Seventh Annual Conference on Carbon Capture & Sequestration

Technical Session: Capture (Membranes/Sorbents) (1)

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

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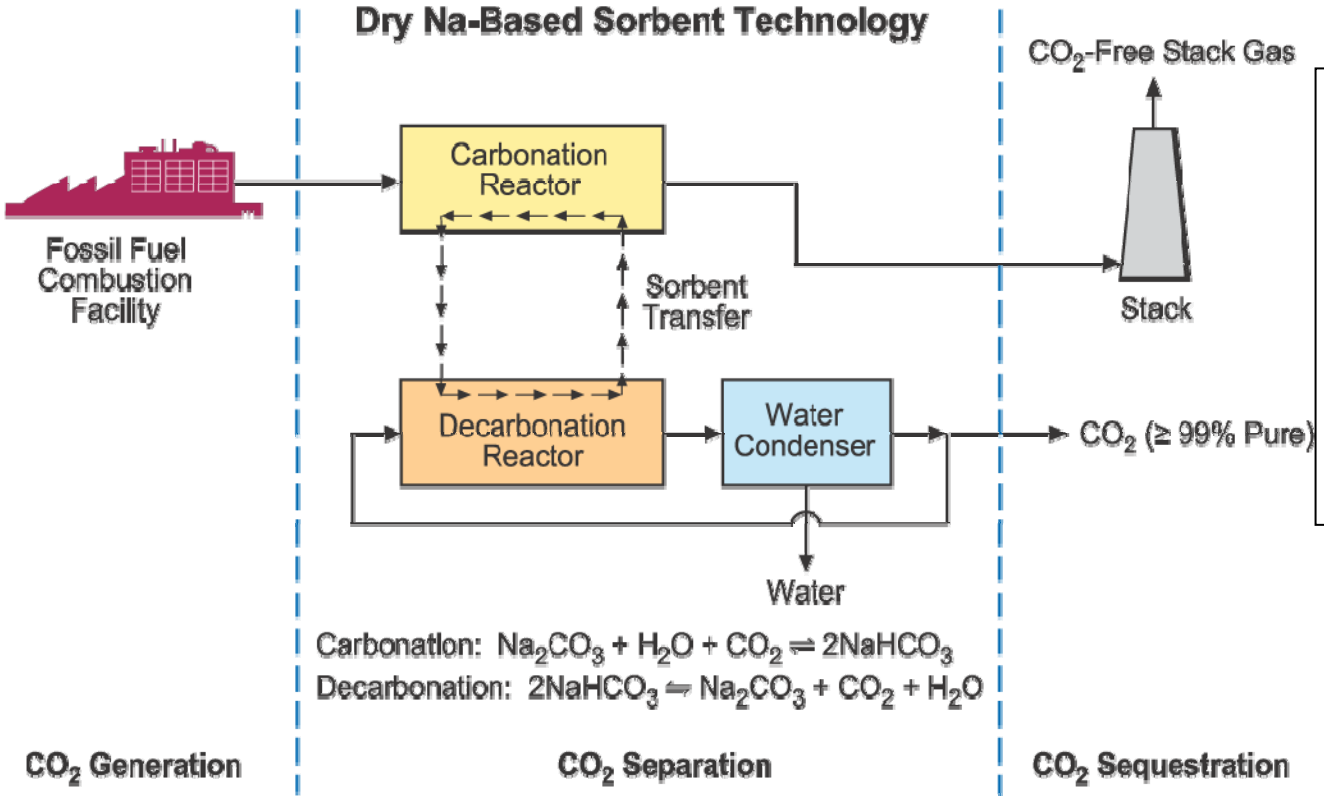
The Dry Carbonate Process

CO_2 Capture from Flue Gas



Key Features

- Dry, sorbent-based
- Known carbonate chemistry
- Regenerable
- Thermal-swing
- Retrofit technology
- Ideal for coal-fired plants

A 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: >120°C

Contaminants

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

Reactions with SO_2 & HCl are irreversible at process conditions

No observed effects by O_2, Hg, and NO_x

Challenges of Post-combustion CO_2 Capture

- Enormous volumes: 1,200,000 acfm, 9,000 tons/day CO_2 captured
  - Large quantities of reactive material, large equipment, short residence time
- Dilute CO_2: concentrations of 10 – 15%
  - Not ppm levels like SO_2 NO_x Hg
- Low pressure
  - Decreased driving force for chemical reactor
- Contaminants: SO_2, Hg, NO_x, particulates, and presence of O_2
  - Potential loss of reactive material, performance hindrance, and unwanted byproducts
- Sequestration requirements: 2,200 psia, 98% pure CO_2
  - Large energy penalty for compression
- Parasitic power load: all processes require energy to operate

Potential Advantages of Using Sodium Carbonate

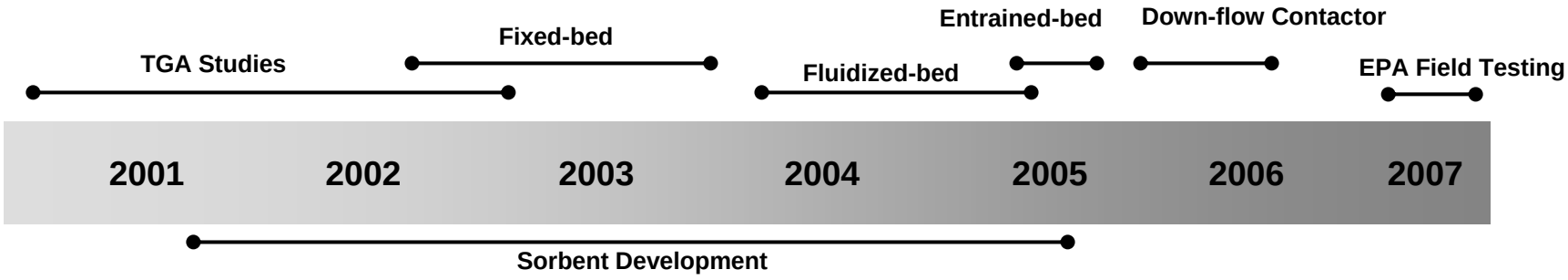
- Energy efficient capture of CO_2
  - lower total regeneration energy requirement than existing amine-based processes
- Potential for lower CO_2 removal cost
  - low raw material cost
  - operating and capital savings
  - lower energy penalty
- Modest temperatures of operation
  - CO_2 adsorption at ~60°C ideal for flue gas from wet FGD
  - regeneration at ~120°C requires modest temperature swing
- Carbonate chemistry is well-known
- Non-hazardous and non-toxic materials
- Tolerance to contaminants in flue gas
- No hazardous waste generated

Challenges of CO_2 Capture with Sodium Carbonate

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

- $Na_2CO_3 : CO_2$ = 2.4 : 1 mass ratio
- Exothermic CO_2 adsorption / equilibrium limited: need efficient temperature control to achieve 90% CO_2 capture
- Sorbent regeneration requires external heat input
- CO_2 adsorption requires water present in stoichiometric ratio
- Na_2CO_3 reacts irreversibly with SO_2 and HCl at process conditions
- Raw sodium carbonate is not physically strong
- Raw sodium carbonate tends to agglomerate in presence of liquid water

Technology Development



- Sorbent Development
  - Evaluated pure sodium bicarbonate, Trona, supported sorbents
  - Supported sorbent advantages: better initial reactivity, physical strength/attrition resistance
  - Supported sorbent manufactured by Süd-Chemie, Inc. (~500 lbs to date)
- Process Development
  - Evaluated fixed-bed, fluidized-bed, and entrained-bed reactor systems
  - >90% CO_2 capture achieved and maintained over multiple cycles
  - Temperature rise during adsorption may be a process issue for fixed-bed and fluidized-bed
  - Problems minimized in entrained-bed system (dispersed solids in gas)
- Proof of concept has been demonstrated with actual coal-fired flue gas

The Dry Carbonate Bench-Scale Unit

System Specifications

- Screw conveyors: 8” diameter and 6’ length
- Sorbent circulation rate: 25 – 250 lb/hr
- Designed to “treat” up to 200 SLPM of flue gas
- Heated screw conveyor is rated to 80 psi (315ºF saturated steam)
- Steam generated by small laboratory boiler
- City water used for cooling

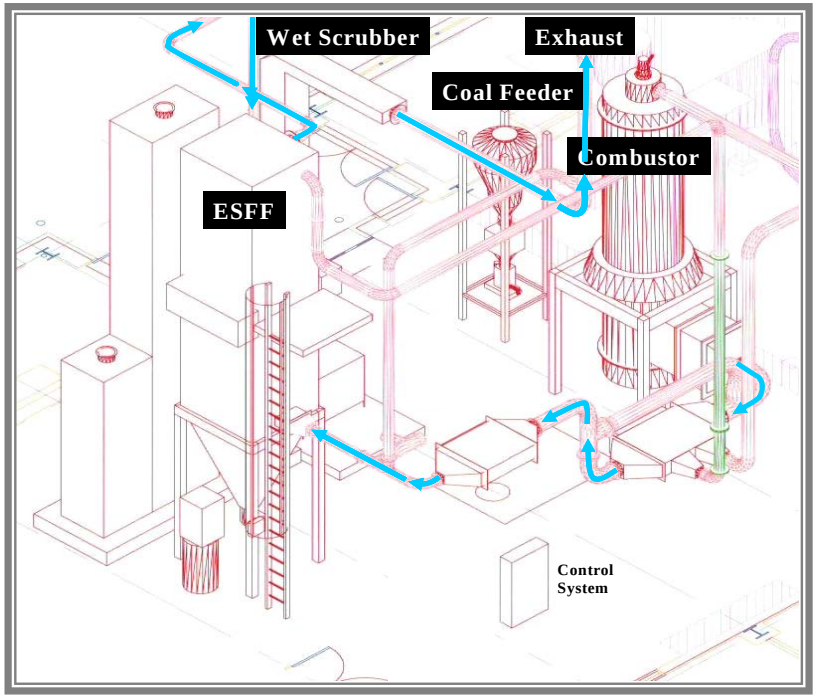
Note:

This “integrated” system was built after individually verifying the performance of each process component

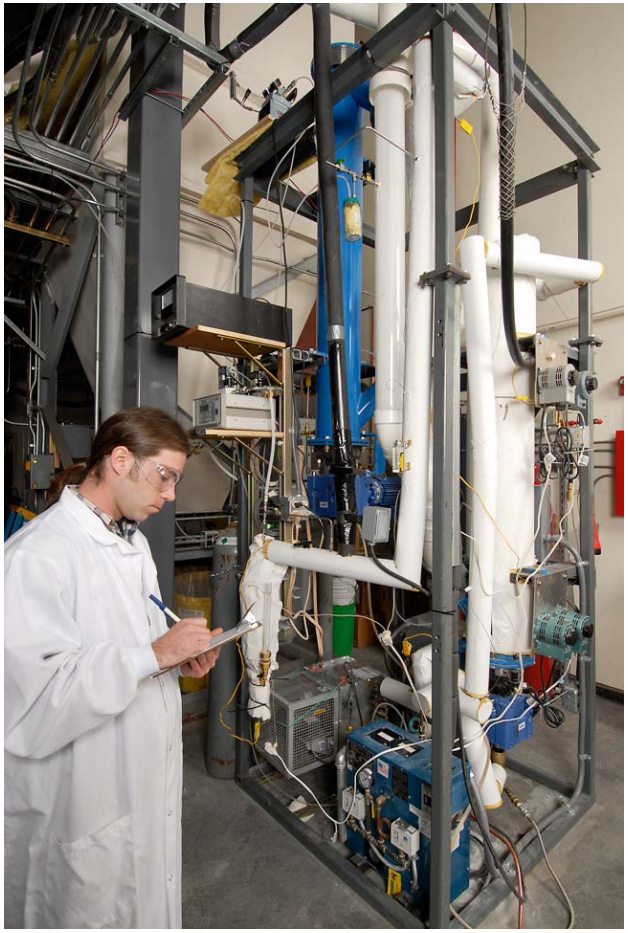
Field Testing of the Dry Carbonate Unit

U.S. EPA – Research Triangle Park, NC

- EPA's Combustion Research Facility
  - 4 Million Btu/hr (1.2 MW_t) multi-fuel fired facility
    - 330 lb/hr bituminous coal
    - 120 m^3/hr natural gas
  - 10 ton/day CO_2 produced (24 hr operation)
  - Designed as a field test site to evaluate different control technologies
    - SCR; wet FGD; Hg control; particulate control
  - Location: RTP, NC (2 mi from RTI)
- RTI's Dry Carbonate Unit was operated at EPA site
  - Testing was coordinated with ARCADIS, Inc, (EPA's on-site contractor)
  - ~1-2% slipstream of EPA's flue gas



Field Testing of the Dry Carbonate Unit



Highlights

Natural Gas Combustion

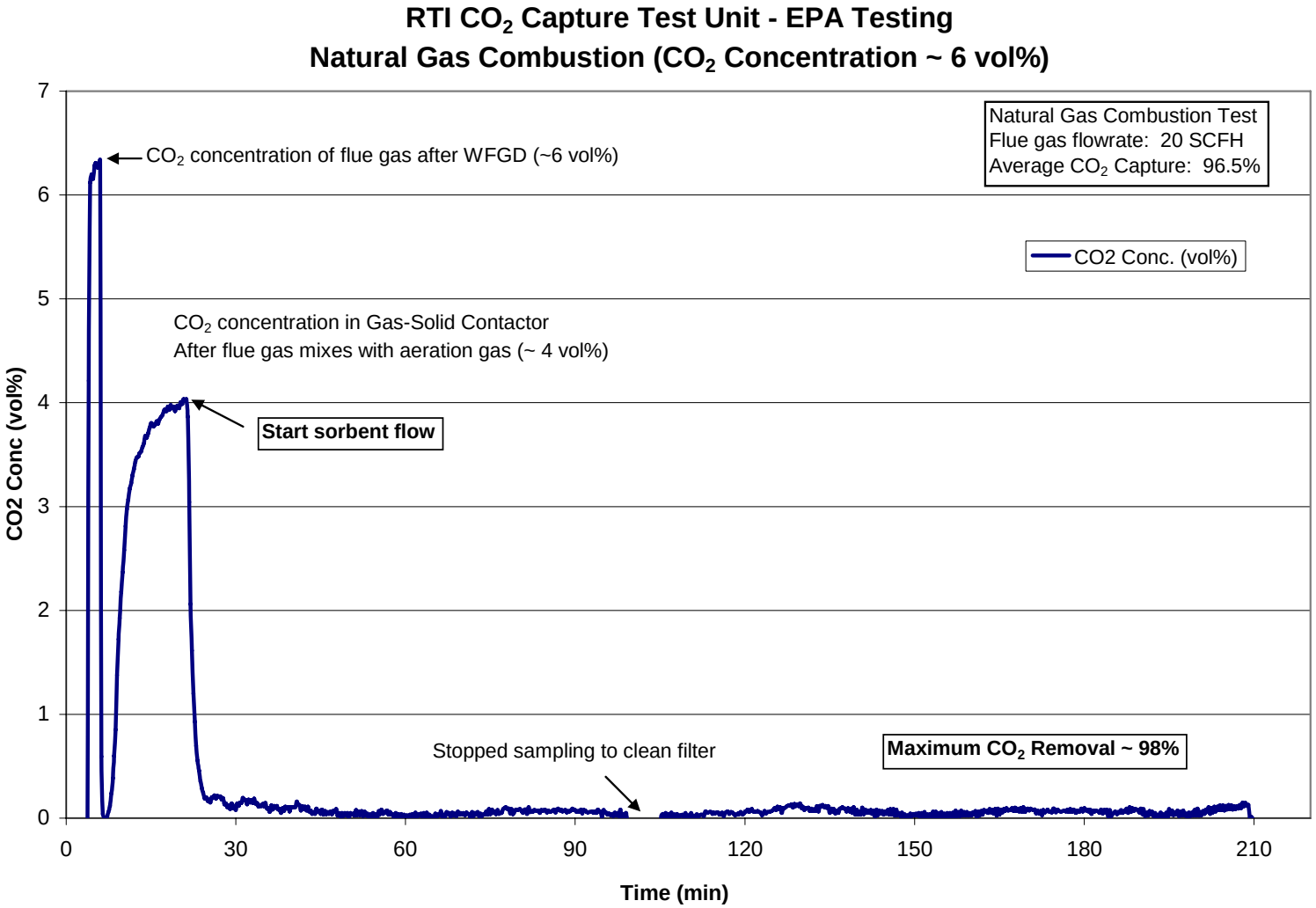
- *130 hrs* exposure to natural gas derived flue gas
- CO_2 concentration in flue gas: *~6 vol% (before dilution)*
- maximum CO_2 removal achieved: *~99%*

Coal Combustion

- *105 hrs* exposure to coal-derived flue gas
- CO_2 concentration in flue gas: *~10.5 vol% (before dilution)*
- SO_2 concentration in flue gas: *~20 ppm*
- coal supply: mixture of eastern bituminous and PRB
- maximum CO_2 removal achieved: *~92%*

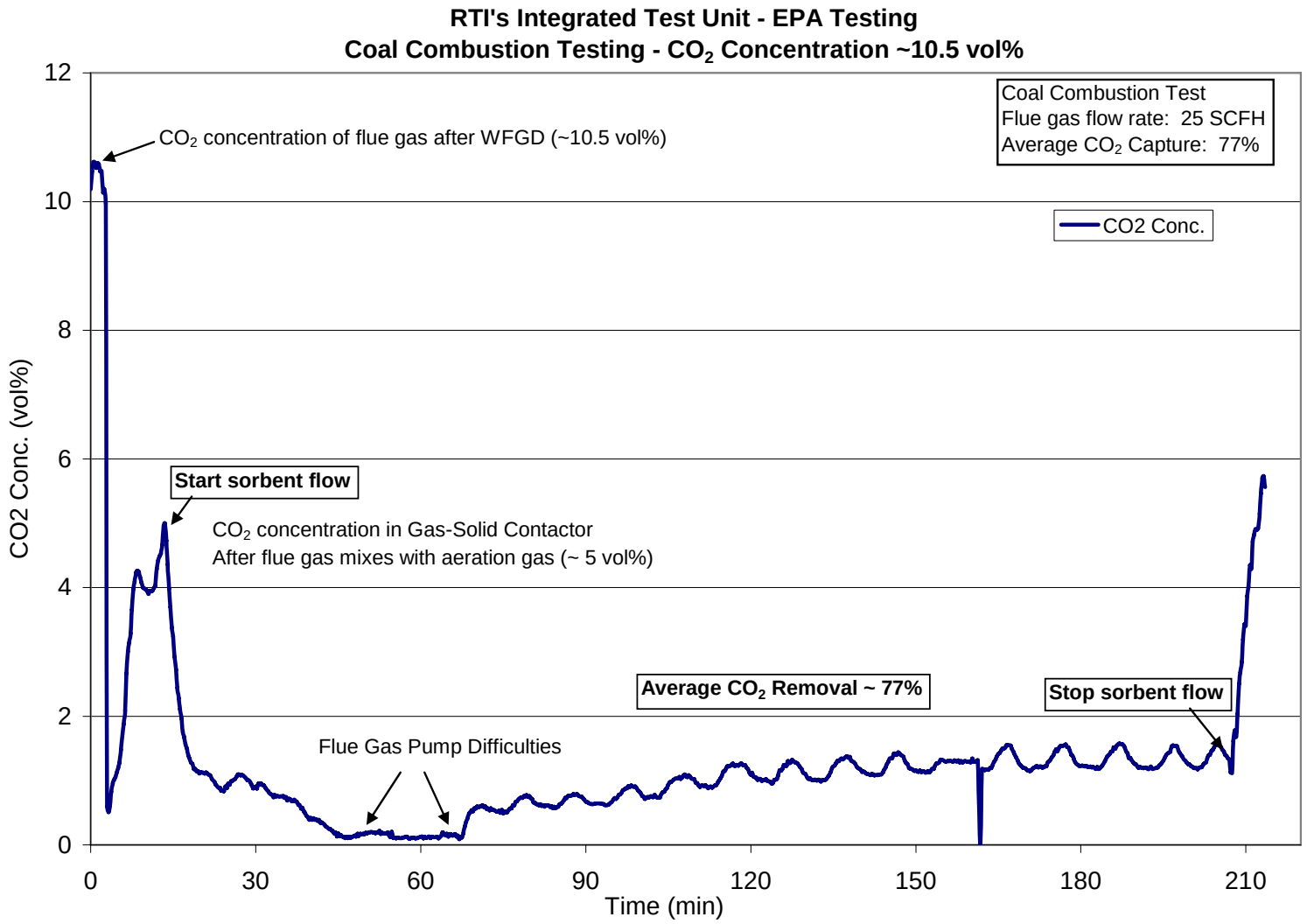
Field Testing at U.S. EPA

Natural Gas Combustion



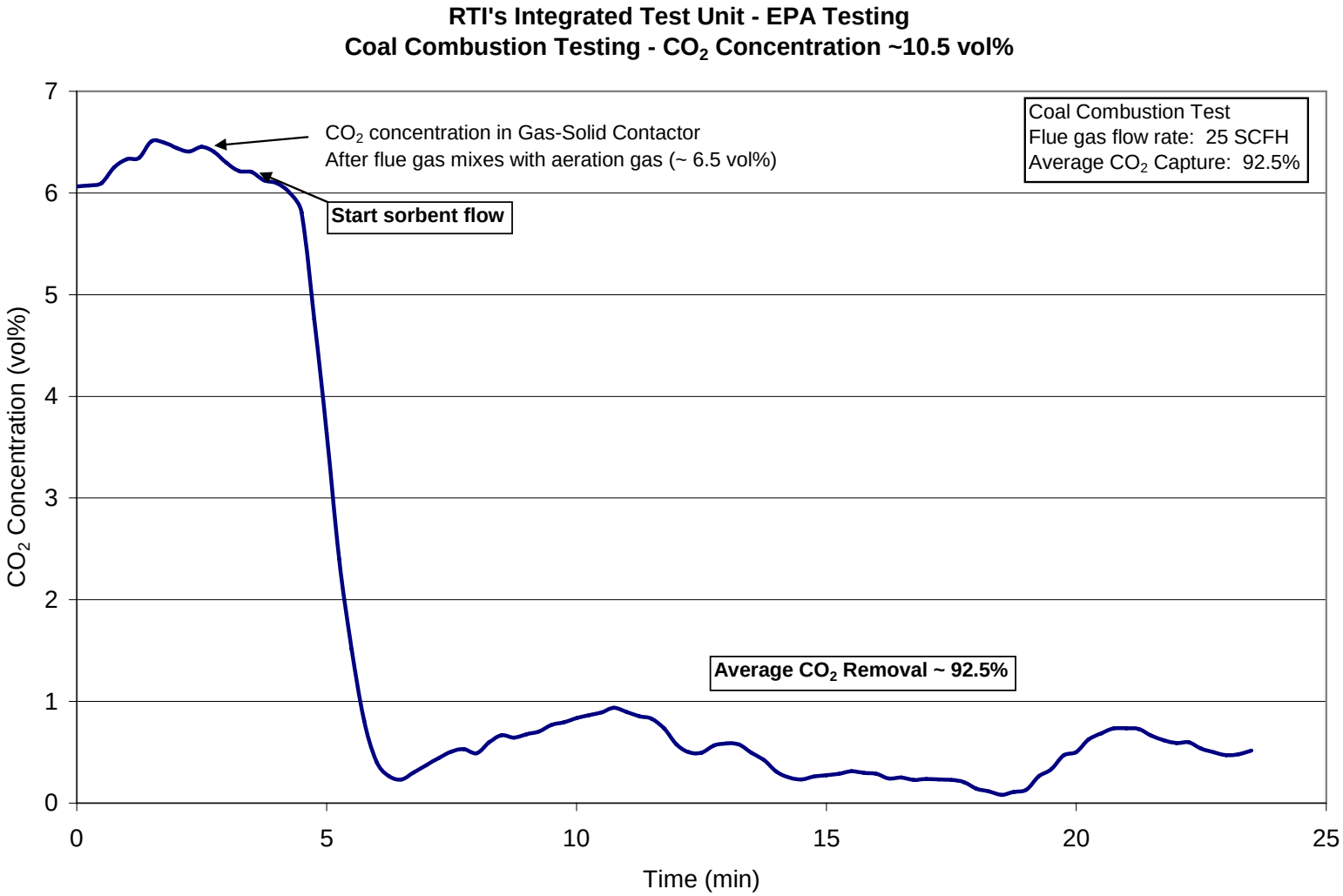
Field Testing at U.S. EPA

Coal Combustion



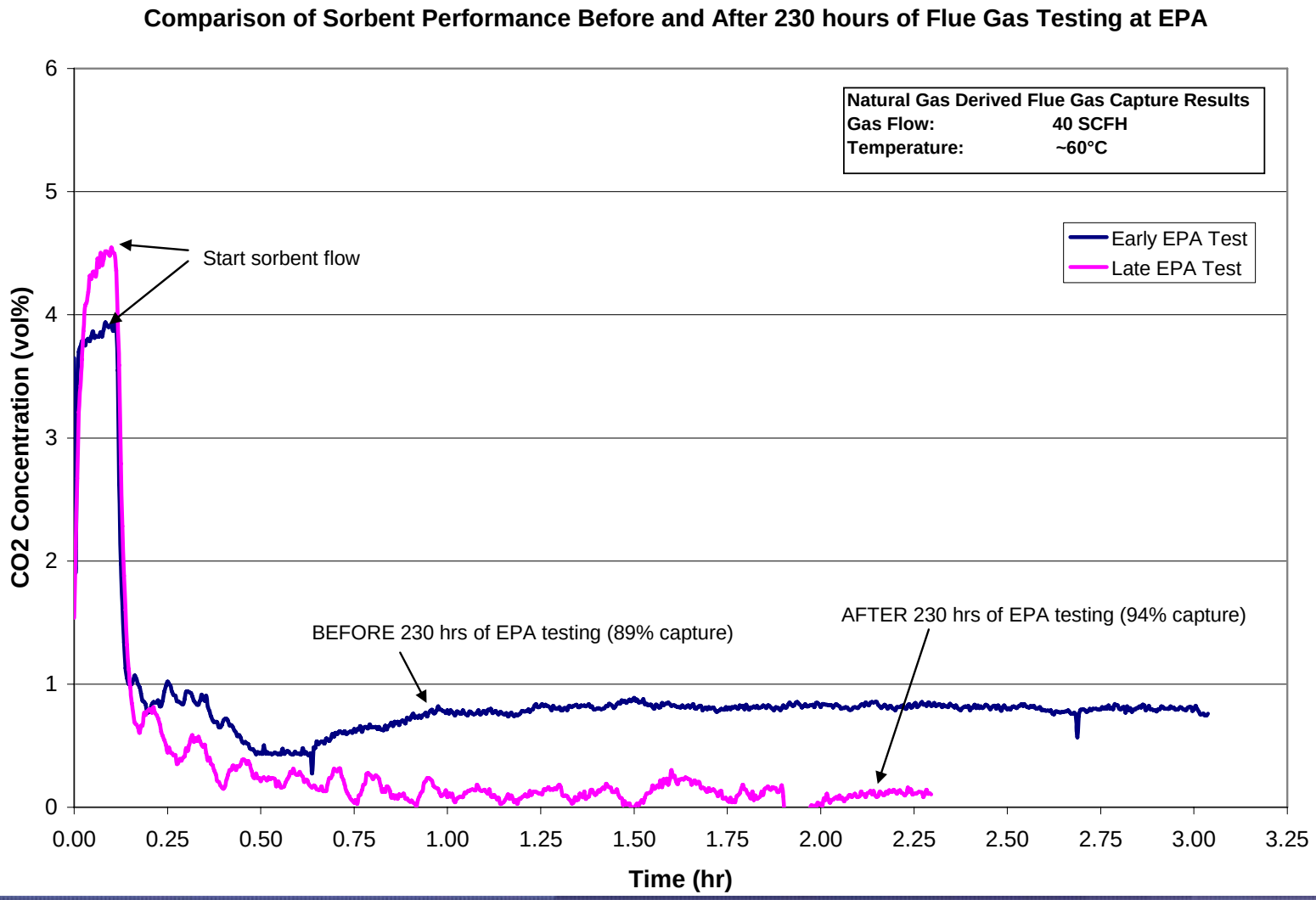
Field Testing at U.S. EPA

Coal Combustion



Field Testing at U.S. EPA

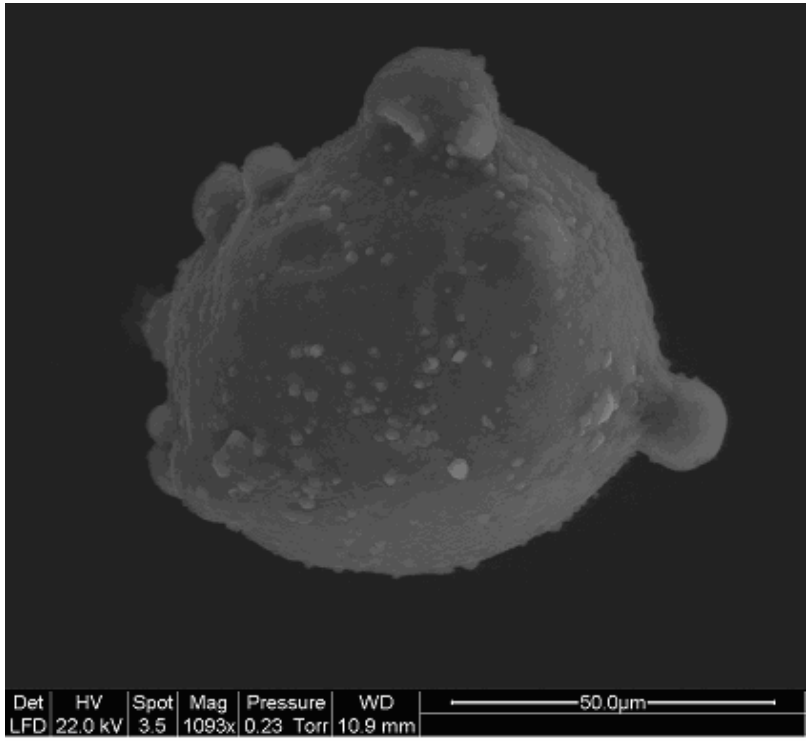
Sorbent Performance after Extended "Real" Flue Gas Testing



Analyses of Fresh and Reacted Sorbent

	Fresh	After EPA Testing
Surface Area (m^2/g)	106	94
Total Pore Area (m^2/g)	160	128
Porosity (%)	47	37
S content (ppm)	N/D*	N/D*
Hg content (ppm)	N/D*	N/D*
As content	N/D*	N/D*

N/D* = not detected



Key Findings of Field Testing at U.S. EPA

Performance Observations

- *Capable of >90% CO_2 capture in both coal and natural gas flue gas*
- *Capable of sustained CO_2 capture*
- *Simulated vs. actual flue gas: observed little difference in capture performance*
- *No negative effects observed due to contaminants in flue gas.*
- *Sorbent properties changed slightly and showed minor signs of physical wear.*

Lessons Learned

- *Regeneration temperatures above 120°C are ideal for full sorbent regeneration.*
- *CO_2 capture performance is better with more complete sorbent regeneration.*
- *Amount of steam delivered is important criteria to achieve target regeneration temp.*
- *Capture performance improves with longer absorber residence time.*
- *Deeper cooling of sorbent improves CO_2 removal – i.e. heat control is more effective.*

Key Findings of Preliminary Economic Analysis

- Dry Carbonate Process has potential to significantly reduce the CO_2 capture costs over amine-based systems
- Potential to meet DOE program goals (90% capture, <20% increase in COE)
- Analysis uncertainties: capital costs (e.g. compressor, reactors); LP steam extraction; land use
- Significant engineering work is needed to develop a commercial system.
  - Heat integration is critical. Utilize available heats from process and power plant.
  - Optimizing sorbent capacity will further reduce equipment sizes and energy required.
  - Limiting flue gas pressure drop is still very important.

Path Forward

- DOE-funded project focused on continued development of Dry Carbonate Process
- Engineering evaluation of adsorber and regenerator process designs
- Finalize process designs
- Evaluate on bench-scale
- Scale-up to “pre-pilot” scale (1 ton CO_2 captured per day)
- Evaluate at EPA facility
- Develop “Slipstream Test Unit” (5MW eq.) Design
- Update economics

Progress to Date

- Evaluated multiple process configurations for Dry Carbonate Process
- One new process design configuration shows most promise

Benefits	Engineering Challenges
• Indirect cooling during CO_2 adsorption • Minimizes solids handling • Less sorbent attrition • Longer flue gas residence time in adsorber • Scalable and modular design • Utilizes latent heat of steam for regeneration	• Pressure drop • Management of water vapor • Multiple trains required

- Constructing bench-scale system to evaluate new process concepts
- Started new, comprehensive economic analysis based on DOE system guidelines
- Optimizing sorbent to maximize dynamic capacity
- Engineering is underway for future “pre-pilot” test (1 ton/day CO_2 removed) at EPA combustion facility

Path to Commercialization

Anticipated 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

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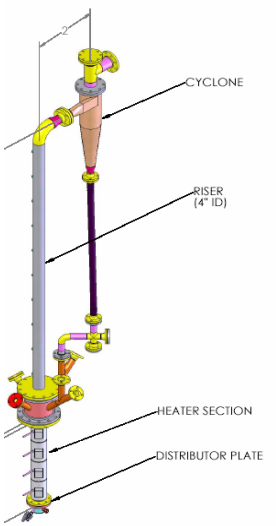
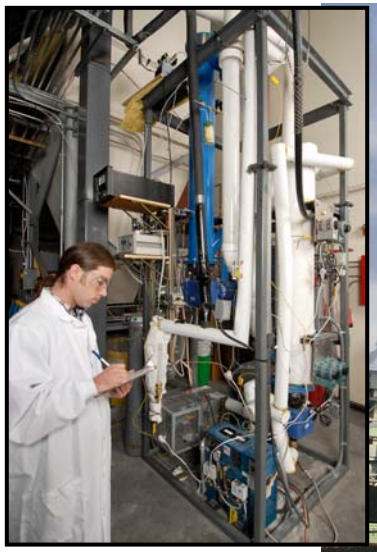
2009
Pilot-scale demonstration of technology – 1 ton CO_2 captured per day

2011
Large-scale demonstration at utility company site – 50 ton CO_2 captured per day

2015
Commercial Technology





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