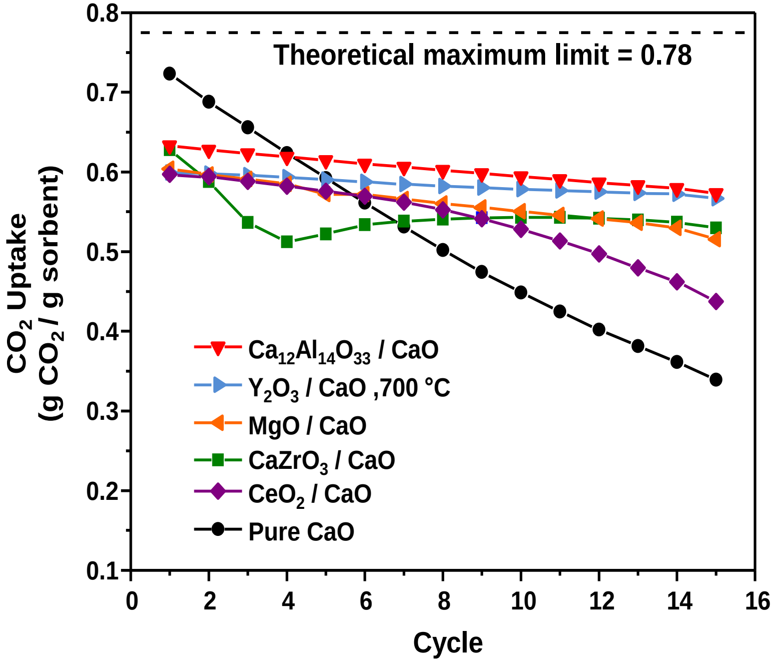
Task 3: FSP Sorbents Synthesized

- Non-porous, FSP nanoparticle sorbents (>20 sorbents)
  - CaO, ZrO_2/CaO, MgO, MgO/CaO, ZrO_2/MgO
- Synthesized at different conditions (composition, precursor type, precursor/solvent ratio, gas flow, etc)

FSP sorbent	BET surface area, m^2/g	d_{BET}, nm
CaO	54	33
ZrO_2/CaO (1:10)	43	40
ZrO_2/CaO (1:1)	21	71
MgO/CaO (1:10)	28	64



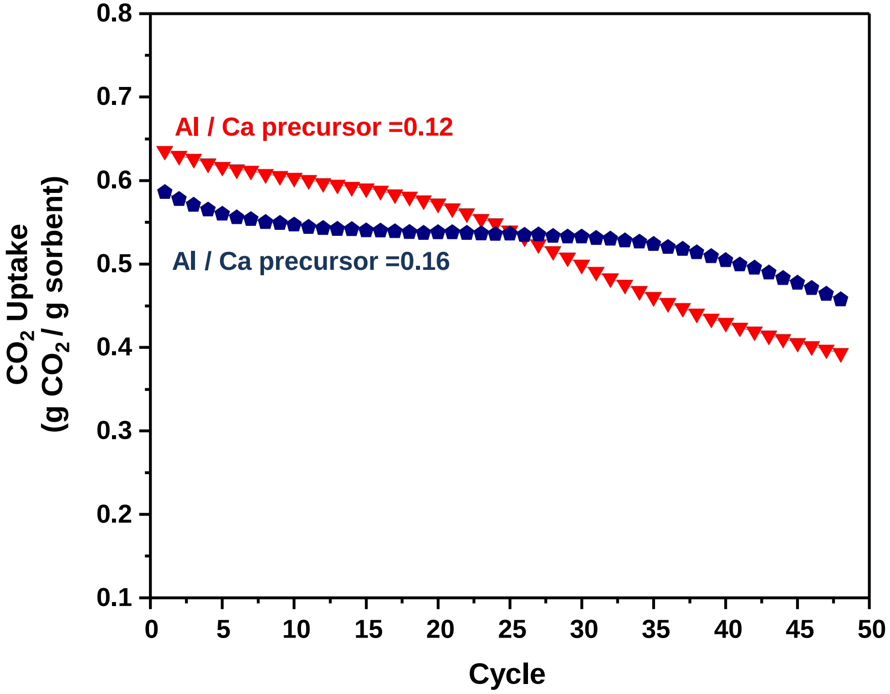
Task 4: 15-Cycle CO_2 Adsorption Performance of USP Sorbents

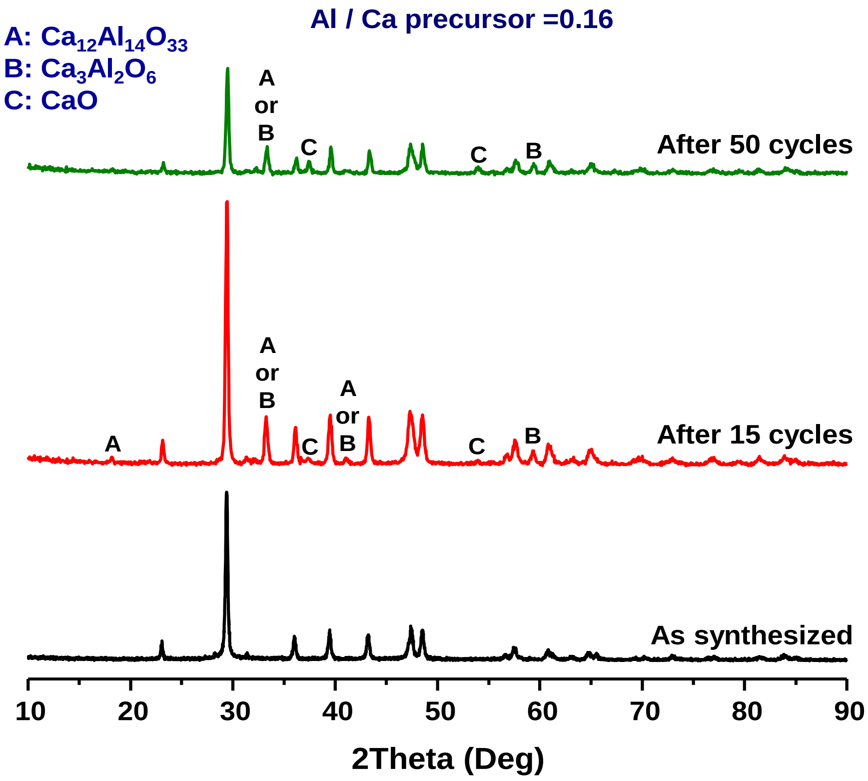


Carbonation at 650 °C for 30 min in CO_2 and calcination at 900 °C for 5 min in N_2

- Reagent grade $CaCO_3$ degraded quickly
- Al, Zr, Y, Mg doped $CaCO_3$ composite sorbents were significantly more stable than pure $CaCO_3$

Task 4: 50-Cycle CO_2 Adsorption Performance of USP Sorbents

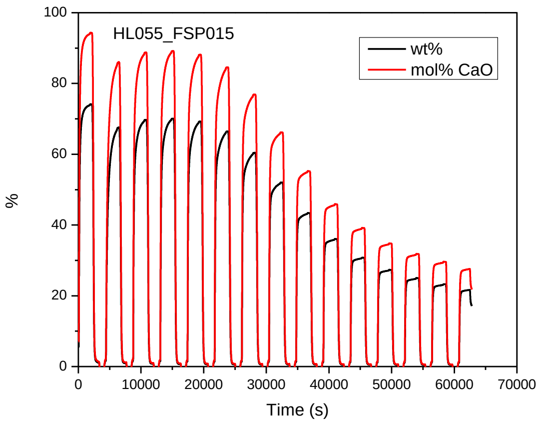




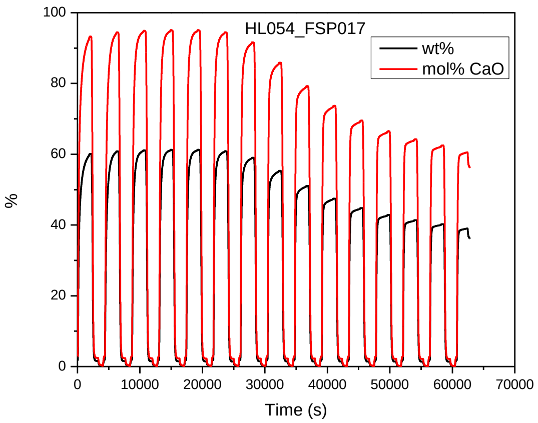
- Increasing Al/Ca weight ratio in sorbent improved performance
- Sorbent stability needs to be tested in longer term cycling

Task 4: Multi-Cyclic CO_2 Adsorption Performance of FSP Sorbents

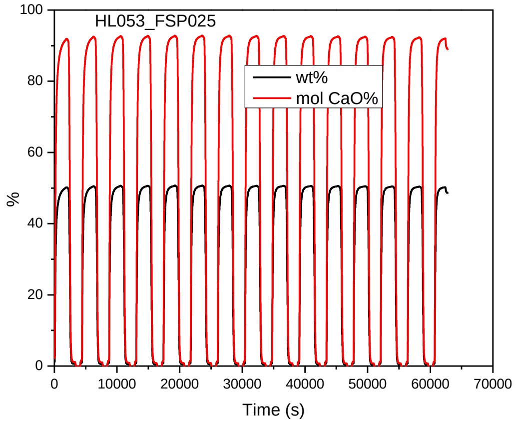
	0 Zr/Ca		0.1 Zr/Ca		0.2 Zr/Ca	
	CO_2 uptake g/g sorbent	CaO molar conv. %	CO_2 uptake g/ g sorbent	CaO molar conv. %	CO_2 uptake g/ g sorbent	CaO molar conv. %
1st cycle	0.74	94	0.60	93	0.50	91
15th cycle	0.21	27	0.39	60	0.50	91



Sorbent with 0 Zr/Ca



Sorbent with 0.1 Zr/Ca

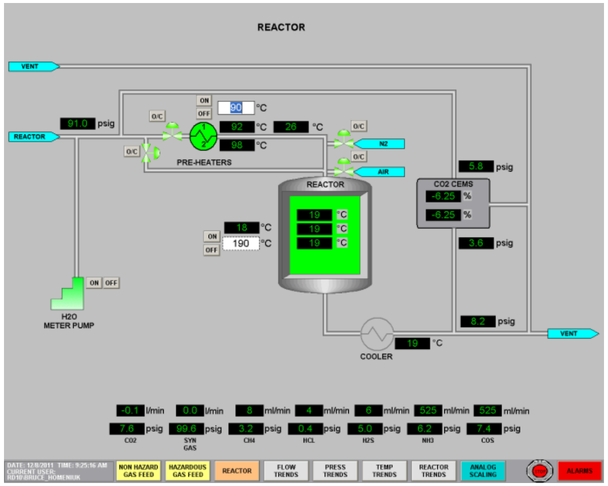


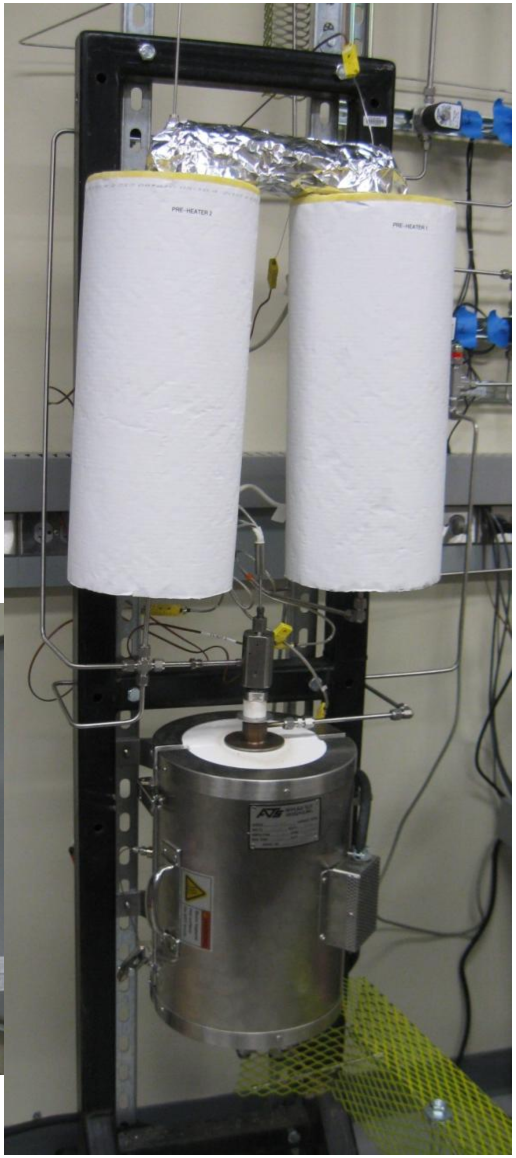
Sorbent with 0.2 Zr/Ca

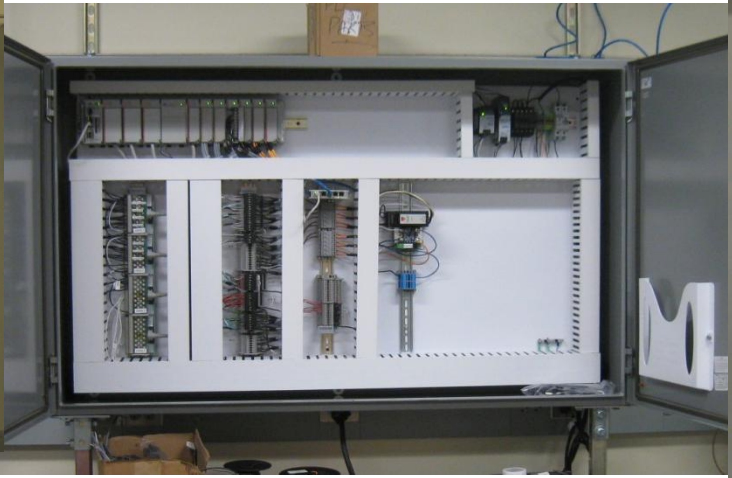
Carbonation and calcination of FSP sorbents

(Black curves: % weight change (g CO_2/g sorbent), red curves: % CaO molar conversion

Task 4: High Temperature, High Pressure Reactor Studies

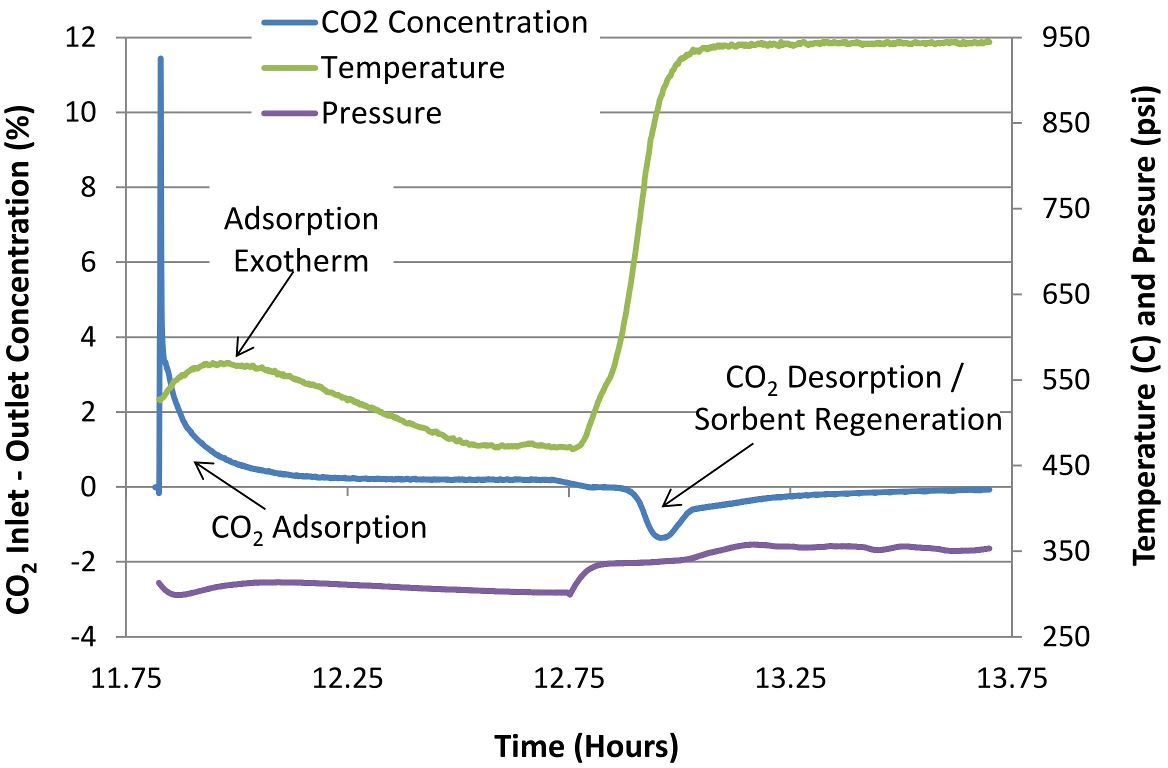






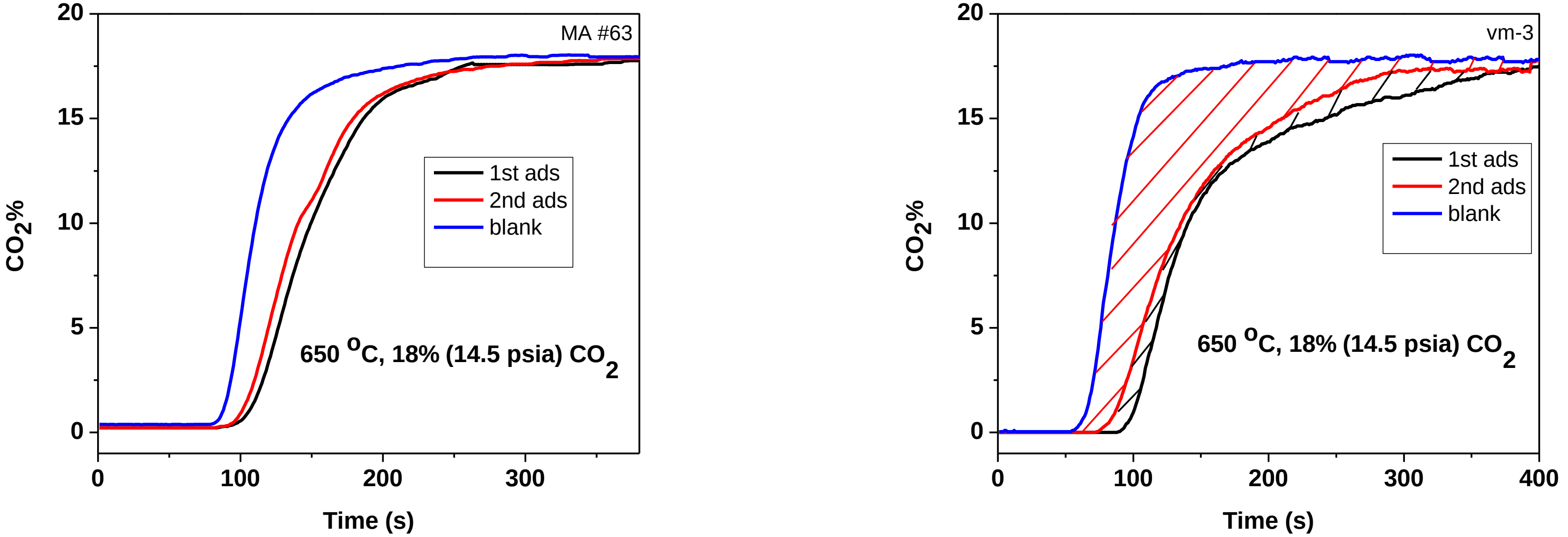
Systems capable of 1000 C, 10 bar & 650 C, 40 bar with corrosive / toxic impurities (e.g., NH_3, H_2S)

Task 4: Sorbent Testing in HTPR



- vm-3: 53:44 wt% calcite: dolomite, natural limestone
- CO$_2$ (8%) in N$_2$, 300 psi and 500 C
- Regeneration in pure N$_2$, temperature swing
- Adsorption exotherm evident

Task 4: Sorbent Testing in HTPR



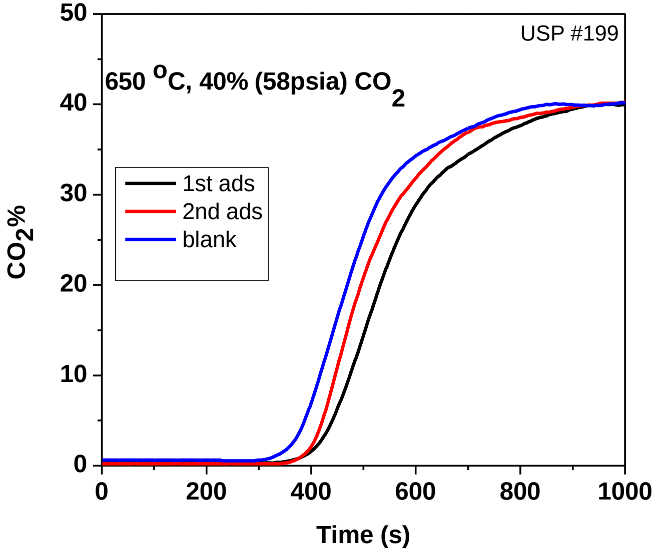
Samples	MA #63	vm-3
Capacity of 2nd cycle: capacity of 1st cycle	83%	80%

Sample MA #63: 77:23 wt% CaO: MgO (mechanical alloying method)

Sample vm-3: 53:44 wt% calcite: dolomite (natural limestone)

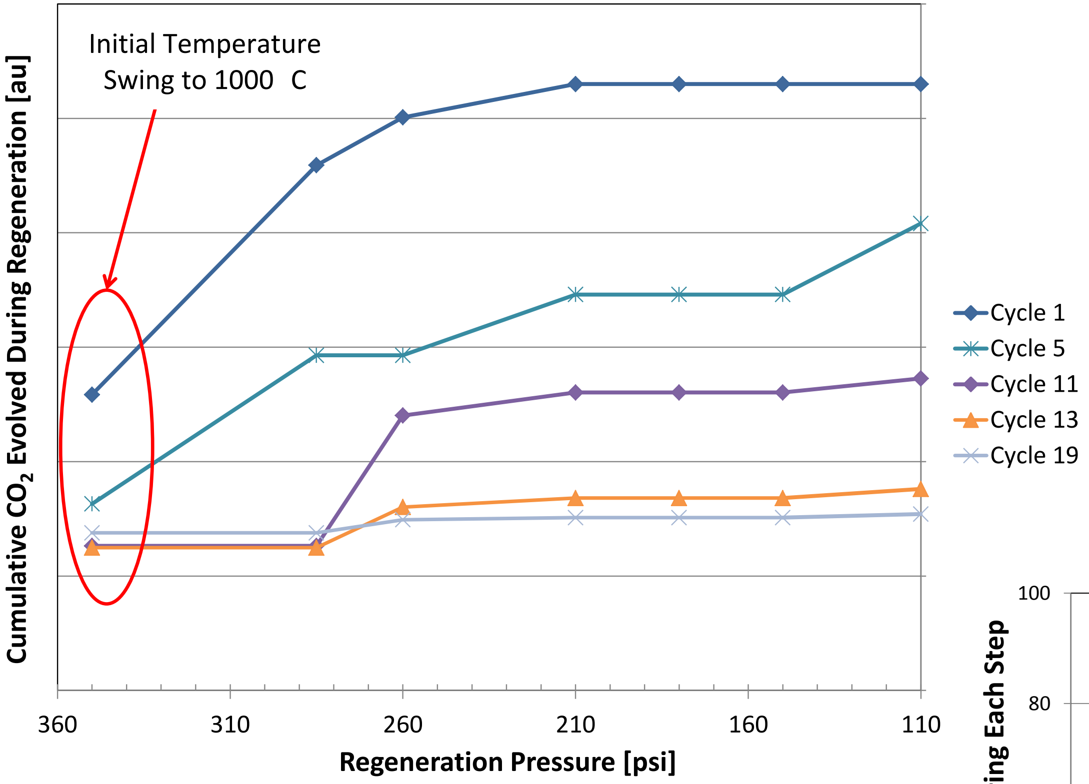
Sorbent Tests for CO_2 Adsorption at P_{CO2}= 58 psia (4 bar) and T = 650°C

Capacity of samples	USP#199 75:25 wt% CaO:meyenite	MA#63 77:23 wt% CaO:MgO	vm-3 53:44 wt% calcite:dolomite
1st cycle, g-CO_2/g-sorbent	0.67	0.45	0.45
2nd cycle, g-CO_2/g-sorbent	0.33	0.20	0.12
Ratio of 2nd cycle : 1st cycle	50%	44%	26%

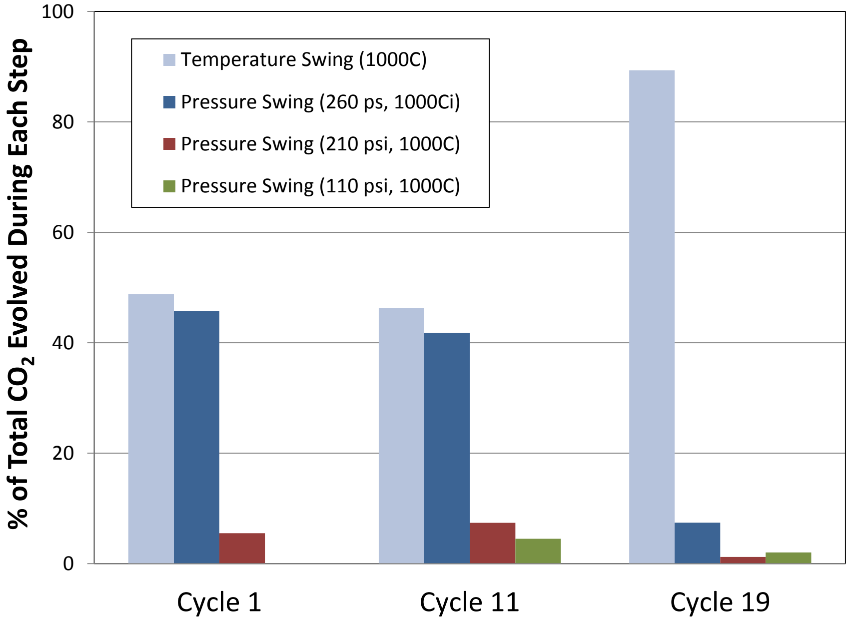


- P_{CO2} of 4 bar is equivalent to concentration level of CO_2 in syngas entering SEWGS process
- Sorbent degraded more quickly at P_{CO2} = 4 bar than at 1 bar
  - Degradation different at higher pressures
  - Some FSP sorbents have shown better performance at higher pressures, achieve stable capacity
- Engineered sorbents perform better than natural limestone

Task 4: High Pressure Testing



- USP-199 (75:25 CaO:meyenite)
- Simulated Syn-Gas
  - CO, CO_2, H_2, H_2O, CH_4, N_2
  - 650 C
- Parametric regeneration testing (pure N_2, 1000 C, various total pressures)



- Capacity lower at higher pressure (0.22 g-CO_2/g-sorbent)
- Inclusion of 0.1% HCl showed no impact
- Temperature swing all that is required?

Summary

- >20 USP and >20 FSP sorbents synthesized
  - Sorbent synthesized with controlled morphology and structure (size, hollow structure, high BET, etc.)
  - Al, Zr, and Y-doped calcium-based sorbents much more stable over multiple test cycles than pure $CaCO_3$
- Sorbents screened in TGA experiments and tested in high pressure environments
  - Engineered sorbents perform better than natural materials
  - Capacity decreases with increasing pressure (evidence that it does stabilize)
  - HCl does not appear to impact USP sorbents
  - Regeneration conditions probed

Plans for Future Work

- Synthesis of WGS catalyst–CO_2 adsorption hybrid materials
- CO_2 adsorption and combined CO_2 adsorption + WGS of selected sorbents using the HTPR setup
- Continue impurity testing and parametric regeneration optimization
- Long term tests on select sorbents
- Techno-economic Analysis
- Final Report

- Continued lab scale HTPR testing, scale up
- Further address reactor design, sorbent attrition, heat management, regeneration, etc.

Acknowledgments

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