



Carbon Dioxide Capture Using Dry Regenerable Sorbents

Presentation at GCEP Energy Workshop
Carbon Capture and Sequestration
Stanford University

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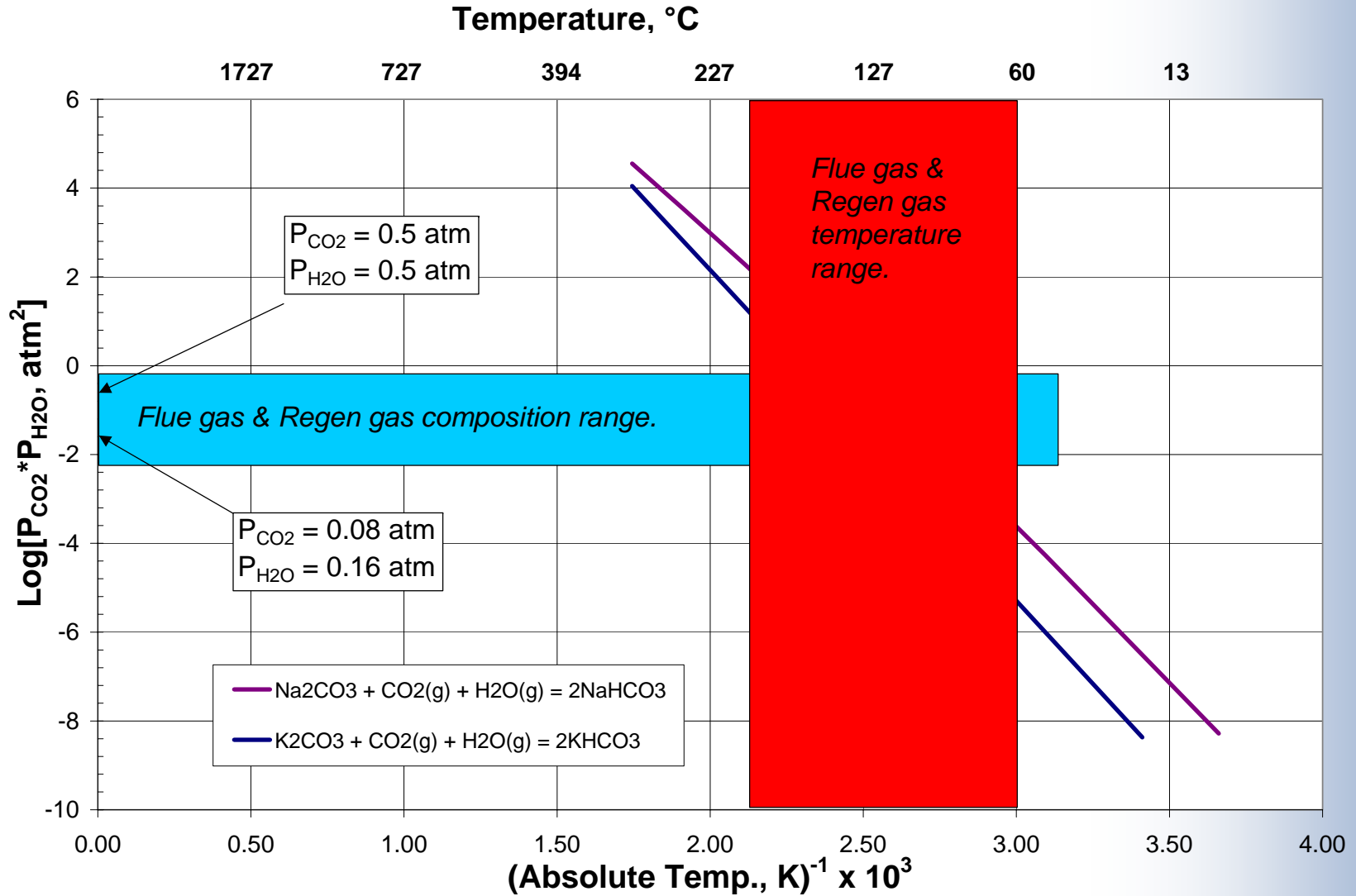
Research Triangle Park, North Carolina

turning knowledge into practice

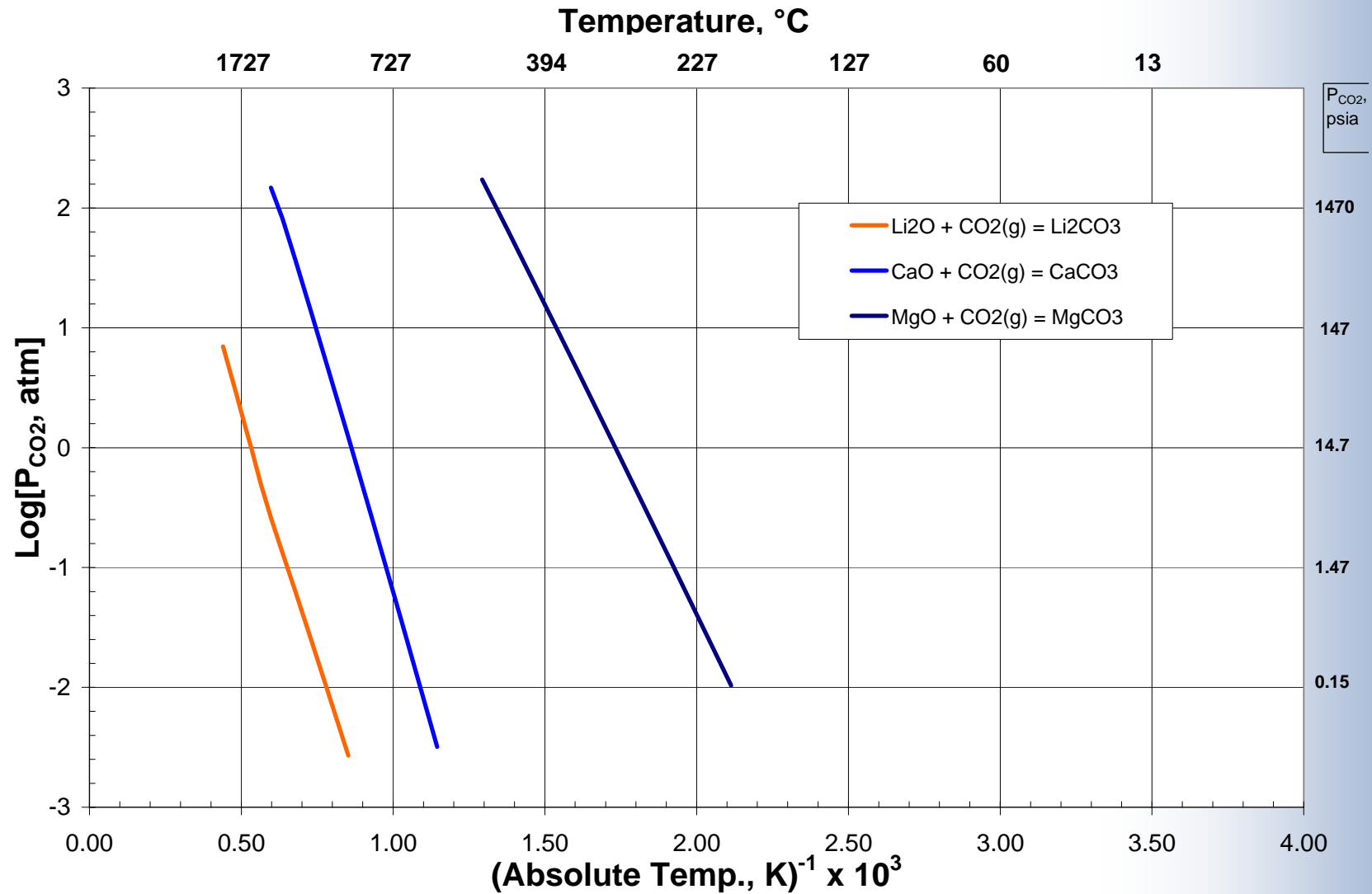
Sorbent / Process Development at RTI

- . Develop sorbents that have desired properties for various CO₂-containing process streams:
 - Flue gas at low temperatures from fossil fuel combustion.
 - Flue gas at elevated temperatures from fossil fuel combustion.
 - Syngas (from carbonaceous fuel gasification) at moderate and elevated temperatures and high pressures.
- . Develop a simple, inexpensive process to separate CO₂ as an essentially pure stream using a reversible reaction and dry chemical sorbents.

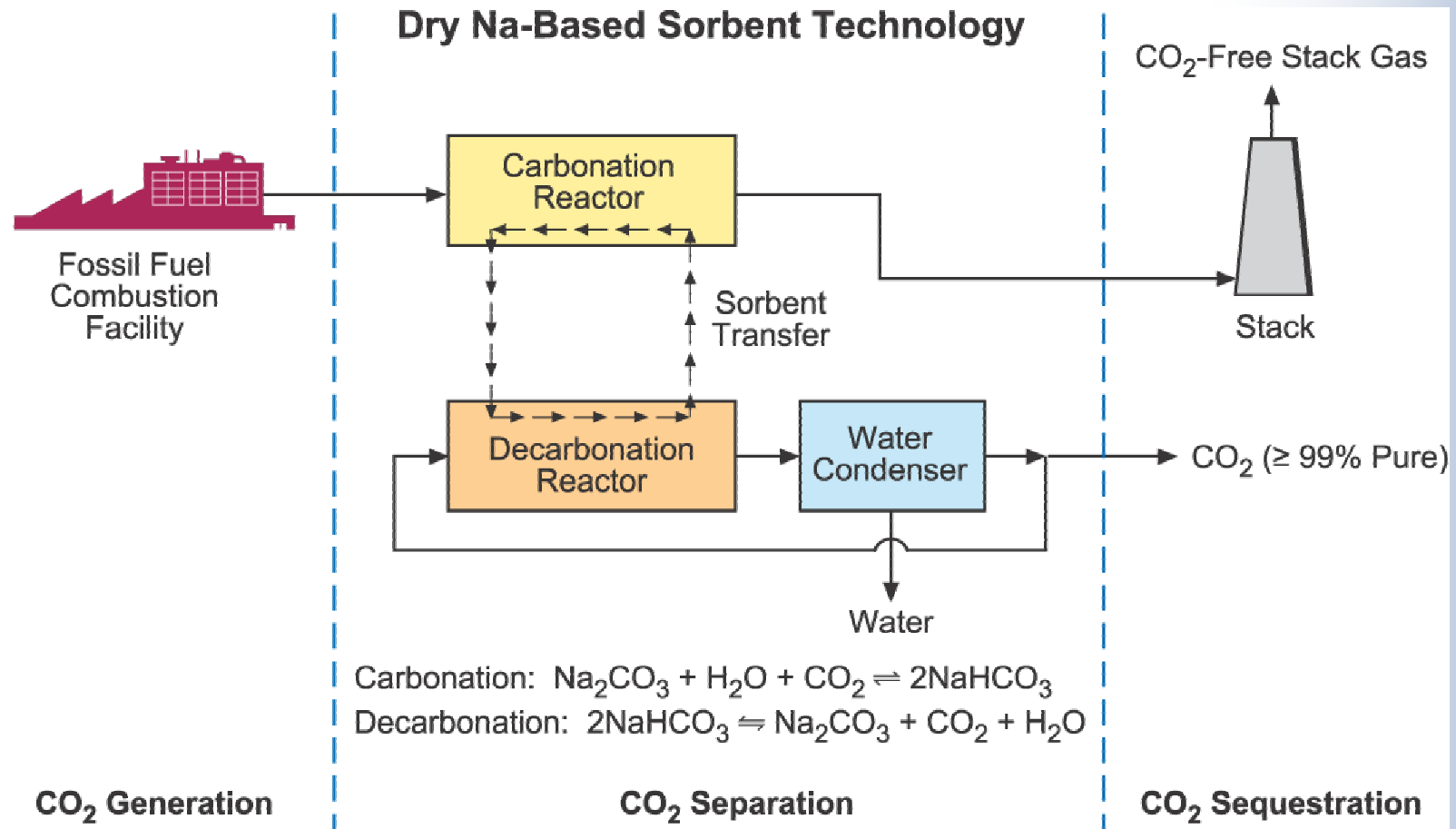
Carbonate-Bicarbonate Equilibrium



Carbonate-Oxide Equilibrium



Integration of the “Dry Carbonate” Process in a Combustion Facility



Key Aspects of Flue Gas Project

- Utilize the known CO₂ removal potential of alkali carbonate materials.
- Overcome known reaction rate limitations with the use of a commercial fast fluidized-bed reactor (“entrained-bed” reactor).
 - Fast initial kinetics
 - Improved heat transfer
- Leverage RTI’s expertise in fluidized-bed sorbents to develop chemically reactive and attrition-resistant sorbent for CO₂ removal.

Reaction Chemistry

- CO₂ absorption (carbonation):



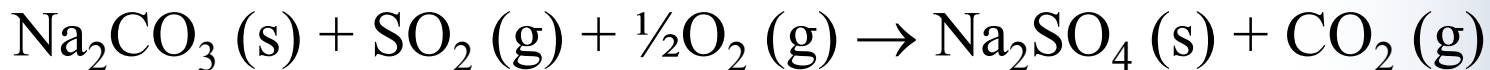
- Sorbent regeneration (decarbonation):



- Wegscheider's Salt:



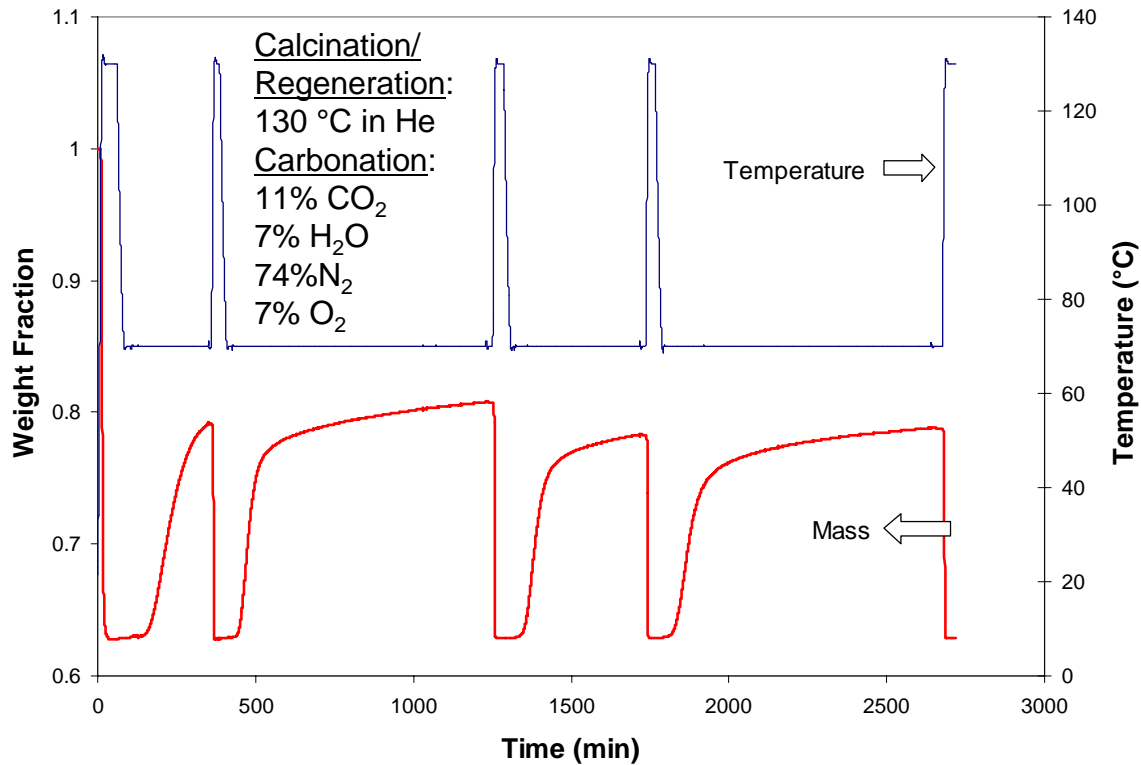
- Effect of HCl and SO₂:



- No Effect of O₂ and NO_x

Concept Evaluation

(Sodium Bicarbonate Sorbent – “Baking Soda”)

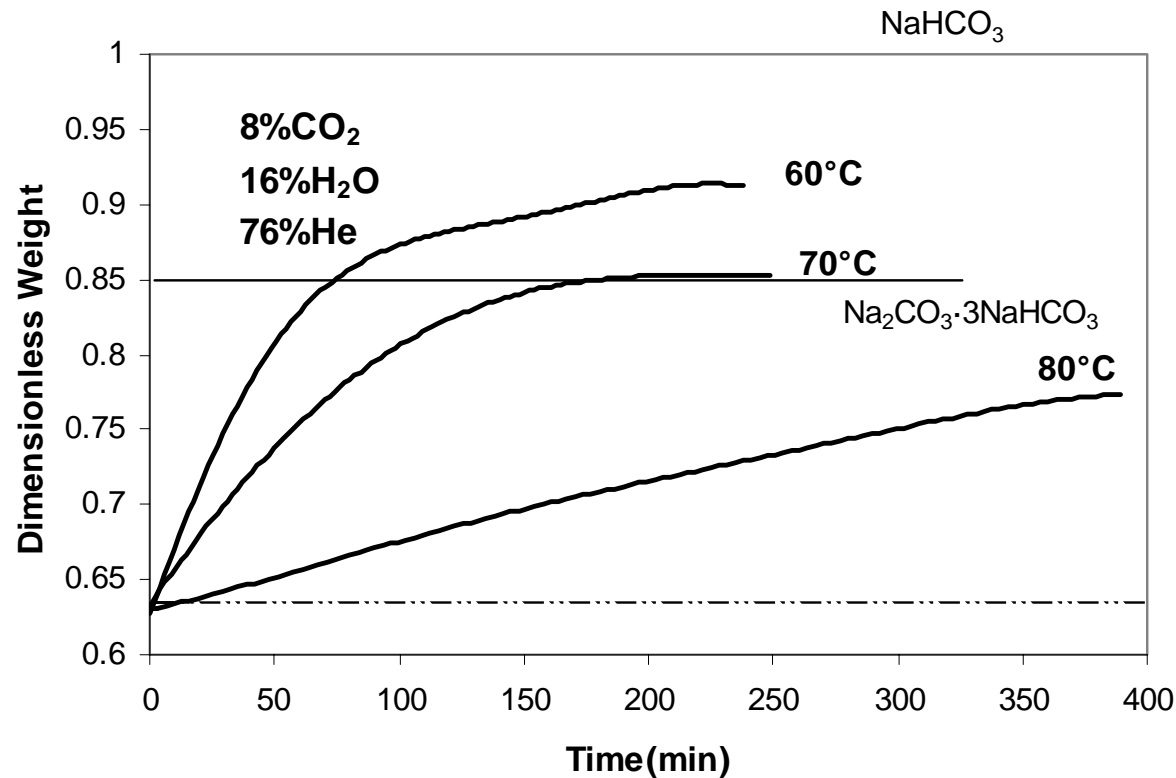


- Inexpensive CO₂ sorbent identified
- Sorbent is readily regenerated
- Low temperature process
- Convenient for flue gas treatment

Material Testing/Material Development

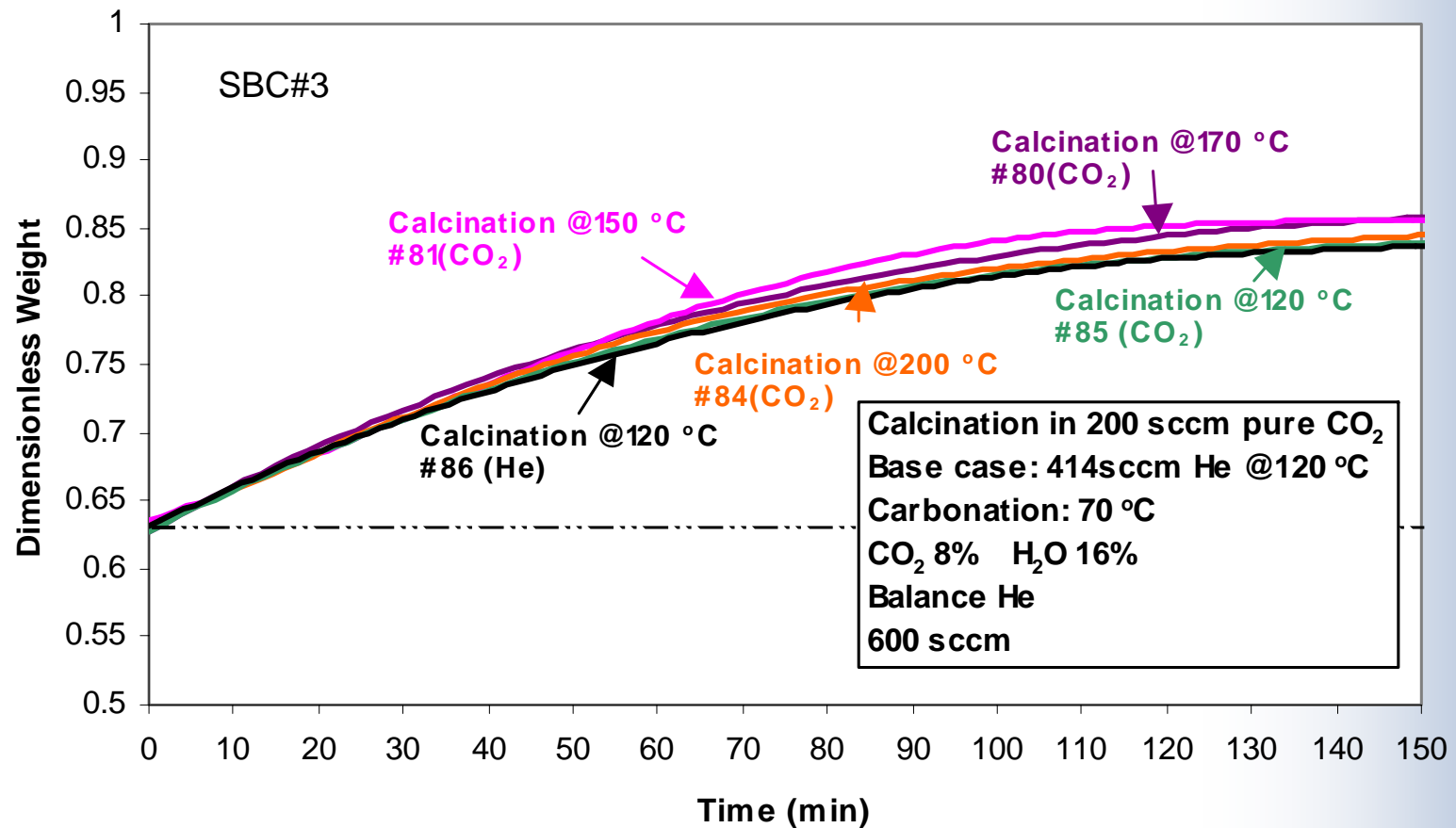
- . Pure chemicals
 - Sodium bicarbonate (SBC) – NaHCO_3
 - Trona – $\text{Na}_2\text{CO}_3 \cdot \text{NaHCO}_3 \cdot 2\text{H}_2\text{O}$
 - Potassium Carbonate – K_2CO_3
 - Soda Ash – dense ash, natural light low density
- . “Supported” sorbent development
 - Carbonate compounds on inert, attrition-resistant metal oxide support
- . Advantages of supported sorbents
 - High surface area (10-200 m^2/g)
 - High porosity and pore volume
 - Good attrition resistance
 - Thermally and chemically stable substrates

Fundamental Kinetic and Thermodynamic Studies (Carbonation)



- First order reaction kinetics
 - CO₂
 - H₂O
- Temperature sensitive kinetics: rate decrease with increased T suggests equilibrium hindrance.
- Sorbent operating temperature ranges
 - Sodium carbonate (60 to 80°C)
 - Potassium carbonate (60 to 120°C)

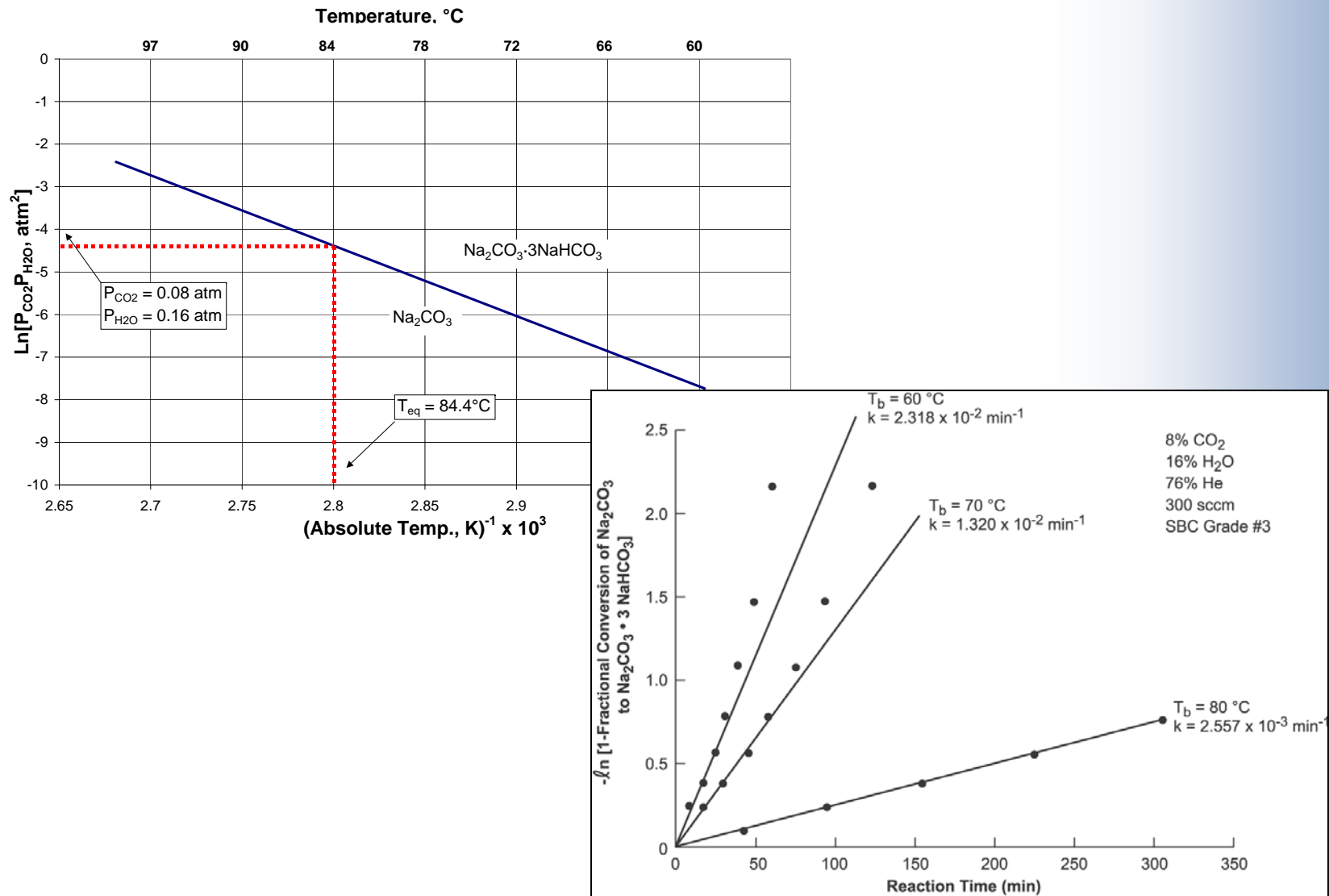
Effect of Regeneration Temperature (in pure CO₂ compared to He)



Engineering Challenges

- Absorption of CO₂ is highly exothermic
 $\Delta H_{298} = -32.1 \text{ kcal/gmol CO}_2 \text{ (1314 Btu/lb)}$
- Absorption of CO₂ is less favorable with increase in temperature.
- Large negative ΔH implies excellent heat removal required to prevent reaction from becoming self-extinguishing.

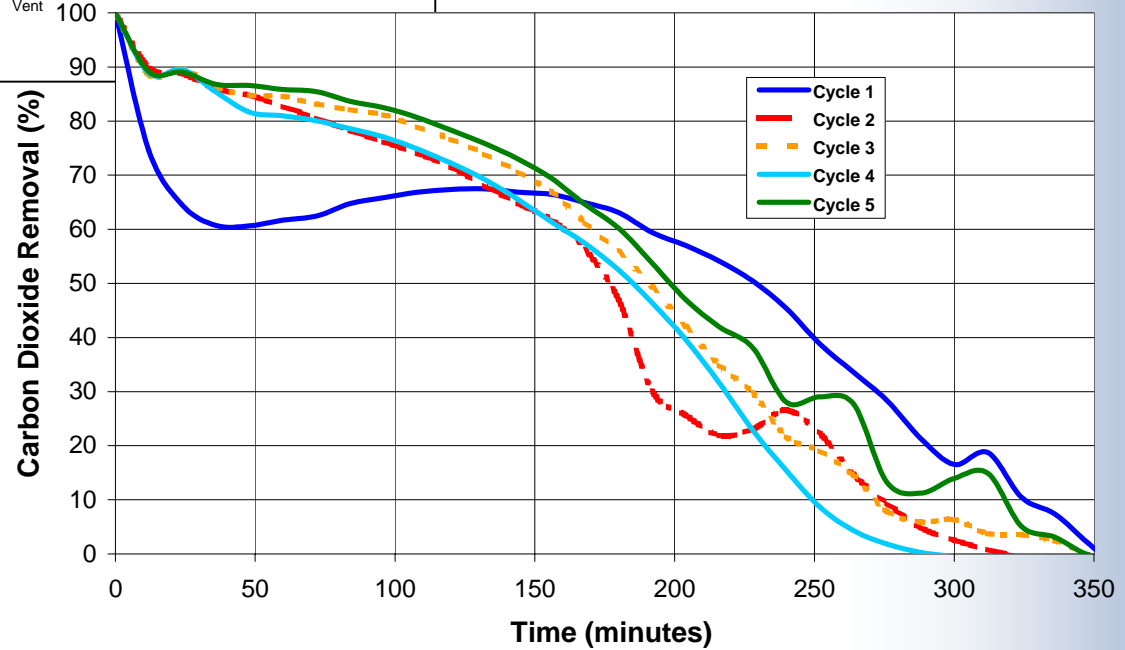
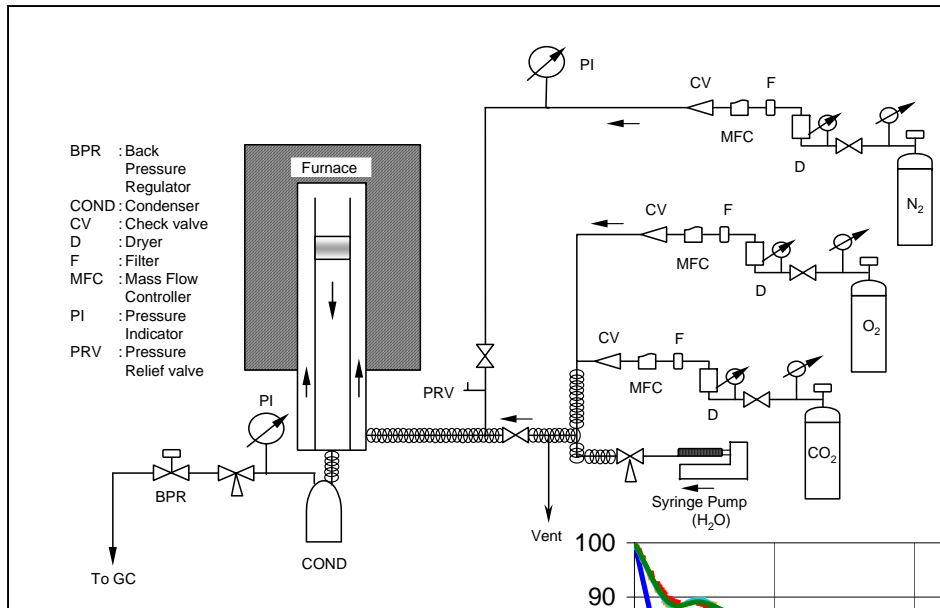
Kinetic Modeling



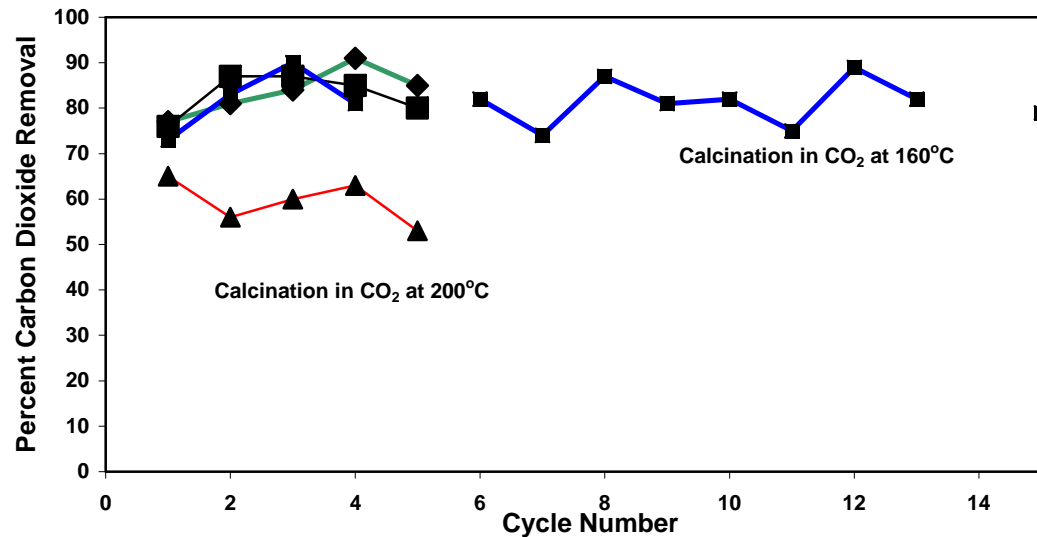
Conclusions from Kinetic Modeling Work

- Initial reaction kinetics (relative to unconverted carbonate) appeared to be first order.
- A “shrinking core” heat transfer model of the sorbent on the TGA pan was also consistent with the observed reaction rate.
- Heat transfer calculations based on bench-scale fluid-bed data showed that temperature difference between the gas and the solid is the driving force.
- The inferred heat transfer coefficient was applied to a conventional “shrinking core” model for a spherical particle (i.e., a sorbent particle in a dilute-phase entrained-bed reactor).
- Shrinking core model extrapolated to small particles and moderate solid loadings in transport gas suggests that:
 - Substantial Na_2CO_3 conversion and CO_2 removal is possible in moderate residence times with effective heat removal from reactor.

Fixed-Bed Testing at LSU

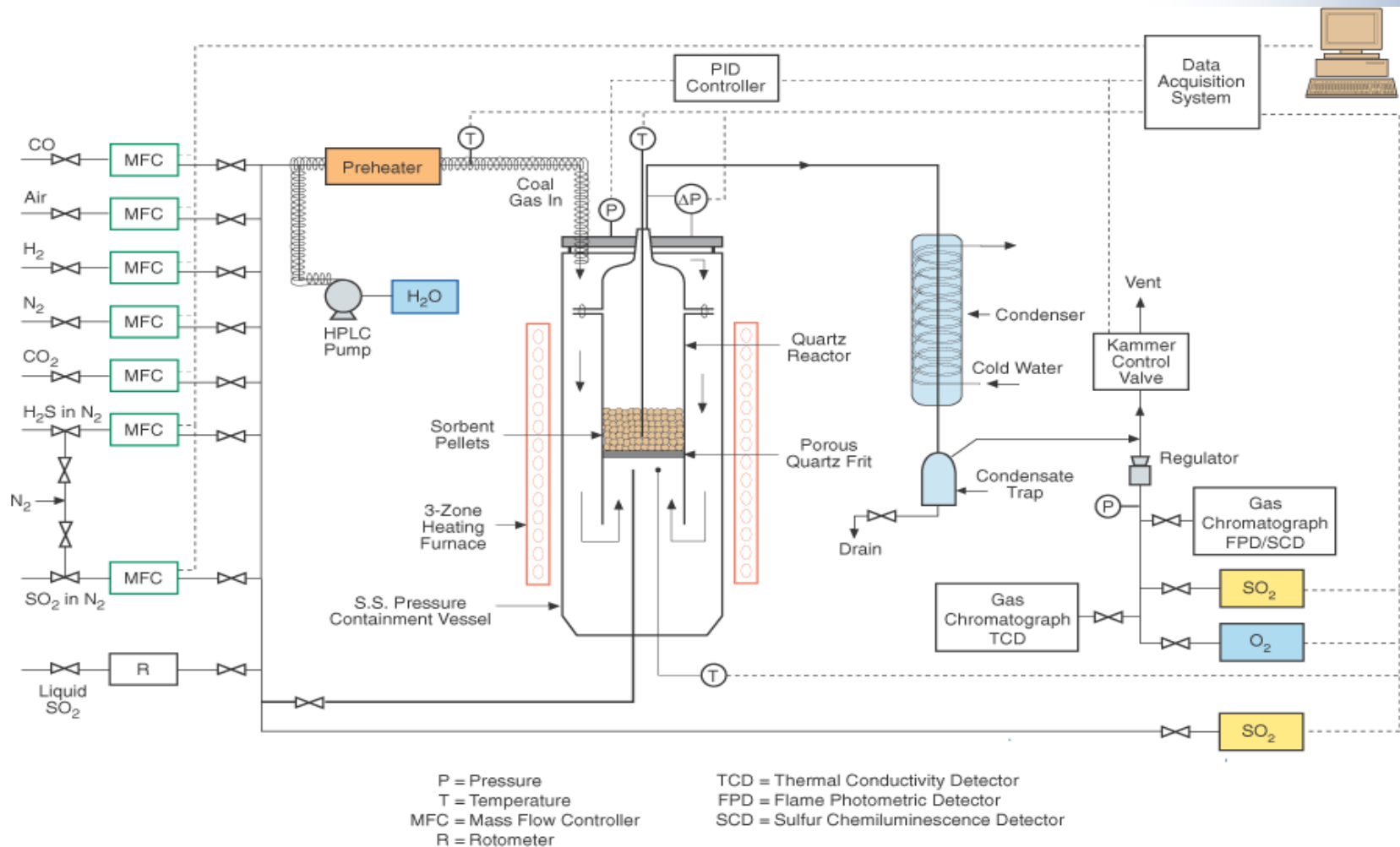


15-Cycle Fixed-Bed Testing at LSU



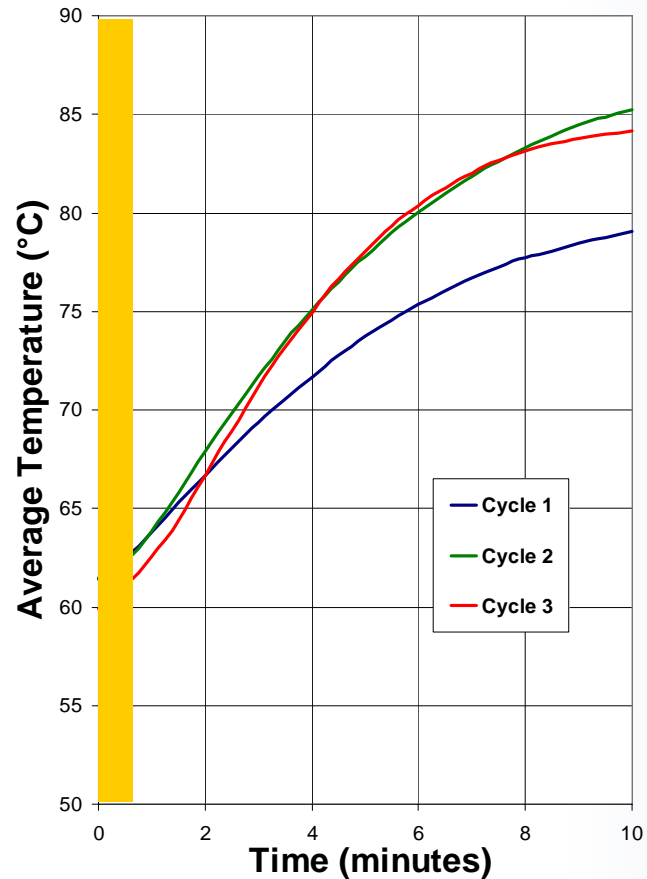
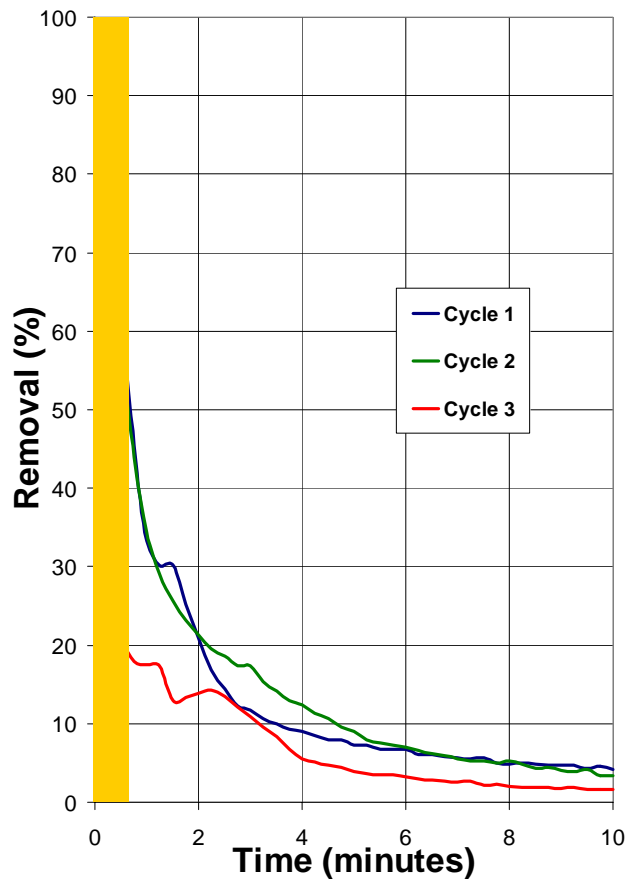
- . High degree (>90%) of sorbent utilization is possible.
- . Apparent improvement in reaction rate after 2nd regeneration.
- . >90% CO₂ removal from flue gas demonstrated.
- . Rapid regeneration rate.
- . No deactivation for 15 cycles.

Fluid-Bed Testing at RTI



Fluid-Bed Testing of 40% Supported Sodium Carbonate

Carbonation in 7% Carbon Dioxide, 6% Water Vapor

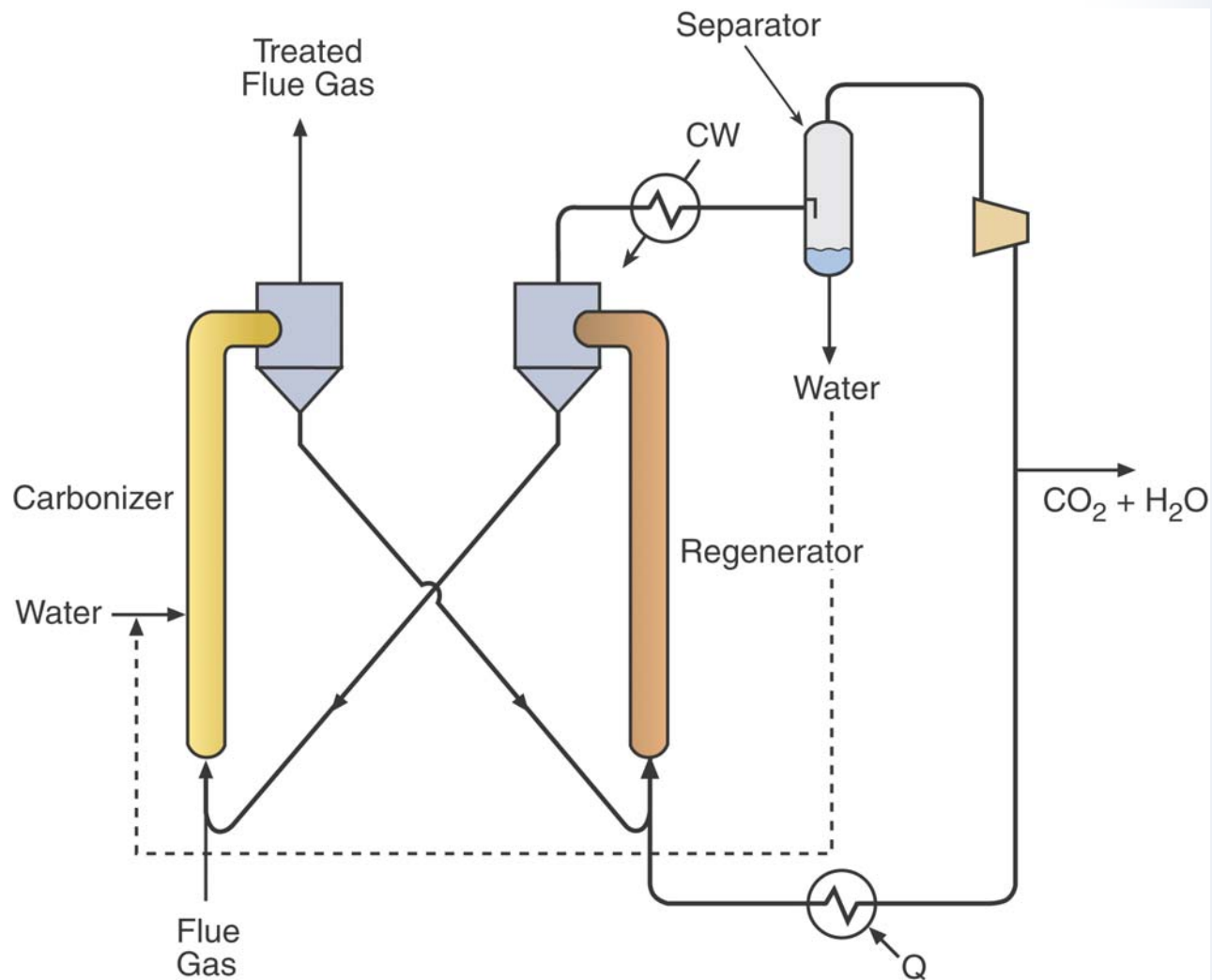


Highlights of Fluid-Bed Studies

- Very rapid initial carbonation rates.
- Rapid increase in bed temperature.
- Little or no decline in carbonation activity over 5 cycles in numerous multicycle tests.
- HCl and SO₂ are irreversibly absorbed.



Commercial Embodiment – Conceptual Reactor System



Heat Duties – Comparative Flue Gas Processes

- Case 7A in EPRI, *Evaluation of Innovative Fossil Fuel Power Plants with CO₂ Removal*, 2000.
 - Btu steam per pound of CO₂: 1617.
- Case 7A recalculated using heat duties documented in Alstom Power, *Engineering Feasibility and Economics of CO₂ Capture on an Existing Coal-Fired Power Plant*, 2002.
 - Btu steam per pound of CO₂: 2350.
- Comparison: heat energy of bicarbonate regeneration to Wegscheider's Salt.
 - Btu per pound of CO₂: 1315

RTI-5 Material: Scale-up at Süd-Chemie

- Drum quantities have been produced by commercial spray drying.
- Formulations and “recipes” developed at RTI, using lab-scale spray dryer.



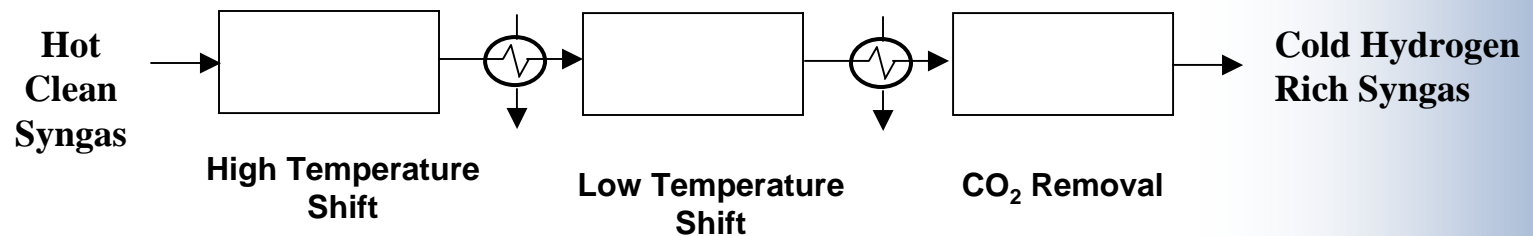
Ongoing Work– Flue Gas Process



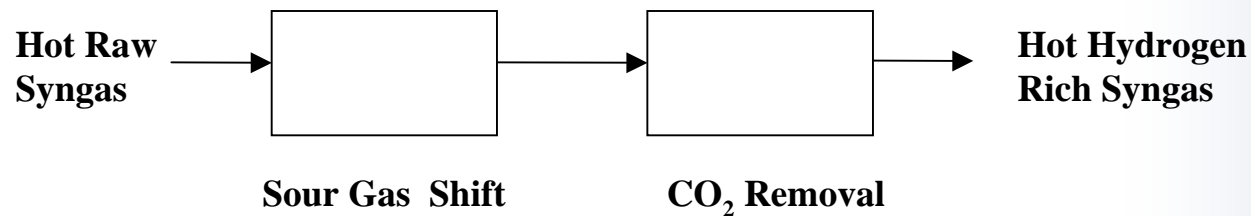
- . Process Modeling
- . Exploration of innovative regeneration concepts to re-use heat of absorption
- . Sorbent optimization
- . Bench-scale/Pilot-scale entrained-bed reactor testing
- . Slipstream field test
- . Technical/Economic Assessment

CO₂ Separation from Syngas

Commercially Practiced Process



Potential Elevated Temperature Process



CO₂ Separation from Syngas at Elevated Temperature

. Benefits

- High CO₂ concentration, smaller treatment volume at high pressure
- High thermal efficiency of IGCC
- Simpler process integration
- Higher quality sequestration-ready stream

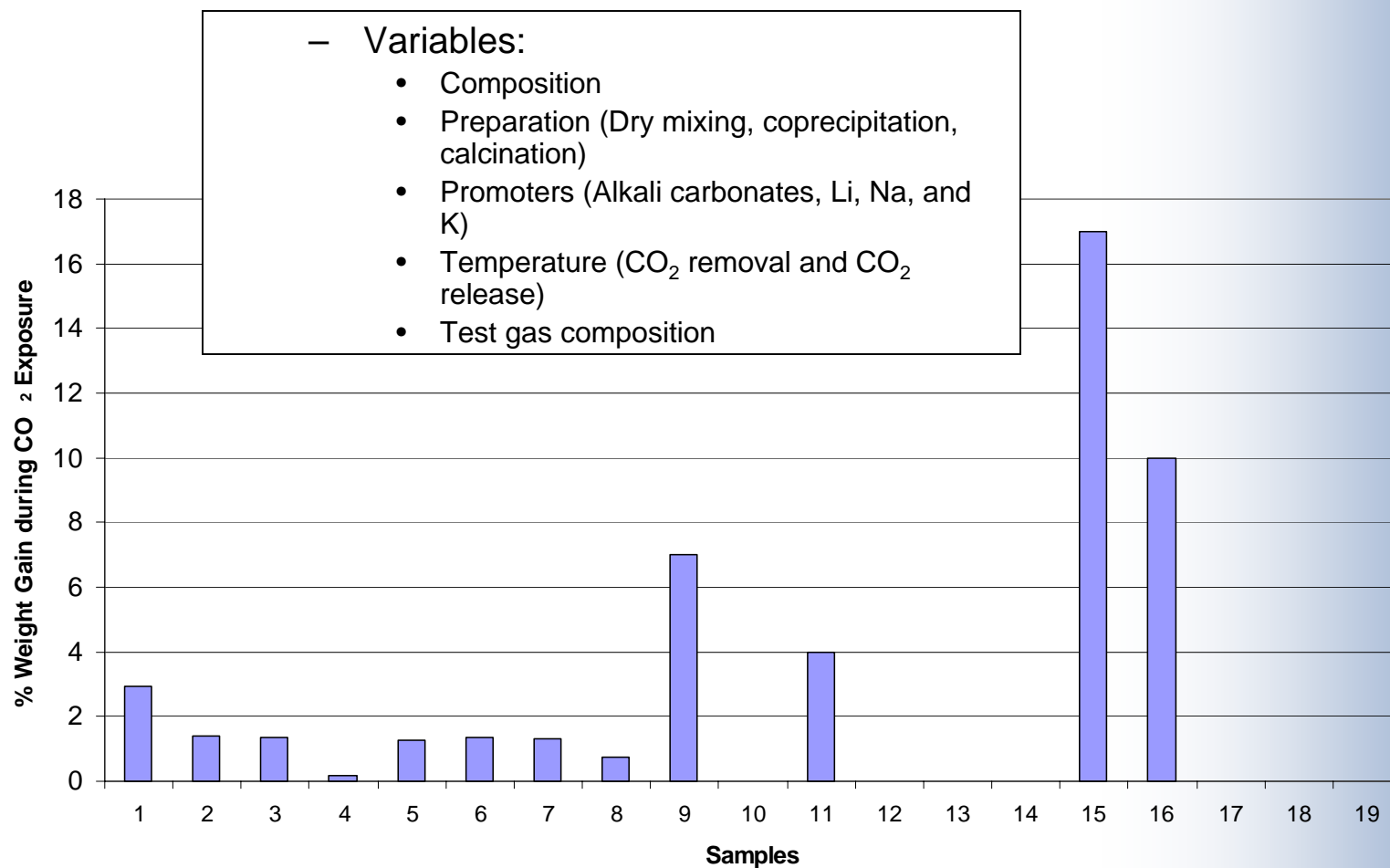
. Challenges

- Complete CO conversion
- Low sulfur tolerance of catalysts
 - Equilibrium limited

Research Objectives

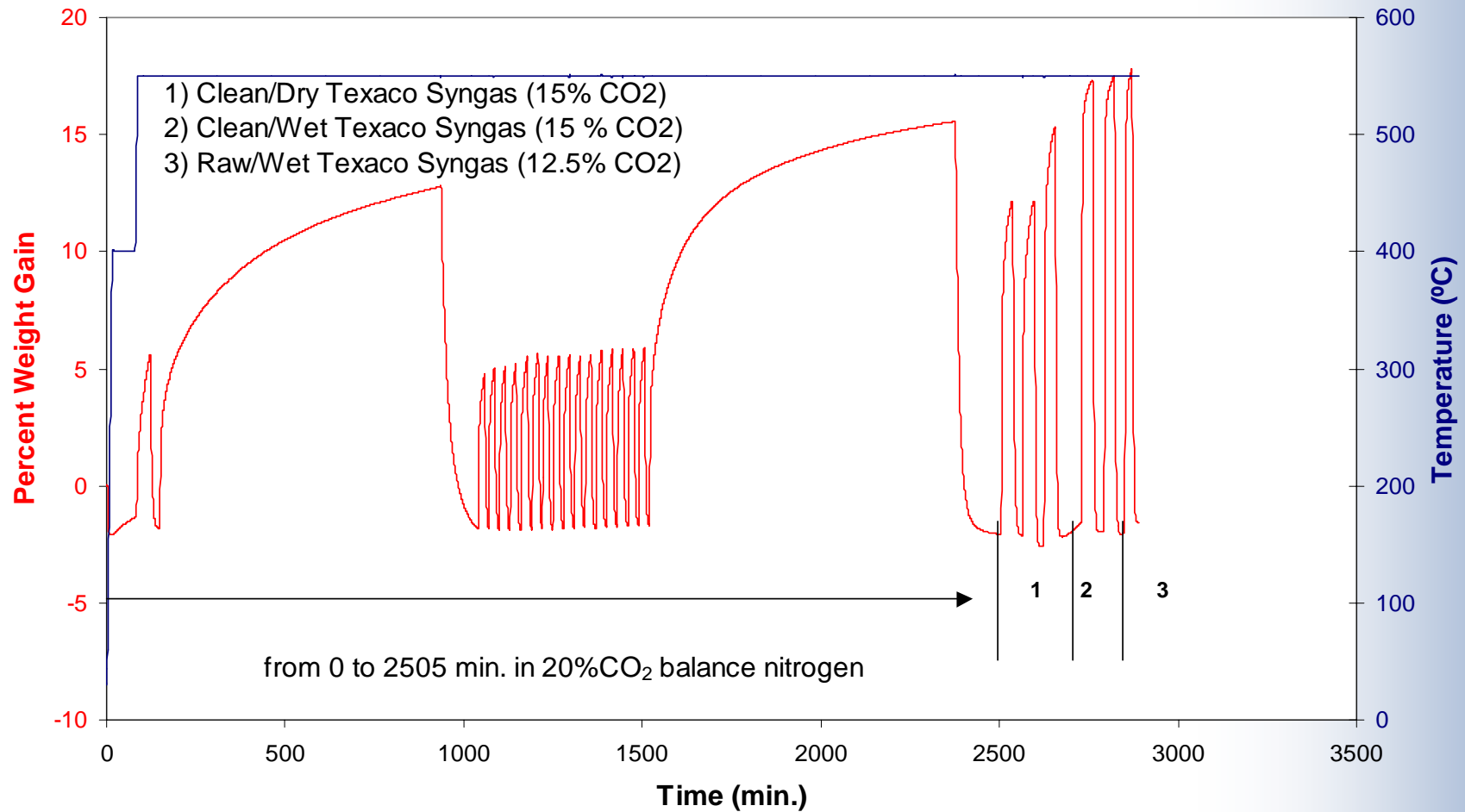
- Identify promising candidates for regenerable CO₂ sorbent
 - CO₂ removal
 - Remove CO₂ from synthesis gas
 - Temperatures 400°F to 1000°F
 - CO₂ release
 - Generate essentially pure, high-pressure CO₂ product ready for sequestration
 - CO₂ release by temperature swing, inert purge, or pressure swing
- Possible candidates:
 - Magnesium Oxide
 - Calcium Oxide
 - Lithium Aluminate
 - Lithium Ferrite
 - Lithium Titanate
- **Especially promising:**
 - **Lithium Zirconate**
 - **Lithium Silicate**
 - **Lithium Silicate – w/ Eutectic salt additions**

Screening Test Results



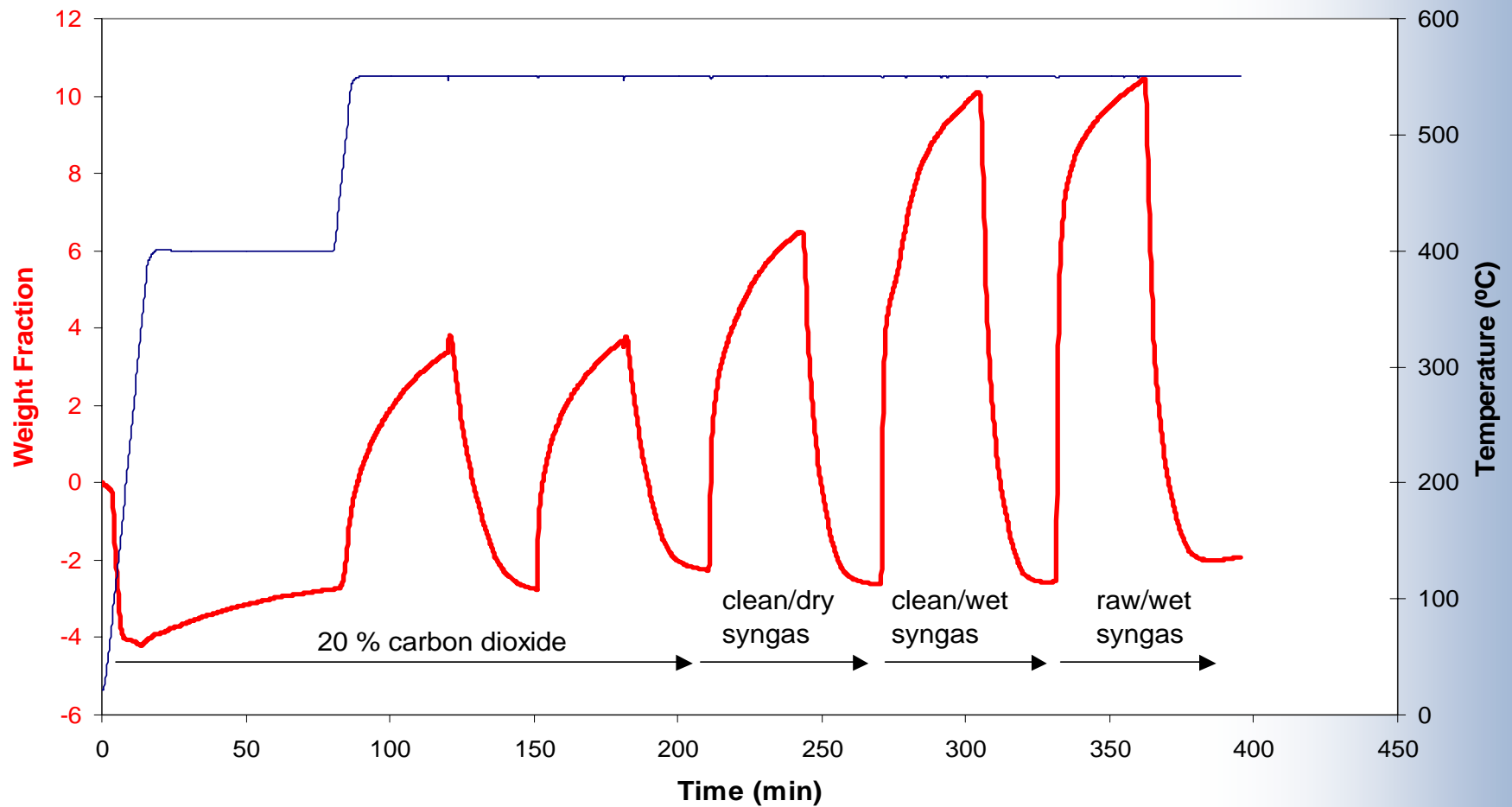
Multicycle Screening Tests

Sample 15

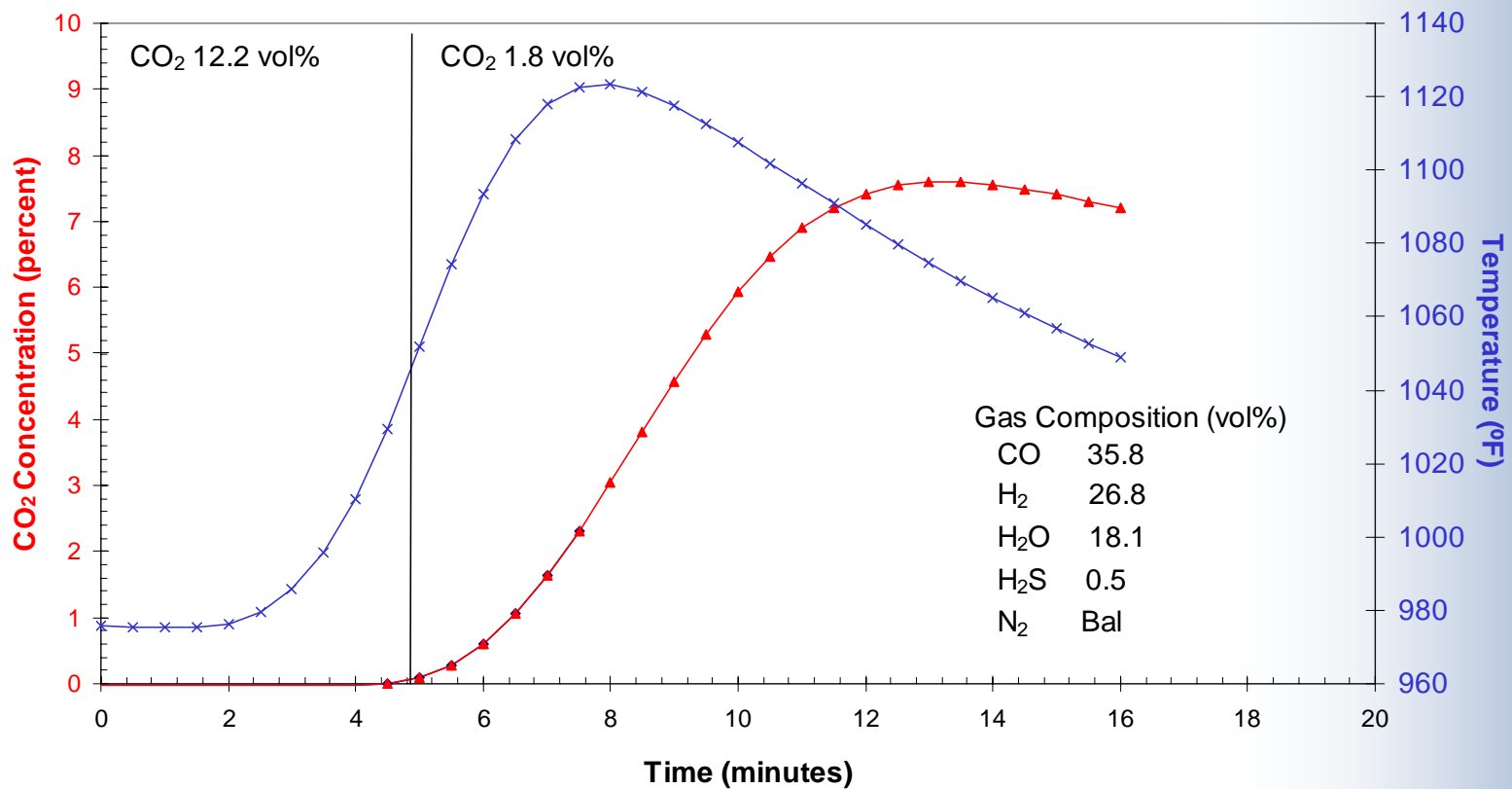


Multicycle Screening Tests

Sample 16



Effluent CO₂ and Temperature Profiles



Accomplishments

- . Demonstrated:
 - Sorbent CO₂ loadings between 4 and 17 wt%
 - Effective regeneration with temperature swings and inert purging
 - CO₂ removal actually improves in the presence of raw synthesis gas
- . Initiated bench scale testing of sorbent formulations

Research Priorities

- . Sorbent development
 - Composition
 - Spray dried production
 - Highly active
 - Attrition resistant
 - Shift activity
- . Bench scale testing
 - Regeneration modes
 - Multicycle testing
- . Process development
 - Reactor design
 - Heat integration
 - Process integration
 - Economic evaluation

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