turning knowledge into practice

Carbon Capture Technologies and Implementation Challenges for the Cement Industry

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RTI International

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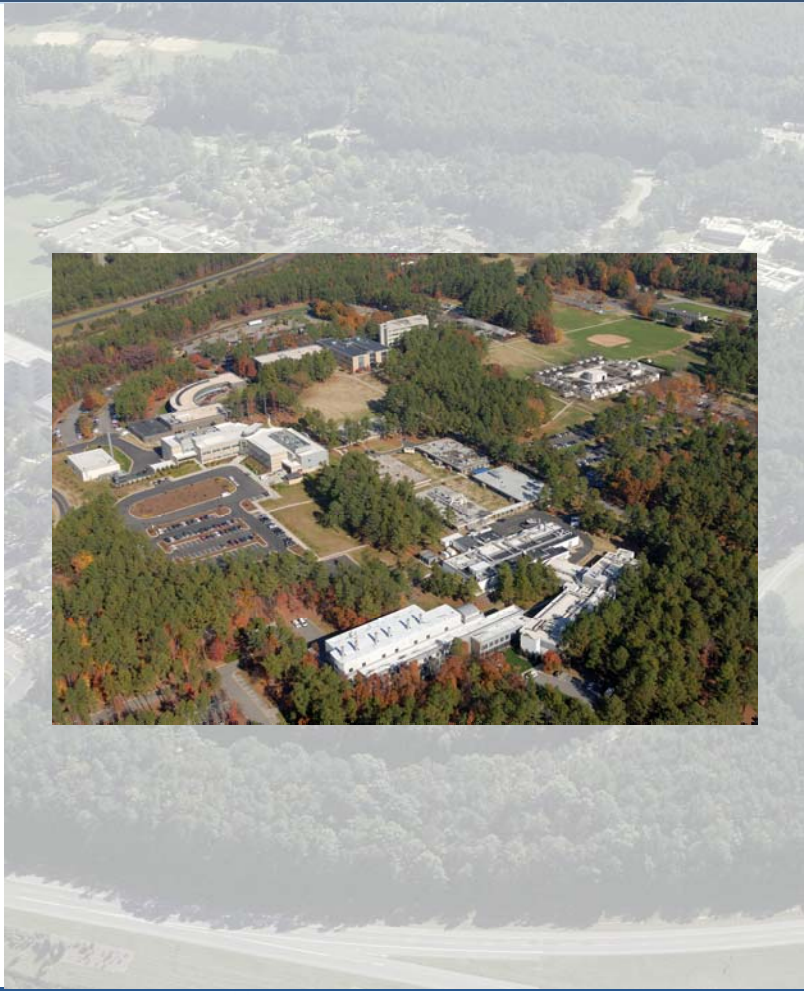
RTI International is a trade name of Research Triangle Institute

RTI International

- The second largest non-profit research institute in the US
- Mission: To improve the human condition by turning knowledge into practice
- Headquartered on 180-acre campus in Research Triangle Park, N.C.
- Founded in 1958
- FY2008 Revenue - $ 710 million
- 2600 staff working in over 40 countries



CO_2 in the Cement Industry

- Cement industry releases 1.3 – 1.7 GtCO_2 annually
  - ~5% of global anthropogenic CO_2 emissions
  - General metric: 1 ton CO_2 emitted for every 1 ton clinker produced
- Two sources of CO_2:
  - *Raw material-derived*: **$CaCO_3 \rightarrow CaO + CO_2$**
  - *Fuel-derived*: **$C + O_2 \rightarrow CO_2$**
- What CO_2 regulatory environment awaits us? Who knows?
  - Multiple Congressional bills proposed (e.g. Lieberman-Warner, etc.); AB 32 legislation in California; Europe's cap and trade
  - Some form of carbon regulations are probably on the horizon
    - Primary target: Fossil-fuel fired power plants (~43% of global CO_2 emissions)
    - Secondary targets: Cement plants, steel mills, refineries

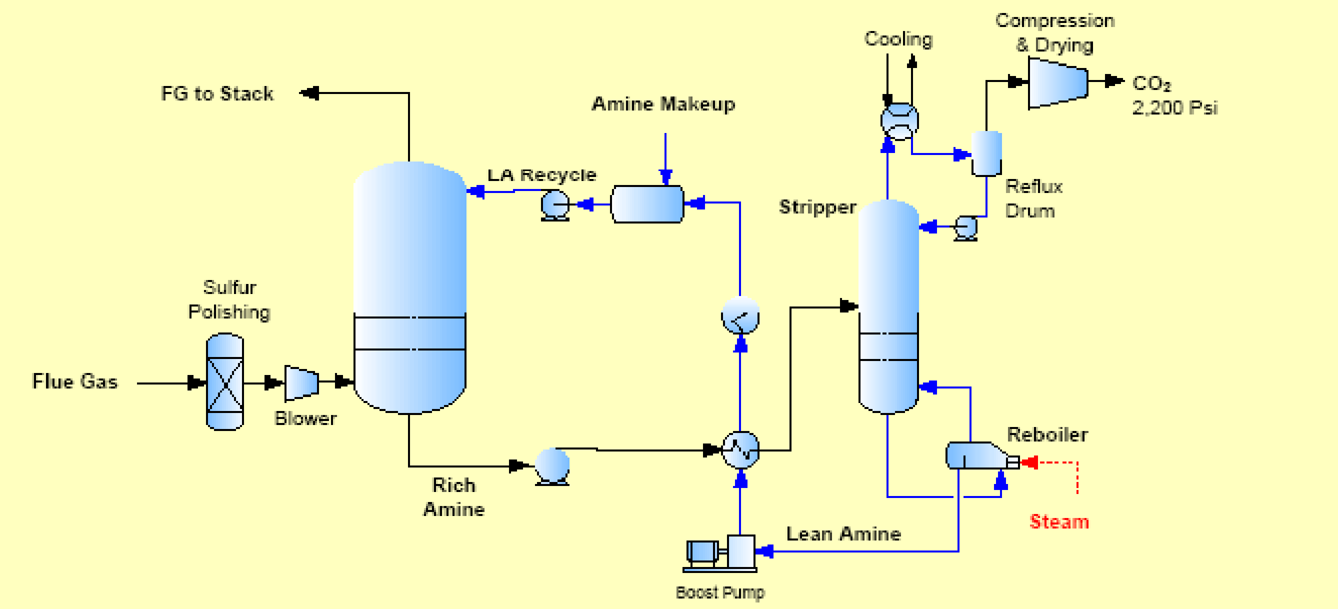
Carbon Mitigation Options

Carbon mitigation options

- Energy efficiency, blended cements, alternative binders, carbon neutral fuels, and…
- …several post-combustion CO_2 capture technologies are compatible with cement plant exhausts
  - Chemical solvents: amines, ammonia, carbonate solvents
  - Physical solvents: methanol, ionic liquids
  - Membranes: polymers, molecular sieves
  - Physical sorbents: metal organic frameworks
  - Chemical sorbents: carbonates, CaO, amine-enhanced zeolites

Conventional Technology: Monoethanolamine (MEA)

Amine CO_2 scrubbing



Absorption (°C)	60	Reboiler Heat Duty (kJ/kg CO2)	3600 - 4200
Regeneration (°C)	120	Auxiliary Power (MW)	19 - 22

MEA Process

- Proven
- Effective

but…

- Energy intensive
- Expensive
- Corrosive
- Hazardous waste produced

Source: *Existing Coal Power Plants and Climate Change…*, 2008 Energy Technology Forum, Ciferno J., DOE/NETL

RTI's Dry Carbonate Process

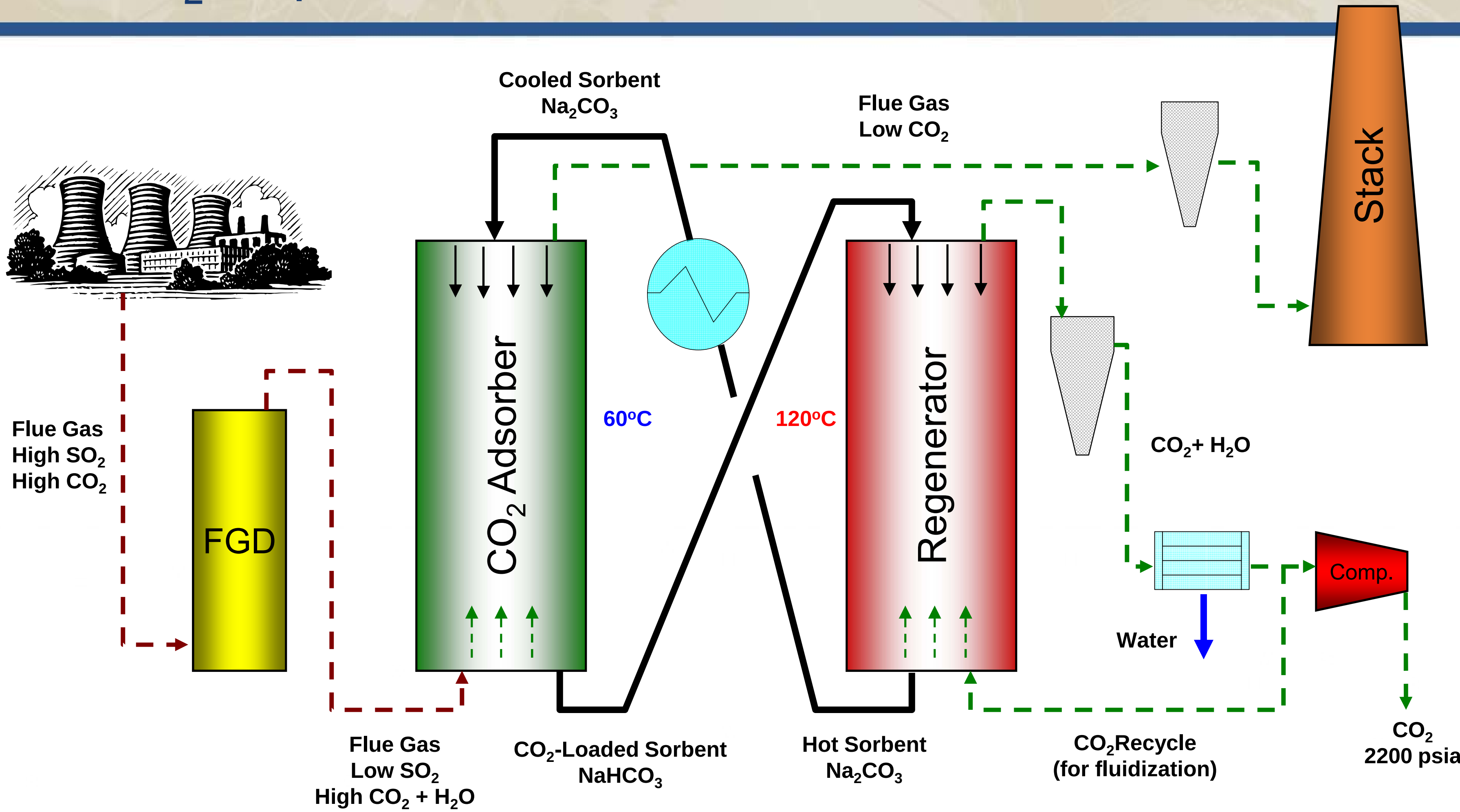
RTI's objective has been to develop a carbon dioxide capture technology that is

- Based on a solid, regenerable, carbonate sorbent
- Applicable to flue gases of coal and natural gas-fired power plants
- Intended for retrofit in existing plants
- Less expensive and less energy intensive than conventional technologies
- Of relatively simple process design

7 years of R&D effort with $7MM of DoE funding committed to date.

The Dry Carbonate Process

CO_2 Capture from Flue Gas



The Dry Carbonate Process

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 $\Delta H_r° = -3082$ kJ/kg CO_2

Operating temperature: < 80°C

Sorbent Regeneration

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

Endothermic $\Delta H_r° = 3082$ kJ/kg CO_2

Operating temperature: > 100°C

Contaminants

$Na_2CO_3(s) + SO_2(g) + \frac{1}{2}O_2(g) \rightarrow Na_2SO_4(s) + CO_2(g)$

$Na_2CO_3(s) + 2HCl(g) \rightarrow 2NaCl(s) + CO_2(g) + H_2O(g)$

Reactions with SO_2 and HCl are irreversible at process conditions

No observed effects by O_2, Hg, and NO_x

Advantages and Challenges of Using Sodium Carbonate

Advantages

- Lower total regeneration energy requirement (vs. conventional MEA)
- Lower CO_2 removal cost
  - Readily available, abundant, and inexpensive sorbent.
  - No flue gas pretreatment (no heating, no cooling, no guard beds)
- Non-hazardous and non-toxic sorbents; no hazardous waste generated

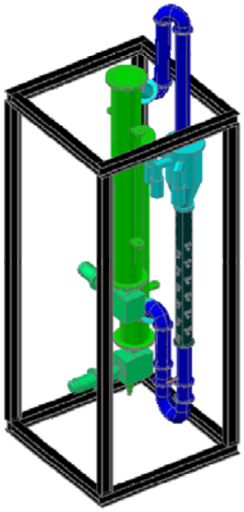
Challenges

- Large solids handling/circulation requirements
  - Best-case scenario → Na_2CO_3 : CO_2 = 2.4 : 1 (mass ratio)
  - *High capacity sorbents; best available solids handling technologies*
- Exothermic CO_2 adsorption affects reaction equilibrium
- CO_2 removal requires equimolar amount of water
- Condensed water causes raw Na_2CO_3 to agglomerate

RTI's Technology Development

Sorbent Development

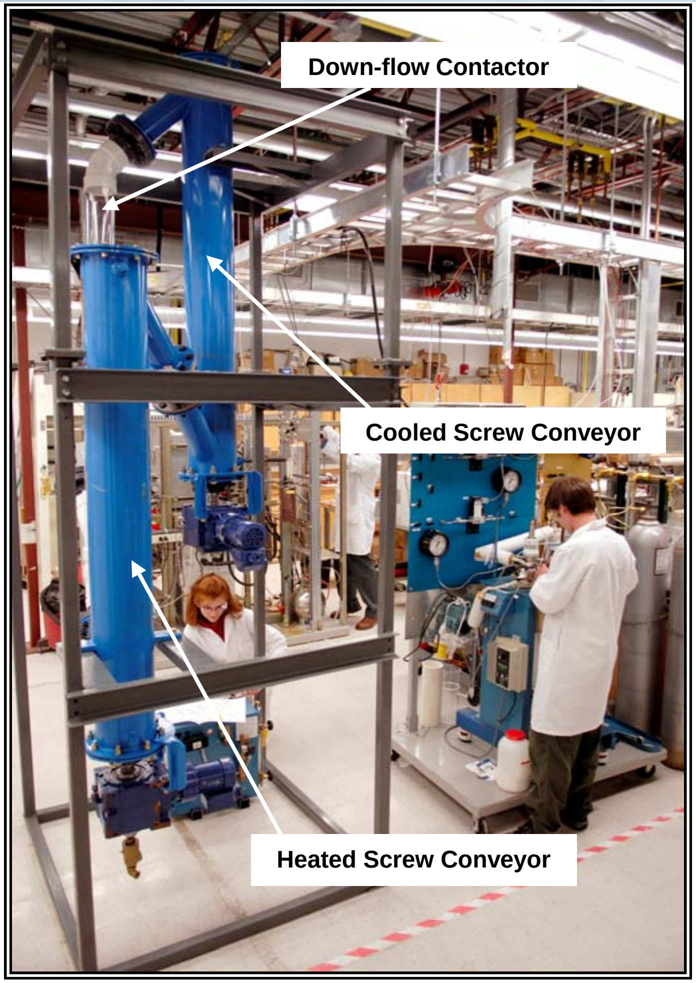
- Raw materials
  - *Higher theoretical capacity (~40%), inexpensive*
- Supported sorbents
  - *Improved reactivity, improved attrition resistance, improved ability to adsorb heat during exothermic CO_2 removal*
- ~225 kg supported sorbent manufactured to date



Process Development

- Entrained-bed reactor (Dispersed phase)
  - > 90% capture achieved
  - *Better heat control, better sustained reactivity*

The Dry Carbonate Bench-Scale Unit



System Specifications

- Designed to "treat" up to 200 SLPM of flue gas
- Sorbent circulation rate: 10 – 150 kg/hr
- Screw conveyors: 20 cm wide and 2 m tall
- Heated screw conveyor is rated to 550 kPa (~160ºC saturated steam)
- City water used for cooling

Note:
This "integrated" system was built after first verifying the performance of each process component individually

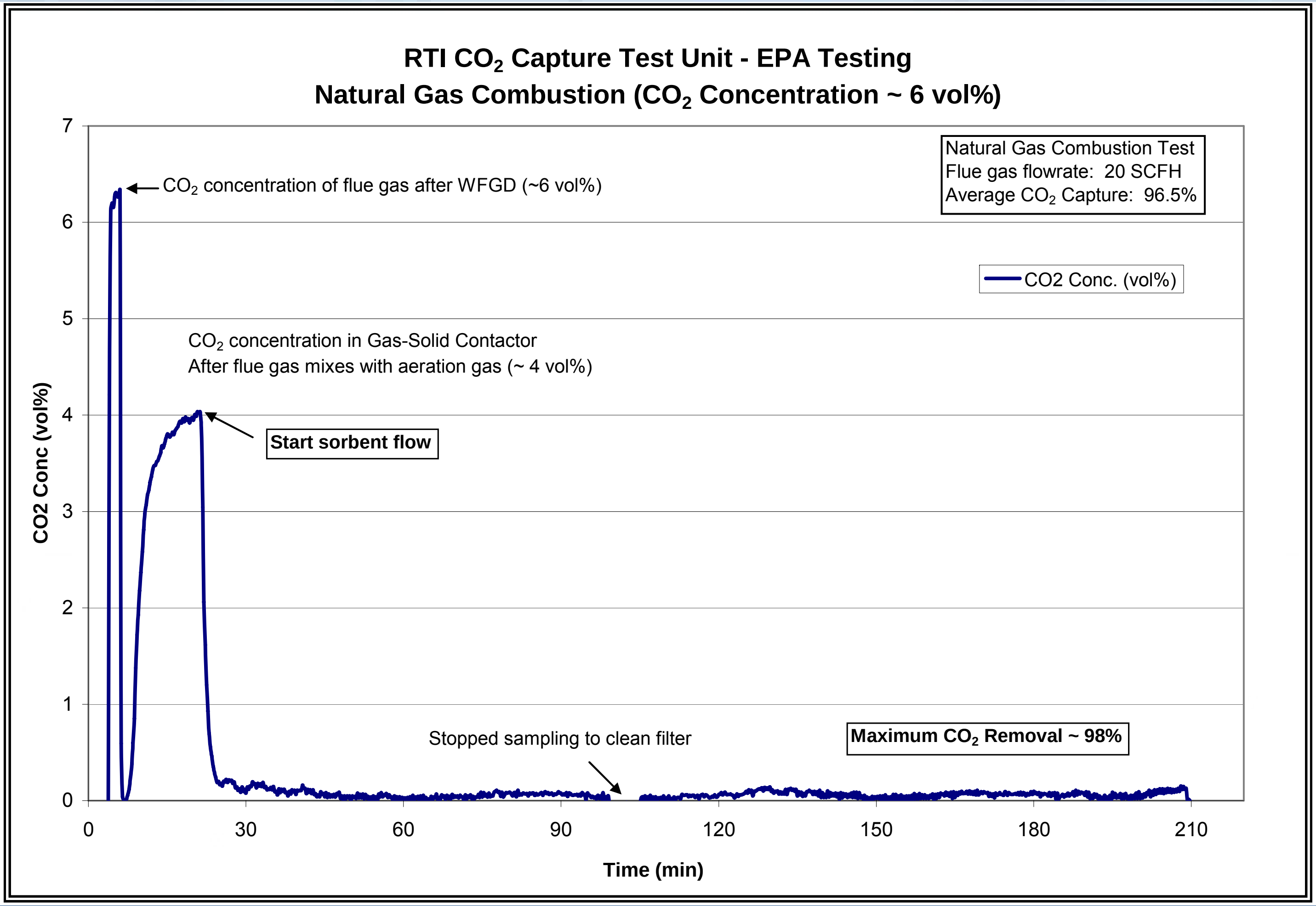
Field Testing of the Dry Carbonate Unit
U.S. EPA – Research Triangle Park, NC

- EPA's Multi-pollutant Control Research Facility
  - 4.2 Million kJ/hr (1.2 MW_t) multi-fuel fired facility
  - ~10 tonne/day CO_2 produced
  - Field test site used to evaluate emission control technologies
- RTI's Dry Carbonate Unit installed and operated at EPA site
  - Testing was coordinated with ARCADIS, Inc. (EPA's on-site contractor)
  - ~3-5% slipstream of EPA's flue gas
- Objectives
  - Evaluate process and sorbent using actual combustion flue gas
  - Identify optimal operating conditions
  - Evaluate sorbent degradation and effects of flue gas contaminants

RTI's Dry Carbonate Process prototype was tested at EPA for >230 hrs using coal & natural gas flue gas

Field Testing at U.S. EPA

Natural Gas Combustion



Key Findings of Field Testing at U.S. EPA

- Sorbent is capable of sustained >90% CO_2 capture in both coal- and natural gas-derived flue gas
- Sorbent regeneration more effective at 120 - 140°C (EPA steam header)
- No negative effects observed due to contaminants
  - No significant particle changes, no agglomeration, CO_2 capture not inhibited
- After > 1000 hrs of circulation, sorbent shows minor signs of wear
  - Slightly lower avg. particle size, surface area
  - Larger scale testing will be better for attrition analyses
- Further work required to optimize:
  - heat control in the adsorption unit to improve heat removal from the sorbent
  - Sorbent loading capacity for economical operation of process

Current R&D Findings and Path Forward

Bench-scale findings

- Sorbents with improved CO_2 loading capacities produced [> 15 wt% CO_2]
- Modified designs for the adsorption and regeneration reactors have been evaluated
- CO_2 capture and loading rate are greatly improved with improved heat transfer in absorber

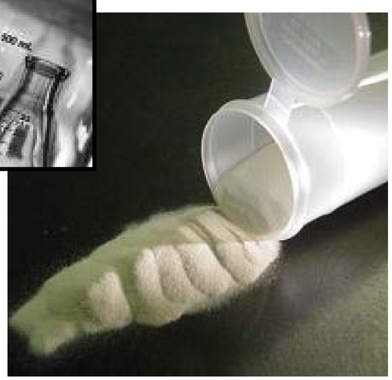
Process development and demonstration

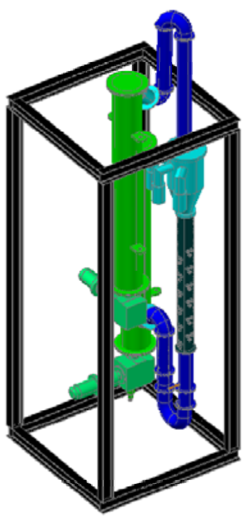
- Construction of a 0.3 MT CO_2 captured per day unit
- Long-term testing planned at RTI's Central Utility Plant and EPA site
- Testing expected to begin in mid-2009, last 8-10 months
- Data will be used to scale-up to 5 - 10 MT CO_2 capture per day
- Perform a comprehensive economic analysis

Path to Commercialization

Anticipated development timeline for RTI's Dry Carbonate Process

2001	2003	2005	2007	→	2010	2013	~2016
Laboratory and "proof of concept" studies	Novel CO_2 capture sorbent developed based on supported sodium carbonate	RTI field testing proves feasibility of dispersed gas-solid reactor design	Bench-scale system successfully tested at coal-fired research facility		Pilot-scale demonstration of technology – up to 10 MT CO_2 captured per day	Large-scale demonstration at utility company site – 500 MT CO_2 captured per day	**Commercial Technology**





Cement Plant vs. Power Plant

Comparison of exhaust gases at "typical" cement plant & power plant

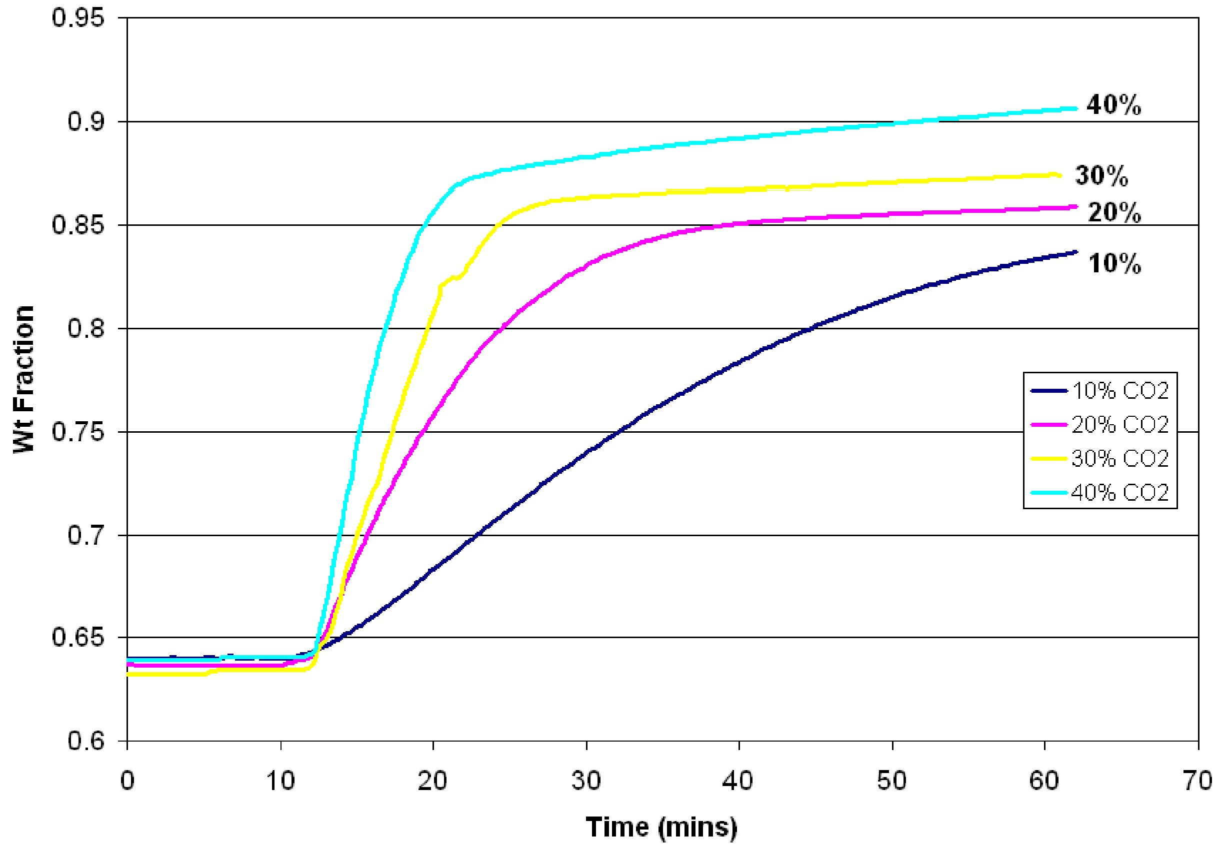
	Cement Plant[1]	**PC Power Plant[2]**
CO_2 (vol%)	22.4	13.1
H_2O (vol%)	7.2	17.3
SO_2 (vol%)	n/a	< 0.01
O_2 (vol%)	2.3	2.4
N_2 (vol%)	68.1	66.4
Temperature	160°C	60°C
Pressure	1 atm	1 atm
Flow rate	3,043 m^3/min	44,886 m^3/min
CO_2 Flow rate	~81 MT/hr	~765 MT/hr
Solids feed rate	~100 MT/hr (kiln feed)	~295 MT/hr (coal feed)

[1]Based on St Marys cement plant case study in S. M. Nazmul Hassan thesis,University of Waterloo, 2005 (2,400 TPD clinker rate)
[2]Based on case study in DOE's *Cost and Performance Baseline for Fossil Energy Plants*, August 2007 – 680 MWe PC power plant

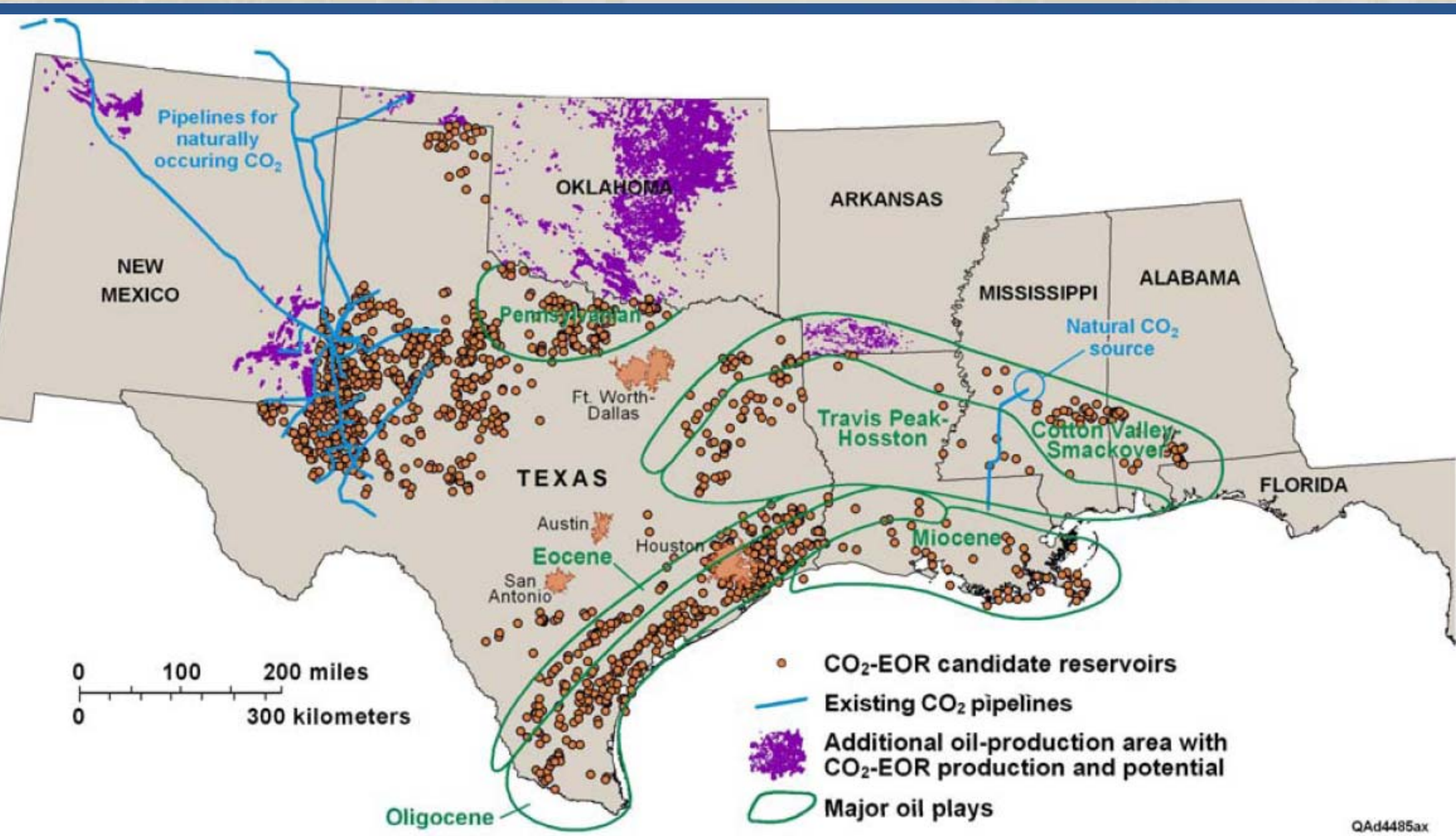
Higher CO_2 Concentration

Comparison of CO_2 capture rates at various CO_2 feed concentrations

TGA Data



CO_2 EOR Potential in the Gulf Coast



Ref: West Texas Geological Society Publ. #05-115
Fall Symposium, October 26-27, 2005
Mark H. Holtz, Vanessa Nunez Lopez, and Caroline L. Breton

Continuation of Cement Plant Evaluations

- Comprehensive economic analysis of Dry Carbonate Process installed at a cement plant
  - Capital & operating costs based on $/kg CO_2 removed & $/ton cement produced
- Evaluation of equipment size, full integration scheme, materials handling & storage, land use, resource availability, etc
- Testing of new sorbents under high CO_2 concentration and simulated cement exhaust gas
- Evaluation of CO_2 compression to pressures needed for pipeline delivery of CO_2 for EOR applications