turning knowledge into practice

Annual NETL CO_2 Capture Technology for Existing Plants R&D Meeting

The Dry Carbonate Process:
Carbon Dioxide Recovery from Power Plant Flue Gas

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RTI International - Center for Energy Technology

March 24 – 26, 2009 • Sheraton Station Square • Pittsburgh, Pennsylvania

RTI International

Center for Energy Technology (CET)

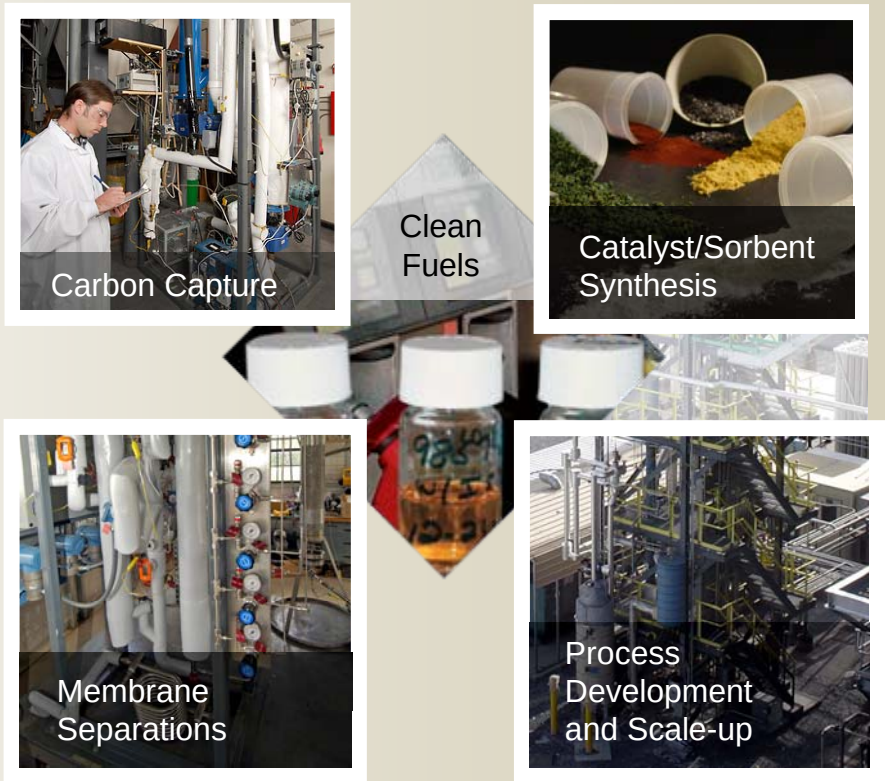
RTI International

- Established in 1958
- One of the world's leading research institutes
- > 2,800 staff; > $700M revenue (2008)
- *Mission:* to improve the human condition by turning knowledge into practice

CET Capabilities

- Advanced Gasification
  - Warm gas desulfurization
  - Multicontaminant removal
  - Substitute natural gas production
- Carbon Capture
  - Post- and Pre-combustion CO_2 capture
  - Chemical Looping Combustion
  - Advanced Membranes
- Clean Fuels
  - Syngas to fuels and chemicals
  - Biofuels
- Hydrogen Production and Purification

CET Application Areas



Project Background

Project Overview

- DOE/NETL Cooperative Agreement # DE-FC26-07NT43089
  - DOE Project Manager: José Figueroa
  - RTI Project Manager: Thomas Nelson

Project Phase	Period of Performance	DOE Share	Cost-Share	Total
Budget Period I	03/07 → 09/08	$757,328	$189,332	$946,660
Budget Period II	10/08 → 08/10	$2,458,753	$614, 688	$3,073,441
Totals	03/07 → 08/10	$3,216,081	$804,020	**$4,020,101**

- Objectives and Scope:
  1. Determine optimal process configuration for Dry Carbonate Process
  2. Build and validate bench-scale "proof-of-concept" components
  3. Build and validate pilot-scale Dry Carbonate Process (1 ton CO_2/day)
  4. Demonstrate >90% CO_2 removal from actual combustion flue gases
  5. Demonstrate long-term chemical & mechanical stability of sorbent
  6. Update process economic analyses
  7. Develop a technology commercialization plan

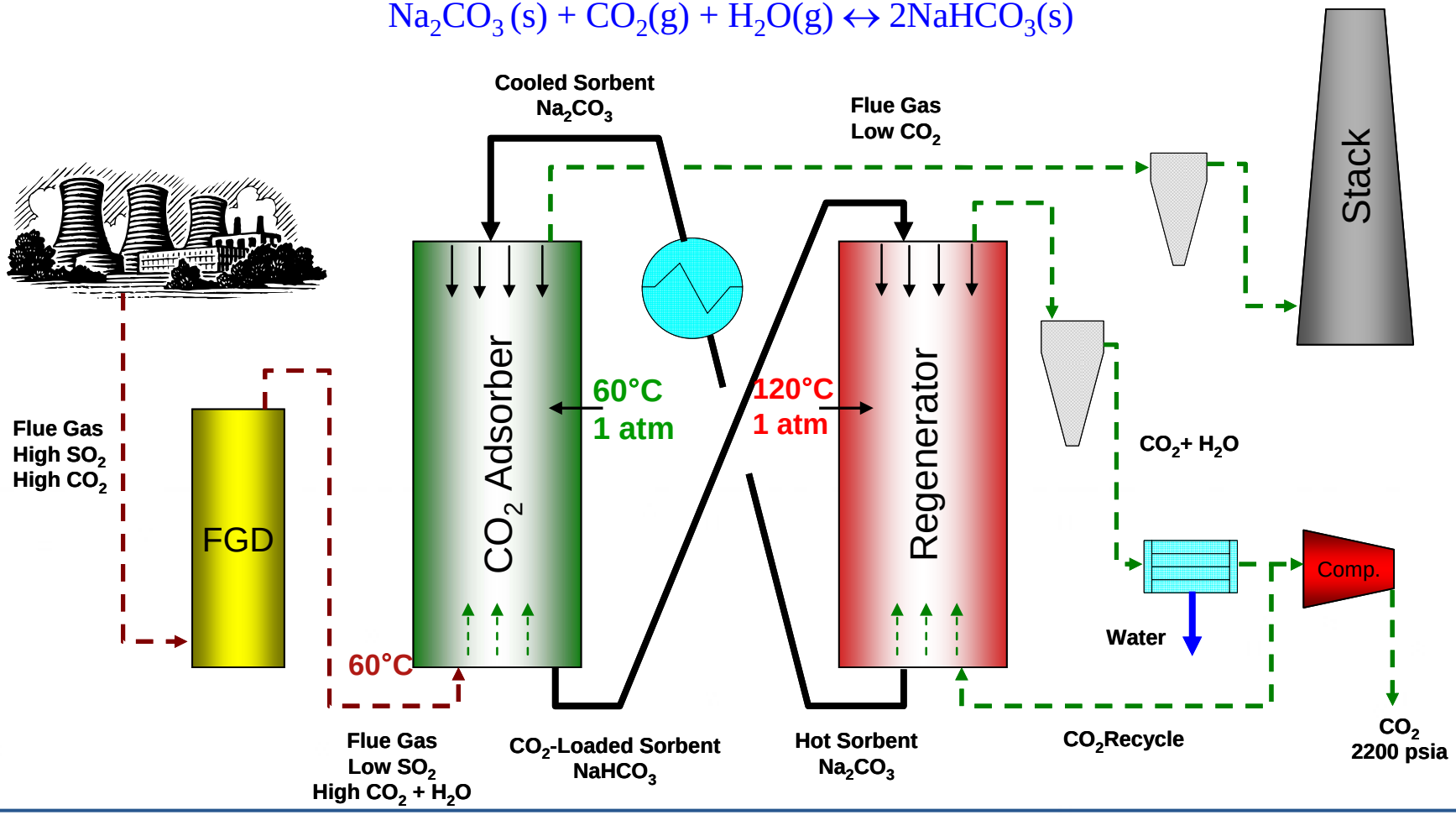
Project Team

Team Member	Key Roles
RTI International	• Technology developer, system engineering & testing, project management
DOE / NETL	• Technical guidance, project evaluation, system analysis
Subcontract Partners	
EPRI	• Economic and technical evaluations, power industry perspective
ARCADIS, Inc.	• Pilot system operation, engineering evaluations
Other Partners	
U.S. EPA	• Facility provider
Süd-Chemie, Inc.	• Sorbent manufacture & scale-up
Nexant	• Subcontractor to EPRI, economic and technical evaluations

Technology Background

RTI's Dry Carbonate Process for CO_2 Capture from Flue Gas

$$Na_2CO_3(s) + CO_2(g) + H_2O(g) \leftrightarrow 2NaHCO_3(s)$$



The Dry Carbonate Process

Closer Look at Reaction Chemistry

CO_2 Adsorption (Carbonation)

$$Na_2CO_3(s) + CO_2(g) + H_2O(g) \leftrightarrow 2NaHCO_3(s)$$

Exothermic $\Delta H_r° = -1325$ Btu/lb CO_2

Operating temperature: < 80°C

Sorbent Regeneration

$$2NaHCO_3(s) \leftrightarrow Na_2CO_3(s) + CO_2(g) + H_2O(g)$$

Endothermic $\Delta H_r° = 1325$ Btu/lb CO_2

Operating temperature: > 100°C

Contaminants

$$Na_2CO_3(s) + SO_2(g) + \tfrac{1}{2}O_2(g) \rightarrow Na_2SO_4(s) + CO_2(g)$$
$$Na_2CO_3(s) + 2HCl(g) \rightarrow 2NaCl(s) + CO_2(g) + H_2O(g)$$

Reactions with SO_2 and HCl are irreversible at process conditions

No observed effects by O_2, Hg, and NO_x

Advantages of a Na_2CO_3-based CO_2 Capture Process
(Compared to conventional amine technology)

- Lower total regeneration energy requirement
- Lower CO_2 removal cost
  - capital savings; operating costs; sorbent make-up savings
- No flue gas pretreatment
  - No heating, No cooling, No guard beds
- Tolerance to contaminants in flue gas (e.g., O_2, SO_2, HCl)
- Readily available and inexpensive sorbent
- Non-hazardous and non-toxic sorbent
- No hazardous waste generated

Challenges of CO_2 Capture with a Na_2CO_3-based Process

- Large solids handling/circulation requirements
  - Best-case scenario → Na_2CO_3 : CO_2 = 2.4 : 1 (mass ratio)

  Solution: *High capacity sorbents; best available solids handling technologies*
- Exothermic CO_2 sorption affects reaction equilibrium
  - CO_2 capture is heat transfer limited

  Solution: *Reactor design is critical; target designs with highly effective heat transfer*
- CO_2 removal requires equimolar amount of water

  Solution: *Target saturated flue gas (downstream of wet FGD); water added if required*
- Na_2CO_3 reacts irreversibly with SO_2 and HCl at process conditions

  Solution: *Continuous sorbent make-up; SO_2 guard bed may improve economics*
- Raw Na_2CO_3 is not physically strong

  Solution: *Engineered sorbent (binders / support materials)*
- Condensed water causes raw Na_2CO_3 to agglomerate

  Solution: *Engineered sorbent; reactor operation above flue gas dew point*

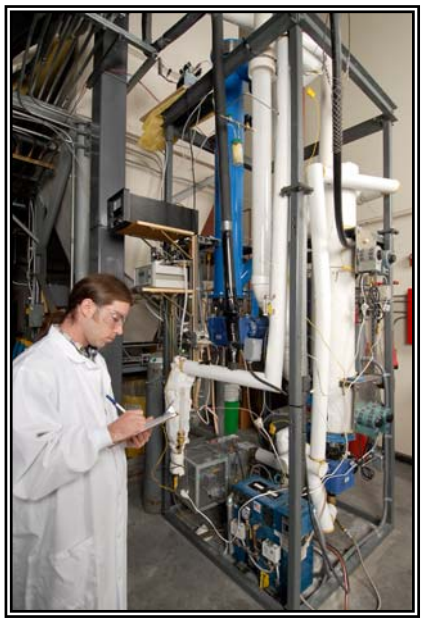
Technology Development

Development Timeline (*Focus*: Process and Sorbent Development)

- Early proof-of-concept testing: Thermogravimetric Analysis
- 2005 – 2006: Sorbent and reactor screening
- 2007 – 2008: Sorbent and process testing with coal-fired flue gas at U.S. EPA's Multi-pollutant Control Research Facility (MPCRF)

EPA Testing

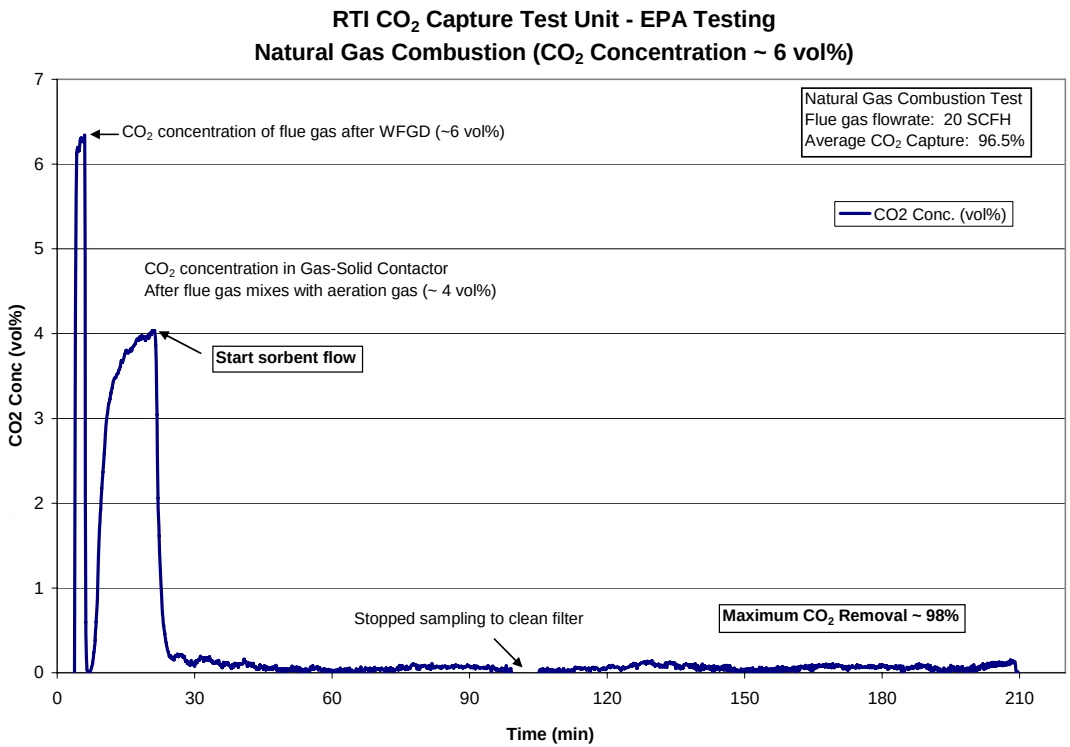
- MPCRF: 1.2 MW_t multi-fuel fired facility (330 lbs/hr coal)
- RTI's Dry Carbonate unit was installed and operated
- Process: Bench-scale Entrained-bed based reactor
- Sorbent: sodium carbonate on support material



Objectives of Coal-fired, EPA Testing

- Operate continuous adsorption and regeneration cycles
- Evaluate process and sorbent performance using actual flue gas
- Evaluate kinetics, heat transfer, solids transport, sorbent degradation
- Identify optimal operating conditions

Field Testing of the Dry Carbonate Unit



Highlights

- Thousands of hours of sorbent circulation testing
- Hundreds of hours of combustion flue gas testing

Natural Gas Combustion

- CO_2 in flue gas: *~6 vol% (before dilution)*
- Maximum CO_2 removal achieved: **~99%**

Coal Combustion

- CO_2 in flue gas: *~10.5 vol% (before dilution)*
- Maximum CO_2 removal achieved: ***~92%***
- Sustained > 90% capture over many cycles
- No negative effects due to contaminants

Lessons Learned

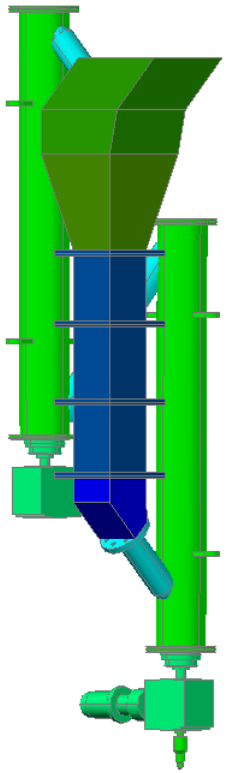
- **Heat control** in adsorber is critical for CO_2 capture rate – reactor design must be optimized
- Sorbent **CO_2 working capacity** was not sufficient for economical operation of process

Current Research & Development

Dry Carbonate Process

- RTI has selected an isothermal, moving, fluidized-bed design for further scale-up
- Most commercially- and technologically-feasible embodiment of the Dry Carbonate Process
- Design specifically addresses key process challenges

Heat Transfer	• Achieves maximum heat transfer rates • Dedicated heating/cooling service systems • Commercial: Coal dryers, Circulating fluidized-bed combustors
Reaction Rate	• Maximizes thermodynamic and concentration driving forces • Maximizes gas-solid contacting • Permits counter-current gas-solids contacting
Solids Handling	• Permits gravity feeding through reactor • Simple gas-solid separation • Commercial: Used in mining, cement plants, power plants



- Focus on scale-up: Dry Carbonate pilot unit capable of 1 ton/day CO_2 capture

RTI's Development Approach

RTI's ongoing R&D effort to prepare for 1 TPD CO_2 capture unit:

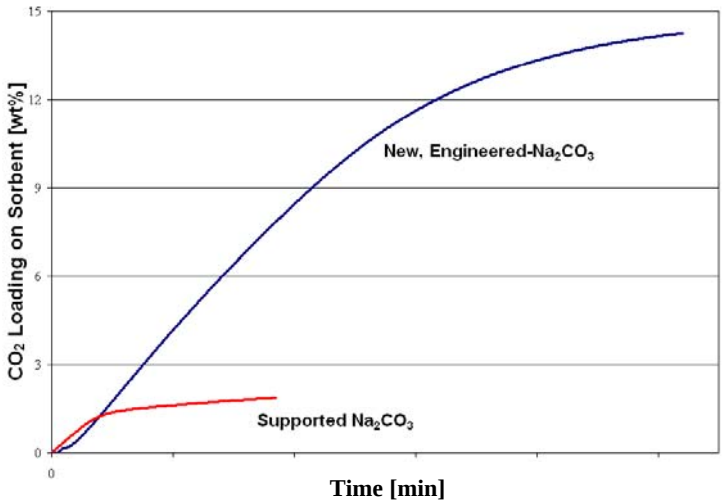
Development Areas	Approach
Improved Sorbent CO_2 Capacity	• Modify sorbent recipe • Screen candidates in lab-scale CO_2 adsorber
Heat Transfer Evaluation	• Bench-scale heat transfer system • Measure heat transfer coefficients • CFD Modeling
Operate in Moving-bed Mode	• Bench-scale evaluation of moving-bed contactor
Evaluate Solids Handling / Control	• Consult with solids/fluidization experts • Bench-scale evaluation of conveyors and control valves
Develop Process Design & Sizing	• Detailed engineering and design for 1 ton/day pilot unit • Bench-scale evaluation of heat transfer arrangements

Sorbent Development Program

- R&D Scope of Work:
  - Construct sorbent test station → Complete
  - Improve sorbent CO_2 capacity → Complete
  - Improve sorbent CO_2 capture rate → In Progress
  - Maintain acceptable attrition resistance → In Progress
  - Scalable manufacturing procedure → May 2009

Status

- Expected Results
  - Na_2CO_3-based sorbent having a minimum dynamic CO_2 capacity of 10 wt%
  - Sorbent with an optimized CO_2 capture rate
  - Attrition resistance consistent with commercial materials used in fluidized-bed applications
  - Production of 200 lb "validation" batches of best-performing sorbents by our partner, Süd-Chemie, Inc.
  - Production of several thousand pounds of optimized sorbent by Süd-Chemie, Inc.

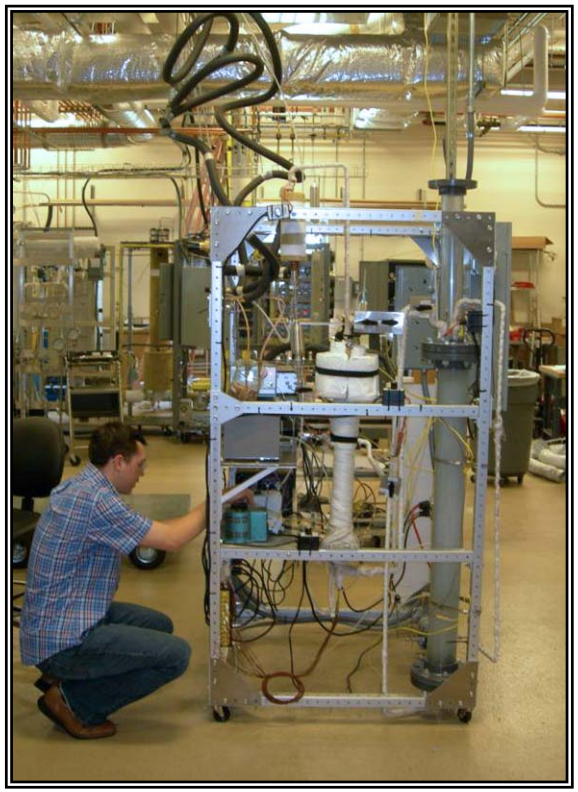


Improved Sorbents

Sorbent	Density [g/cm^3]	Davidson Attrition Index	CO_2 Capacity [wt%]
Supported-Na_2CO_3	0.96	12	2.2
Sorbent A	0.67	29	13.3
Sorbent B	0.57	23	16.3
Sorbent C	0.65	32	24.3

- April / May 2009: Scale-up at Sud-Chemie manufacturing plant

Lab-scale CO_2 Sorbent Test Station

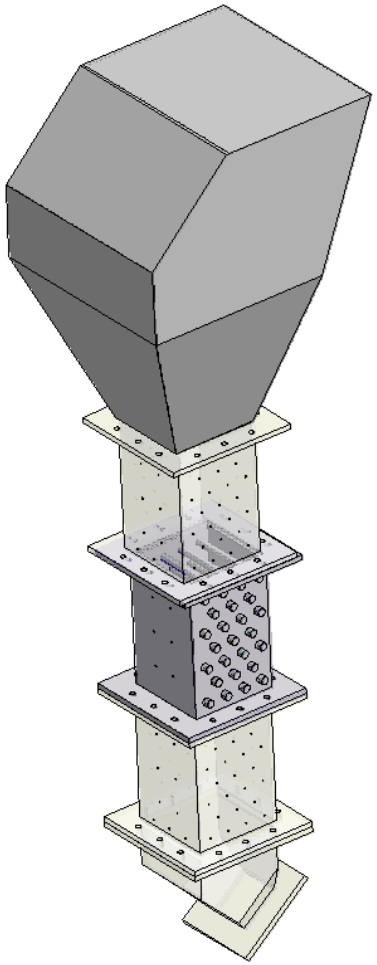


Heat Transfer Evaluations

- R&D Scope of Work: **Status**
  - Design heat transfer evaluation system → Complete
  - Build heat transfer evaluation system → In Progress
  - Test heat transfer evaluation system → April 2009

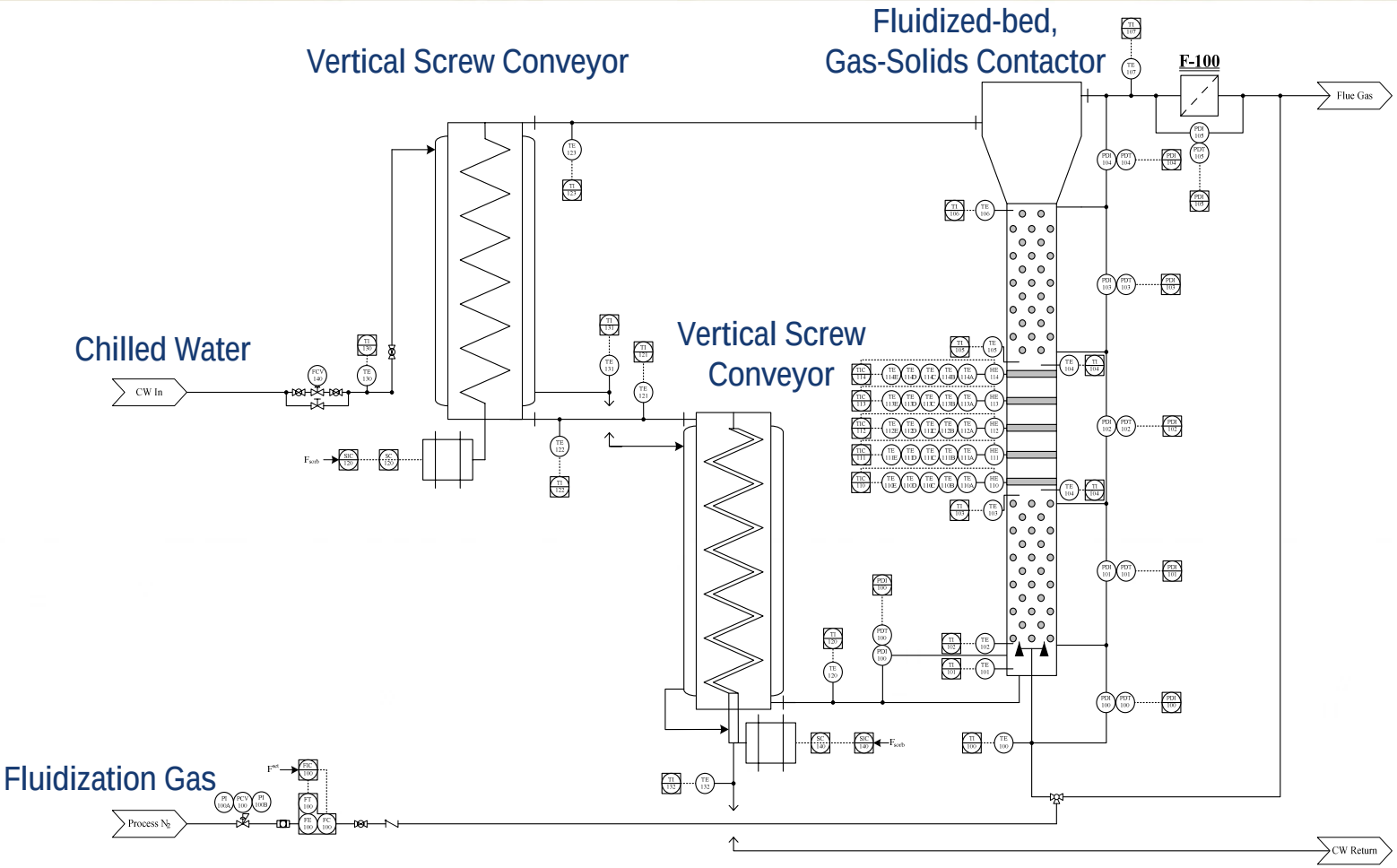
- Expected Results
  - Optimal contactor design identified
  - Heat transfer coefficients measured
  - Able to properly design and size pilot-scale CO_2 Capture and Regeneration reactors

Approach	Description
Flexible / Modular design	• Design and build multiple contactors • Utilize various heat transfer internal patterns (pitch ratio, layout, orientation) • Well instrumented • Utilize existing screw conveyors for sorbent delivery
Evaluate bed hydrodynamics	• Measure bed densities, pressure drop, fluidization • Define regions of operability for gas and solids flow
Evaluate heat transfer	• Measure heat transfer coefficients • Determine heat transfer efficiency throughout bed



Heat Transfer Evaluations

Process and Instrumentation Diagram



CFD Modeling

Support for bench-scale and pilot-scale R&D

- R&D Scope of Work
  - Validate MFIX model with experimental results
  - Develop MFIX predictive model to guide reactor designs
- Expected Results
  - Functional model to predict how design of heat transfer internals affects hydrodynamic and heat transfer properties
  - Fundamental understanding of:
    - gas/solids movement
    - mass transfer
    - heat transfer between gas-solid-surface
  - Reduced time to select optimal contactor designs for heat transfer system and 1 TPD pre-pilot unit

Status

→ In Progress

→ In Progress

Solids Handling and Control

Status

→ In Progress

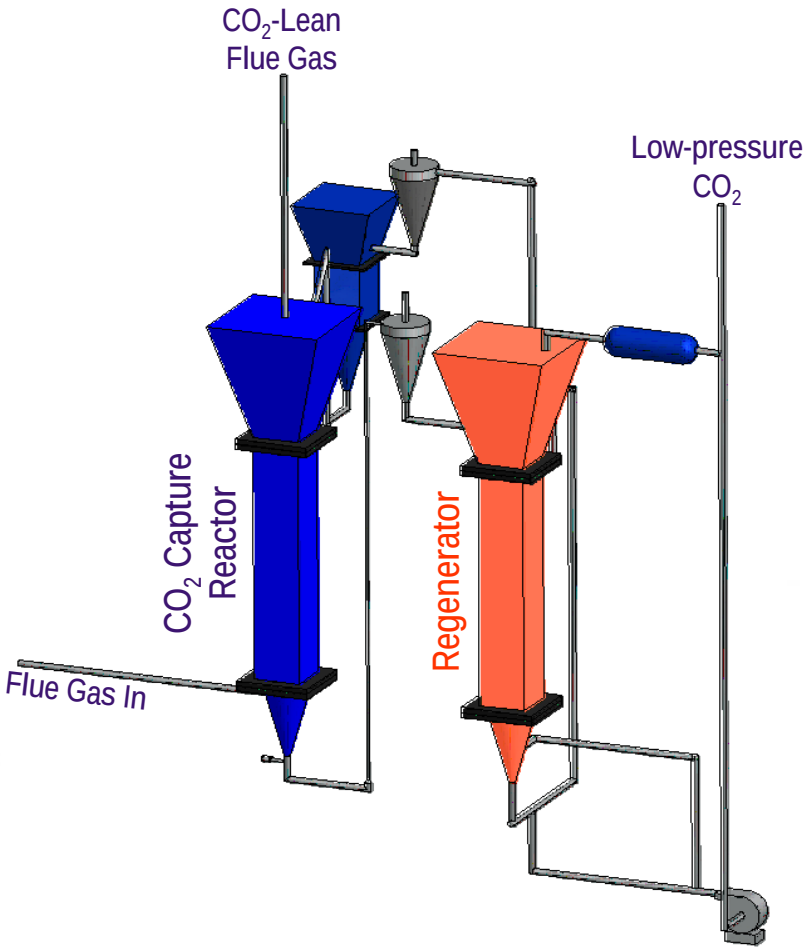
- R&D Scope of Work
  - Evaluate solids control valves
  - Pneumatic conveying of carbonate sorbent
  - Evaluate gas-solids separation and filtering
  - Consult with solids handling experts
- Expected Results
  - Determine optimal solids control technique for 1 TPD
  - Determine operating ranges for pneumatic conveyor
  - Determine optimal gas-solids separation technique
- Approach
  - Utilize solids flow equipment developed under DOE-funded project DE-FG36-04GO14312
  - Parametric testing of control valves, seals, conveying, and separation techniques

Design of Pilot-Scale Dry Carbonate Process

- Pilot-scale: 1 ton per day CO_2 Capture Unit
- Sizing:

CO_2 Captured (90%)	2000 lbs/day, 84 lbs/hr
Flue Gas Flowrate (wet)	8,730 SCFH
Initial Sorbent Loading	1,500 lbs
Sorbent Circulation	500 – 1500 lb/hr
Sizing of Test Unit	12' tall - 4' X 4' footprint
Cooling Load (water)	10 gpm
Heating Load (steam)	140 lb/hr

- Modular design
- <u>Current work</u>: sizing, reviewing fabrication needs, creating PFDs and P&IDs, process control



Path Forward

EPA Field Testing of Pilot Dry Carbonate Process

Objectives:

- 2,500 hours online
- Utilize 10-20% slipstream of flue gas
- Multiple coals: bituminous, sub-bit., lignite

Expected Outcomes:

- Long-term reliability proven
- True measure of:
  - sorbent attrition
  - sorbent degradation
  - regeneration gas purity
- Parametric/sensitivity studies exhibit optimal conditions for Dry Carbonate Process

Slipstream Test Unit Design

Project Objective: Design for next scale-up phase – Slipstream Test Unit (STU)

Sizing: 5 MW equivalent slipstream at utility site

CO_2 Captured (90%)	~100 tons/day
Flue Gas Flowrate (wet)	700,000 SCFH
Initial Sorbent Loading	125,000 lbs
Footprint	400 – 500 ft^2
Cooling Load (water)	500 gpm
Heating Load (steam)	10,000 lb/hr

Potential demonstration site:

- UNC Chapel Hill power plant
- Power equivalent: ~ 60 MW_e
- CO_2 produced: ~ 1500 tons/day
- Potential to utilize plant for additional testing of 1 TPD unit

UNC Chapel Hill Coal-fired power plant

Source: Microsoft Live Maps

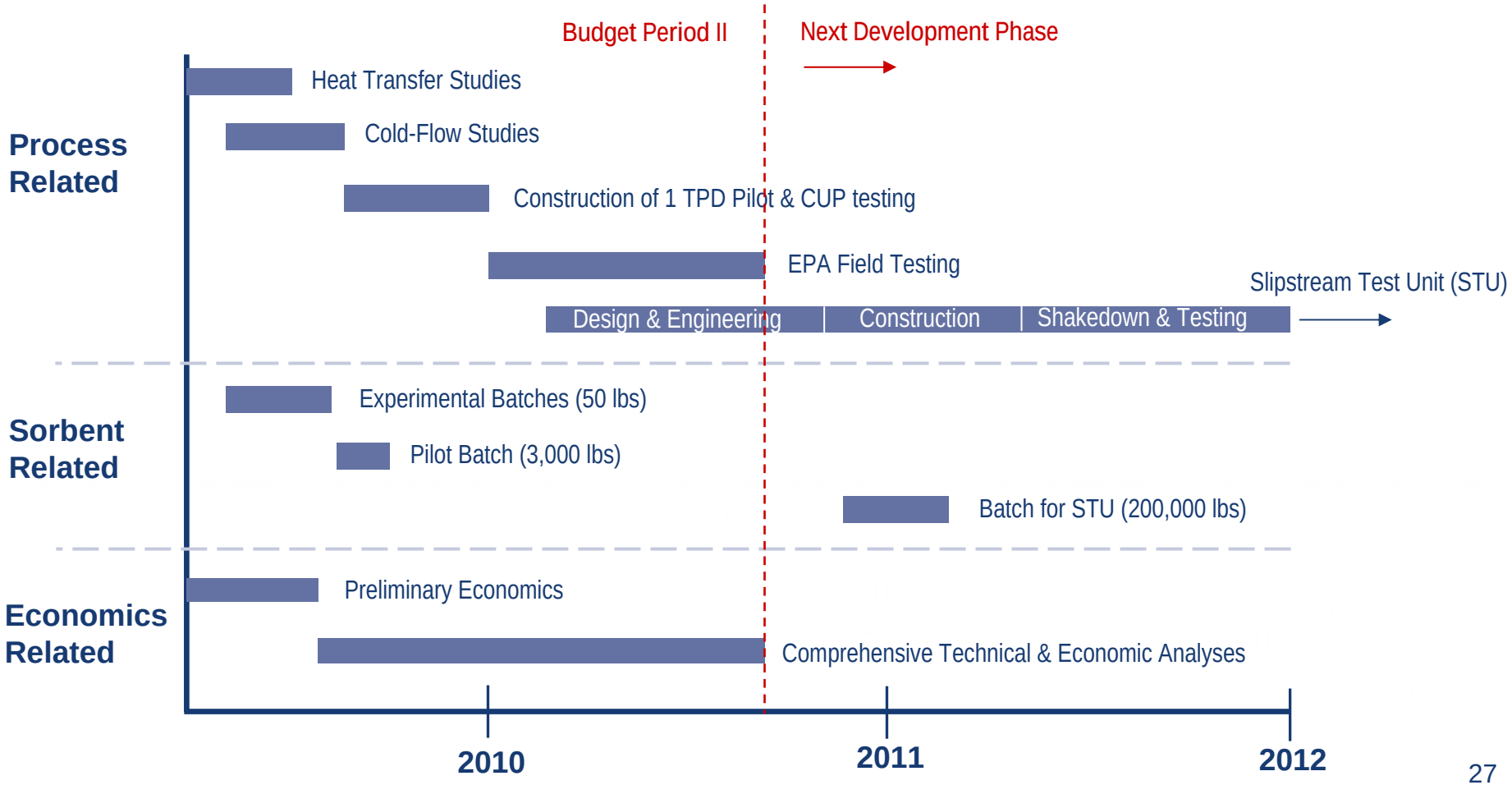
Detailed Economic Analyses

- Current work: Independent analyses of Dry Carbonate Process by EPRI and Nexant
- Phase I: Update cost analysis for new process design (Apr 2009)
- Phase II: Comprehensive technoeconomic analysis of Dry Carbonate Process (2010)
  - Baseline: Fluor's Econamine FG+ CO_2 capture process
  - Utilize data from pilot-scale testing
- Expected Outcomes: CAPEX, OPEX, Power Performance, Novel heat integration schemes, novel compression schemes
- Previous Preliminary Analyses:

Cost Summary	No CO_2 Capture[1]	With CO_2 Capture (MEA)[1]	With CO_2 Capture (Dry Carbonate)
Net Plant Power (MW_e)	462	329	**381**
Total Plant Capital Requirement ($ X 1000)	$ 591,714	$ 733,000	**$ 695,598**
Total COE, c/kWh	5.51	8.73	**7.46**
$/ton CO_2 removed	NA	29.2	**17.7**

[1] Source: *"Evaluation of Innovative Fossil Fuel Power Plants with CO2 Removal"*, DOE/EPRI, 1000316, December 2000

Development Timeline



Path to Commercialization

Development timeline for RTI's Dry Carbonate Process

2001
Laboratory and "proof of concept" studies

2003
Novel CO_2 capture sorbent developed based on supported sodium carbonate

2005
RTI field testing proves feasibility of dispersed gas-solid reactor design

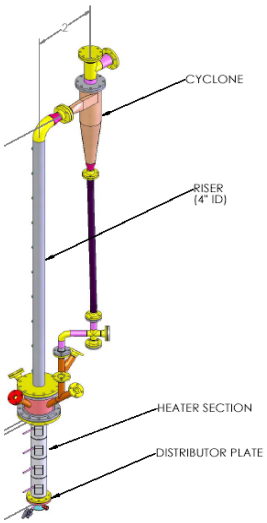
2007
Bench-scale system successfully tested at coal-fired research facility

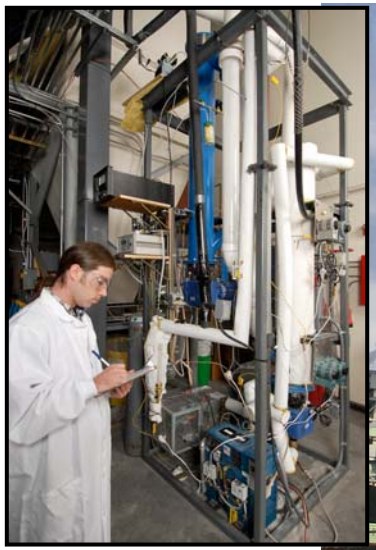
→

2010
Pilot-scale demonstration of technology – up to 1 ton CO_2 captured per day

2012
Large-scale demonstration at utility company site – 100 ton CO_2 captured per day

>2015
Commercial Technology





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