The Partnership for CO₂ Capture Project Kickoff Meeting

Brandon Pavlish, Mike Jones, Steve Benson, Jason Laumb, John Kay, Josh Stanislowski, and Scott Tolbert

March 26, 2008
Energy & Environmental Research Center

Introductions



Brandon M. Pavlish Michael L. Jones Steven A. Benson Jason D. Laumb

Energy & Environmental Research Center University of North Dakota 15 North 23rd Street, Stop 9018 Grand Forks, ND 58202-9018





Agenda

Time	Activity	Discussion Leader(s)	
8:00 a.m.	Continental Breakfast	All	
8:30 a.m.	Welcome and Introductions	Steve Benson	
8:35 a.m.	Welcome by the EERC Director	Gerry Groenewold	
8:45 a.m.	CO ₂ Capture Background	Mike Jones	
10:15 a.m.	Break	All	
10:45 a.m.	CO ₂ Capture Challenges	Brandon Pavlish	
11:45 a.m.	The Partnership for CO ₂ Capture – Overview Brandon Pavl		
12:00 Noon	Business Lunch [Discovery Hall Lobby Area]	All	
1:00 p.m.	Work Plan •Task 1: Design and Construction (postcombustion) •Task 2: Oxycombustion Retrofit •Task 3: Shakedown and Testing •Task 4: Systems Engineering Studies	Scott Tolbert Jason Laumb John Kay Josh Stanislowski	
2:00 p.m.	Deliverables, Schedule, and Management (Task 5)	Brandon Pavlish	
2:30 p.m.	m. Project Sponsor Role Brandon Pavlish		
3:00 p.m.	Wrap-Up and Questions		
3:15 p.m.	Optional Tour of the EERC	Jason Laumb Brandon Pavlish	
3:45 p.m.	Adjourn		



Meeting Goals and Objectives

- Provide a synopsis of the current views of the impact of carbon dioxide (CO₂) on the climate
- Identify challenges facing industry
- Demonstrate how this program is addressing these challenges



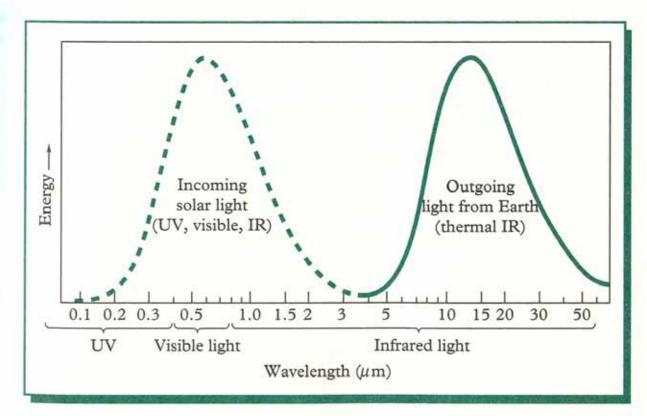
CO₂ Capture Background

CO₂ and the Environment

Mike Jones



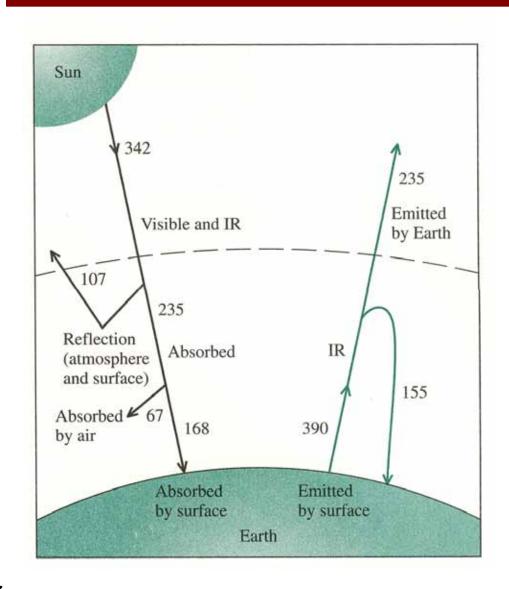
Earth's Energy Balance



Wavelength distribution for light from the sun and by earth surface and troposphere



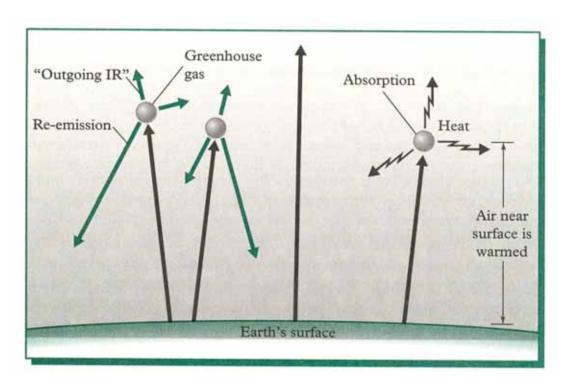
Average Energy Fluxes to and from the Earth (watts/m²)



Averaged day and night over all latitudes and longitudes and all seasons



Greenhouse Effect



- Outgoing infrared (IR) absorbed by greenhouse gases is either reemitted or converted to heat.
- Examples thermal IR region (4 to 50 μm):
 - Carbon dioxide absorbs light in two regions – maximum in the thermal IR region of 15 µm and at 4.26 µm.
 - CFC Light frequency matches of internal motion of molecule. resulting in vibrations – C–F bonds will absorb outgoing thermal IR light.



Contributions to Global Warming and Cooling

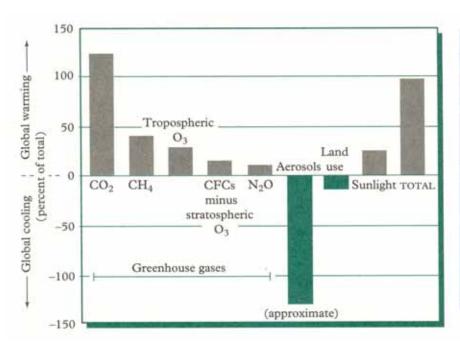
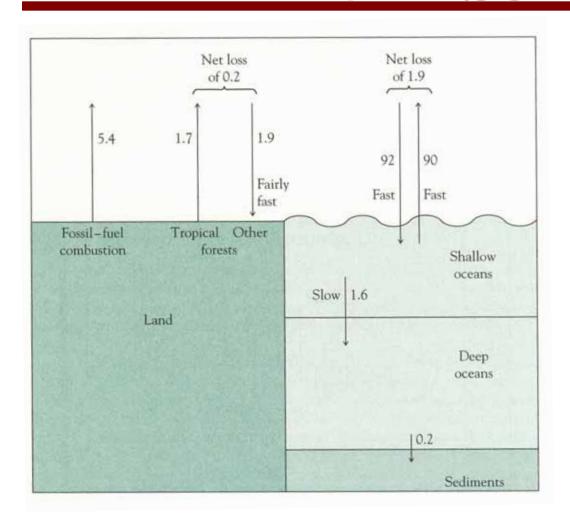


TABLE 4-1	Summary of Information About Some Greenhouse Gases				
Gas	Current concentration	Residence time, in years	Relative global warming efficiency, 100-year horizon		
CO ₂	373 ppm 50-200		1		
CH ₄	1.77 ppm	12	23		
N ₂ O	316 ppb	120	296		
CFC-11	0.26 ppb	45	4600		
HCFC-22	0.15 ppb	12	1700		
HFC-134a	0.01 ppb	14	1300		
Halon-1301	0.003 ppb	65	6900		



Annual CO₂ Fluxes to and from the Atmosphere (gigatonnes)



Mid-1980s data in gigatonnes of carbon (only) Note: 3.3 gigatonnes did not find a sink.



Carbon Dioxide

- One atom carbon and two atoms oxygen.
- Natural atmospheric constituent.
- 0.04% of atmosphere.
- Critical to plant life.
- Like water vapor and other greenhouse gases, supports the natural greenhouse effect that keeps the Earth livable.



CO₂ Capture Background

- Introduction
- Capture technologies
 - Postcombustion
 - Precombustion
 - Oxycombustion
- Challenges
- Current cost estimates

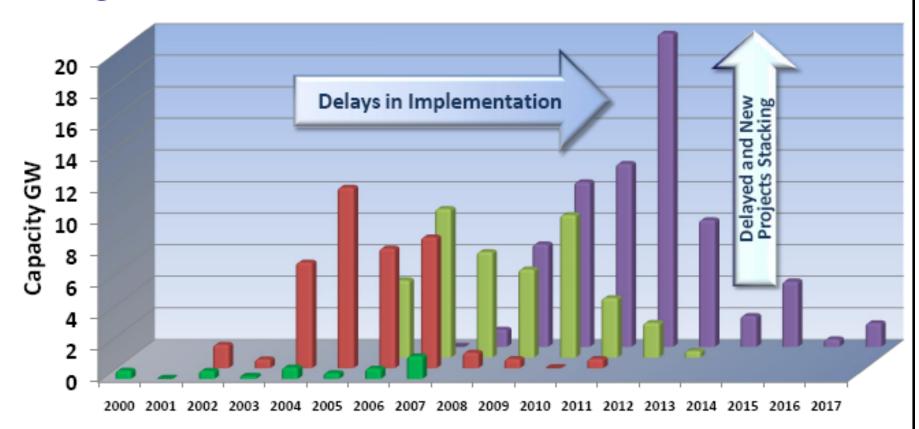


Introduction

Need for Research and Development



Past Capacity Announcements vs. Actual Figure 1



Historically, actual capacity has been seen to be significantly less than proposed capacity. For example, the 2002 report listed 36,161 MW of proposed capacity by the year 2007 when actually only 4,478 MW (12%) were constructed.



Actual



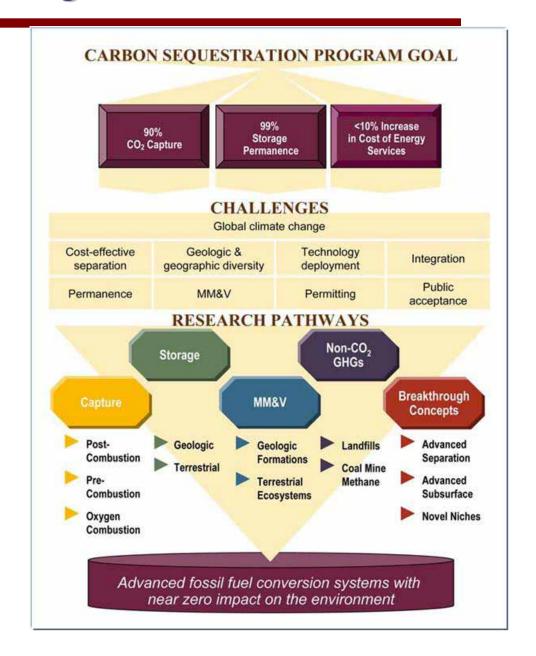
December 2007

DOE NETL Program Goals

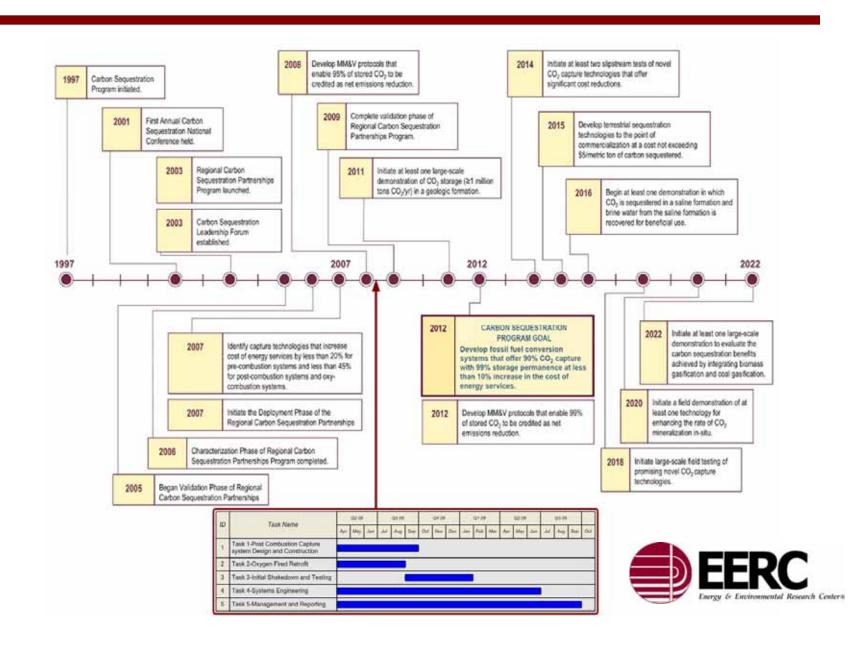
Carbon Sequestration Program Goal and Research Pathways:

The U.S. Department of Energy (DOE) National Energy Technology Laboratory (NETL) technology goal: "To develop, by 2012, fossil fuel conversion systems that offer 90% CO₂ capture with 99% storage permanence at less than a 10% increase in the cost of energy services."

Source: DOE NETL, "Carbon Sequestration Technology Roadmap and Program Plan 2007," www.netl.doe.gov (Accessed March 2008)



Time Line of Research Activities



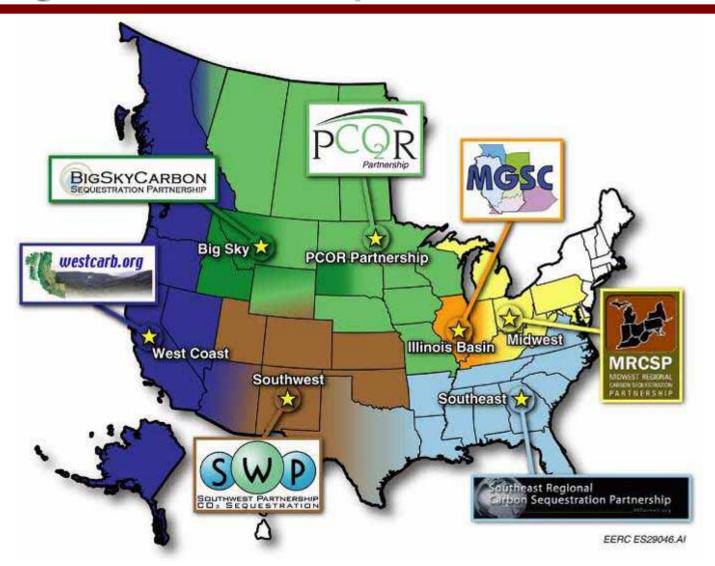
PCOR Partnership

The Plains CO₂ Reduction (PCOR) Partnership, one of seven regional partnerships funded by DOE NETL's Regional Carbon Sequestration Partnership (RCSP) Program, is managed by the Energy & Environmental Research Center (EERC) at the University of North Dakota in Grand Forks, North Dakota.



EERC Facilities in Grand Forks, North Dakota

Regional Carbon Sequestration Partnerships



The RCSP Program represents more than 350 organizations in 41 states, three Indian nations, and four Canadian provinces.

What Is our Region Doing?



PCOR Partnership Region

Nine states and four provinces
Over 1.4 million square miles

The PCOR Partnership is assessing the technical and economic feasibility of capturing and storing (sequestering) CO₂ emissions from stationary sources in the central interior of North America.



The PCOR Partnership currently has over 80 partners representing public agencies, utilities, oil and gas companies, engineering firms, associations and nonprofit organizations, and universities.



PCOR Partnership Phase I Goals

- Gauged public understanding
- Developed database for:
 - Sources
 - Sinks
 - Separation and transportation options
 - Regulatory and permitting requirements
 - Environmental benefits and risks
- Identified sequestration opportunities
- Conducted public outreach campaign
- Developed action plan for Phase II (field validation tests)

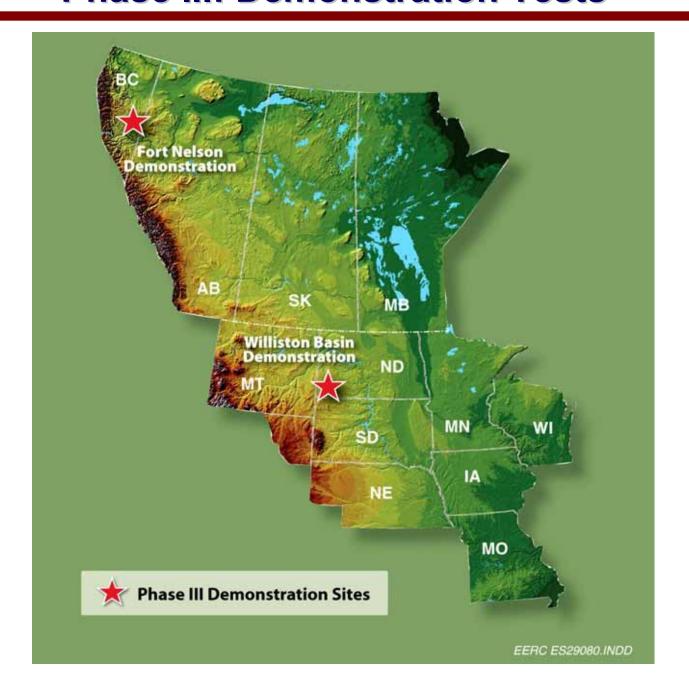


- Increase public understanding of CO₂ sequestration
- Perform field validation tests that develop:
 - Monitoring, mitigation, and verification (MMV) protocols
 - Regional sequestration strategies
 - Best separation—source matches
 - Regulatory and permitting strategies
 - Environmental benefits and risks
 - Information needed to monetize C credits
- Continued regional characterization
- Regional partnership program integration

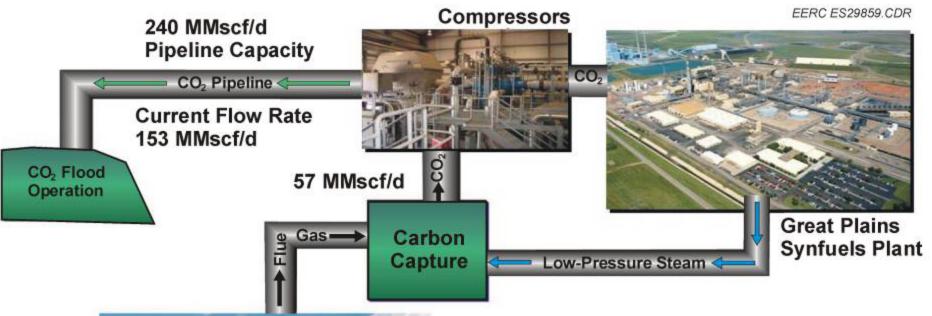
Phase II: Field Validation Tests



Phase III: Demonstration Tests



Phase III Williston Basin Project Overview



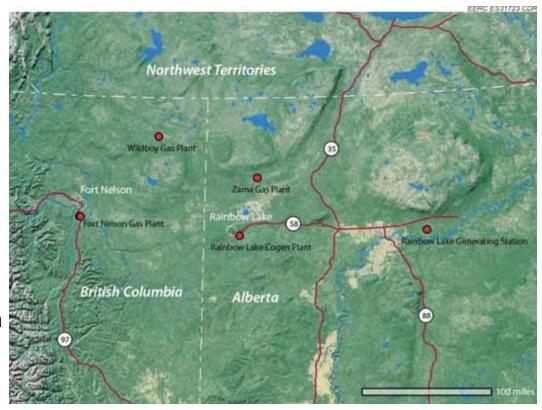


Antelope Valley Station

- Capture at least 500,000 tons/yr of CO₂ at existing coal-fired power plant in central North Dakota.
- Transport via pipeline to Williston Basin oil field.
- Meet or exceed all of the DOE Phase III objectives.
- Conduct activities to document the efficacy of carbon capture and storage.
- Ultimately monetize credits.

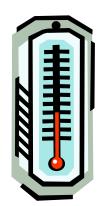
Phase III Canadian Project Overview

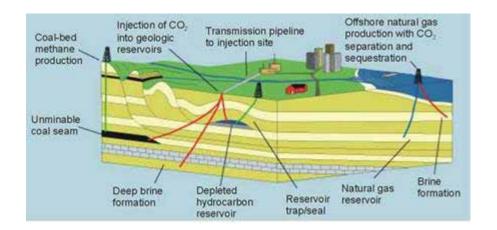
- The PCOR Partnership Phase III Canadian (Fort Nelson) Demonstration Test will develop detailed and previously unavailable insight regarding a wide variety of issues associated with the geological sequestration of CO₂. The primary research and development targets are:
 - Cost-effective MMV approaches for large-scale CO₂ sequestration in brine formations will be suggested for deployment and evaluation.
 - Modeling simulation approaches to predict and estimate CO₂ injectivity, plume areal extent, mobility, and fate within the target formation will be recommended for field testing.
 - Approaches to predict the effects of CO₂ on the integrity of overlying sealing formations will be suggested for verification and validation with field- and laboratory-based data.

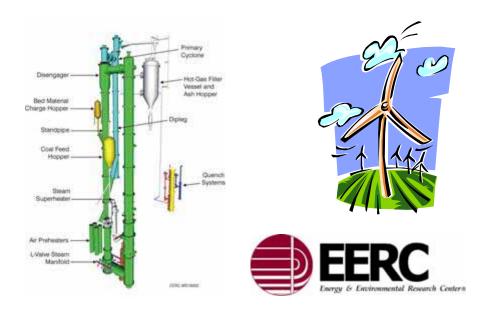


Options to Reduce and Manage Anthropogenic Greenhouse Gas (GHG) Emissions, Including CO₂

- Renewable energy technologies
- Advanced highefficiency energy systems
- Improve efficiency on existing systems
- Reduce consumption of energy
- Capture and Sequester GHG emissions



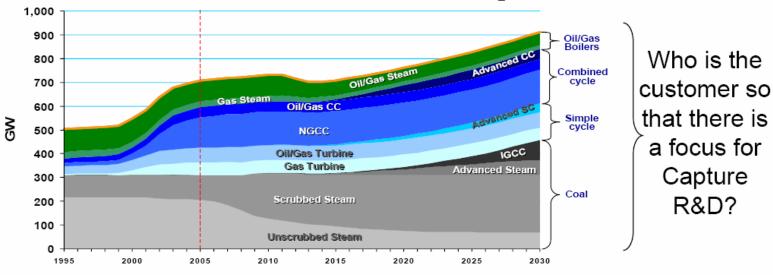




What Is the U.S. CO₂ Capture Market?

- Total 9,877 units installed in the U.S.
 - 337 GW of coal-fired units
 - 422 GW of gas-fired units
 - 64 GW of oil-fired units

- 423 existing coal-fired power plants
 - Comprise of 1,089 boiler units
 - Generate 323 GW (Phase 1&2)
 - Emit 1,917.2 million metric tons of CO₂



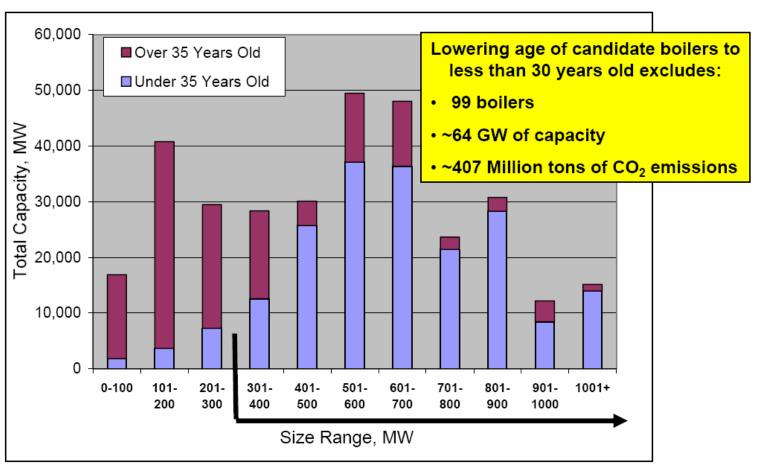
Fossil Power Generation Technology Types

José D. Figueroa et. al./5th Annual Conference on Carbon Capture and Sequestration / May 8-11, 2006

Source: EIA, UDI, EPA



U.S. Power Market Sector Most Likely to Adopt CO₂ Capture and Separation



José D. Figueroa et. al. / 5th Annual Conference on Carbon Capture and Sequestration / May 8-11, 2006



The Need to Focus on CO₂ Capture R&D in the United States

Energy Penalty due to CO ₂ Capture	10%	20%	30%	40%
Target Market, GW	184	184	184	184
Fleet CO ₂ Reduction, %	50.2	49.2	47.9	46.3
New Capacity Req'd, GW	25.5	57.5	98.5	153.3
Additional Coal Req'd., tons x 10 ³	79,940	179,864	308,338	479,637
Cost of New Capacity, MM\$	45,975	103,444	177,332	275,850
Cost of CO ₂ Retrofits, MM\$	91,950	91,950	91,950	91,950
Total New Cost, MM\$	137,925	195,394	269,282	367,800

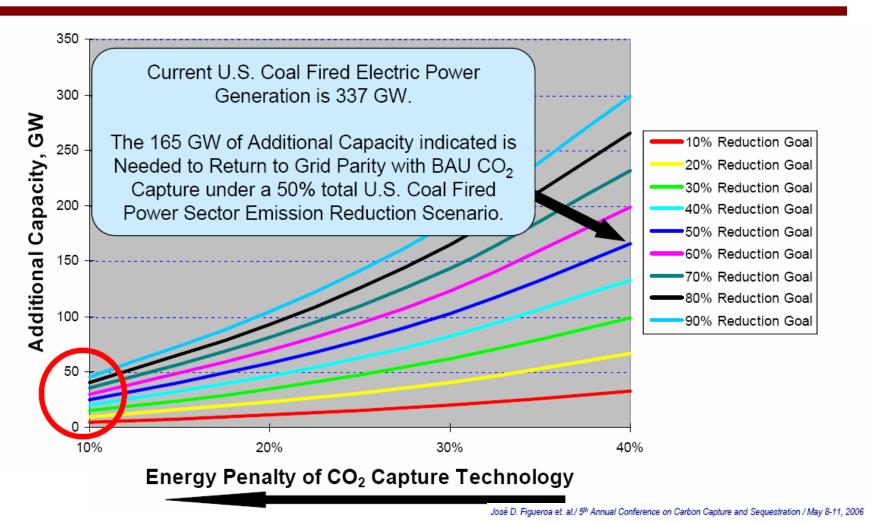
Need for further R&DD to minimize the cost and externalities impact due to CO₂ Capture and Storage.

Current Energy Penalty of CO₂ BACT MEA Absorption System

José D. Figueroa et. al./ 5th Annual Conference on Carbon Capture and Sequestration / May 8-11, 2006



Additional Capacity Required to Meet Increased Targets for U.S. CO₂ Emission Reduction





CO₂ Point Source Contributions

Sources	Total Tonnes		
Power Generation ¹	2,239,700,000		
Coal ¹	1,868,400,000		
Natural Gas ¹	299,100,000		
Oil ¹	72,200,000		
Industries	324,789,000		
Refinery ²	184,918,000		
Iron and Steel ³	54,411,000		
Cement ³	42,898,000		
Ammonia ³	17,652,000		
Aluminum ³	4,223,000		
Lime ³	12,304,000		
Ethanol ³	8,383,000		
Total	2,564,489,000		

¹ Environmental Protection Agency Greenhouse Gas Inventory Sector Analysis (3). ² Estimate from U.S. DOE, 2002 BPD totals (5).



³ EPA (2004) Greenhouse Gas Inventory Industrial Process Analysis (6).

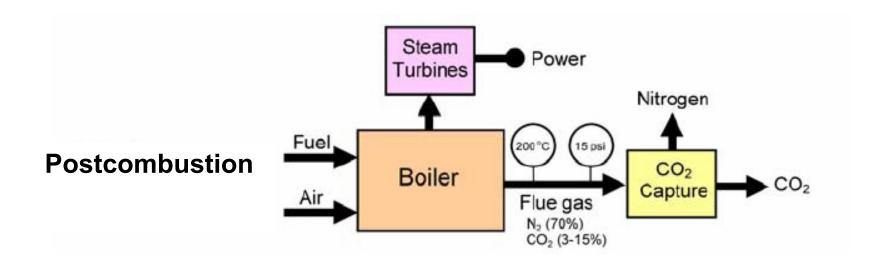
Capture Technologies

Outline

- 1. Postcombustion and precombustion
 - Capture technology options
 - Challenges
- 2. Oxyfuel combustion
 - Oxygen separation
 - Fireside performance issues heat transfer, ash deposition, corrosion
- 3. Other technologies
- Research, development, and commercial projects



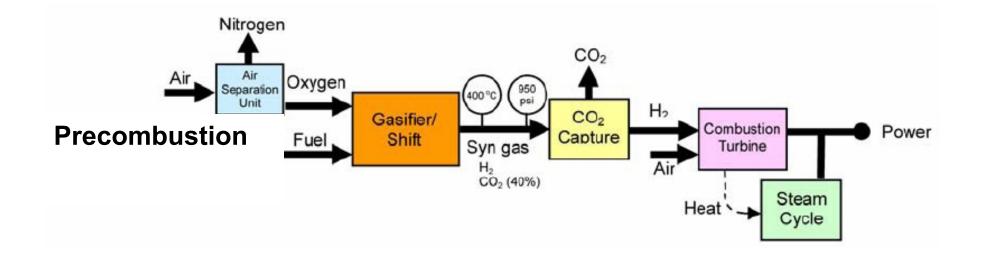
Postcombustion



Source: U.S. DOE Carbon Sequestration Technology Roadmap and Program Plan 2006



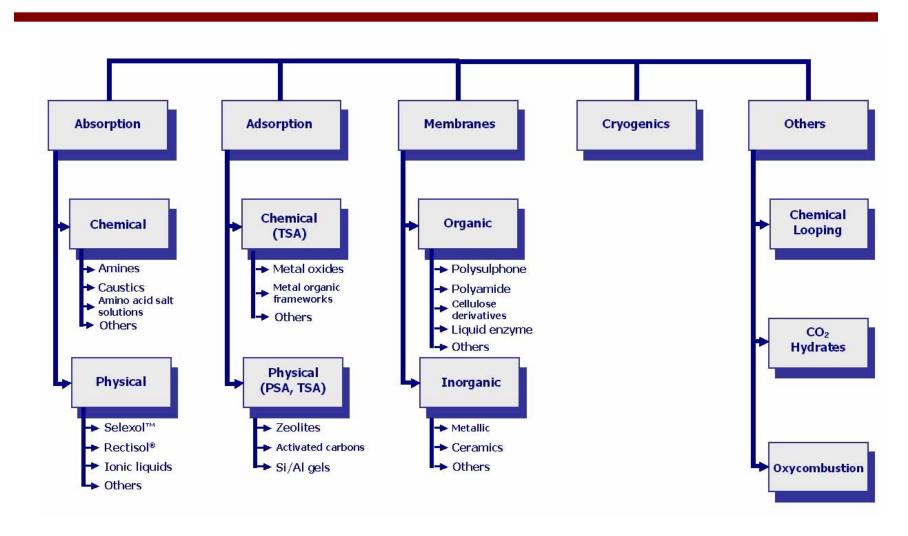
Precombustion



Source: U.S. DOE Carbon Sequestration Technology Roadmap and Program Plan 2006



Summary of CO₂ Capture Technologies





Commercially Available Technologies

Chemical absorbents

- MEA (monoethanolamine)
- MDEA (methyldiethanolamine)
- Designer amines
- Hot potassium carbonate (Catacarb[®], Benfield)

Physical absorbents

- Dimethyl ether of polyethylene glycol (Selexol™)
- Methanol (Rectisol®)



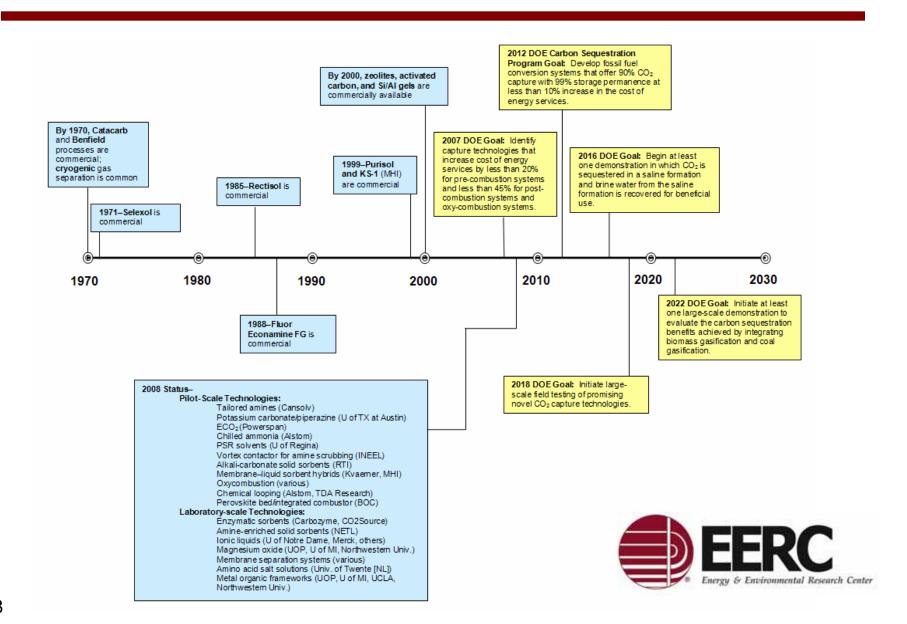








CO₂ Capture Technology Time Line



Absorption

Chemical



Absorption – Amines

State-of-the-Art Postcombustion Capture

- Fluor Daniel Econamine FGSM
 - 30% MEA solution incorporating additives to control corrosion and (oxidative and thermal) degradation
 - >20 commercial plants ranging in size from 5 to 400 tons CO₂/day
- ABB-Lummus
 - 15%–20% MEA solution
 - Four commercial plants ranging in size from 150 to 850 tons CO₂/day
- Mitsubishi Heavy Industries
 - KS-1 sterically hindered amines
 - Two commercial plants: ~210 and 330 ton CO₂/day
- Cansolv
 - Mixture of amines
 - Commercial plant case study at NSC (Japan)
- Praxair
 - Mixture of amines no commercial plant



Absorption Processes

- Commonly used in commercial systems to remove CO₂ from mixedgas streams over a wide range of pressures and CO₂ concentrations.
- Two types of solvents used for CO₂ removal:
 - Physical solvents dissolve CO₂ following Henry's law but do not react with it. Physical solvents are more suitable for mixed-gas streams that are under high pressure. The elevated pressure increases CO₂ solubility. Physical solvent recovered by flashing off CO₂ at lower pressures.
 - Chemically reactive solvents first dissolve CO₂ and then react with it.
 Pressure does not affect the performance of chemically reactive solvents.
 Chemically reactive solvents require heat to separate CO₂ from solvent.
 - Hybrid solvents combine the best characteristics of both chemical and physical solvents and are usually composed of a number of complementary solvents – under development.



Chemical Absorption

Amine scrubbing

- Alkanolamines are a group of amines used for CO₂ removal that includes MEA, diethanolamine (DEA), diglycolamine (DGA), disopropanolamine (DIPA), and triethanolamine (TEA).
- MEA is considered state-of-the-art.
 - Advantages high capacity for CO₂ and high rate of absorption.
 - Limitations include high heat of absorption and corrosion issues.
 - Improving MEA solvent performance is conducted by blending amines or promoting with potassium carbonate.



Common Amines Used in Gas Treating

Class	Name (Abbr.)	Structure
Primary Amine	Monoethanolamine (MEA)	HO-CH2-CH2-N H
	Diglycolamine® (DGA)*	HO-CH ² -CH ² -O-CH ² -CH ² -N H
Secondary Amine	Diethanolamine (DEA)	HO-CH2-CH2N-H
	Diisopropanolamine (DIPA)	CH CH CH CH
Tertiary Amine	Triethanolamine (TEA)	но—сн ₂ —сн ₂ N—сн ₂ —сн ₂ -он но—сн ₂ —сн ₂
	Methyldiethanolamine (MDEA)	HO-CH2-CH2 N-CH3
Hindered Amine	Isobutanolamine (AMP)	но-сн ₂ -с

a. Diglycolamine (DGA) is a registered trademark of Huntsman Chemical.

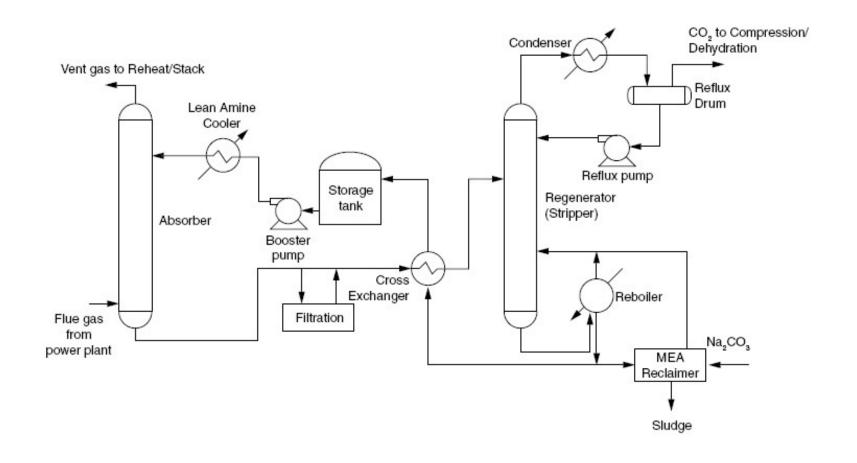


Commercial Facilities Use MEA-Based Solvents

- Food industry and oil industry (enhanced oil recovery [EOR])
 - Capture CO₂ from coal-, fuel oil-, and natural gasderived flue gas streams.
 - Capacities in the range of 100 to 1100 tons/day, (500-MW power plant produces 5500 tons/day).
 - Commercial providers of MEA technology include Fluor Daniel and ABB Lummus Global.



Schematic of an MEA Absorption System for Capturing CO₂ from Flue Gas





How the MEA System Works

- Flue gas is cooled to about 110°F.
- The flue gas is partially compressed to 17.5 psia by a centrifugal blower to overcome the gas path pressure drop.
- Flue gas enters the absorber base and flows upward countercurrent to the lean MEA solution.
- CO₂ is removed from the flue gas in the packed-bed absorber column through direct contact with MEA.
- The CO₂-depleted flue gas is exhausted to the atmosphere.
- The CO₂-rich solution is heated to liberate the CO₂.
- The CO₂ vapor is condensed, cooled, and sent to a multistaged compressor where the CO₂ is compressed to a pressure of over 1200 psia.
- The CO₂-laden stream is dehydrated using glycol or molecular sieve processes.



Other Chemical Absorption Methods

- KS-family of sterically hindered amines (Mitsubishi Heavy Industries [MHI]).
- Potassium carbonate/piperazine complex (University of Texas at Austin).
- Ammonia Processes (Powerspan, NETL, Alstom [Chilled Ammonia]).
- PSR solvents (University of Regina, Saskatchewan), which are proprietary designer solvents formulated for optimized separation of CO₂ from any gas stream.
- Advanced amine scrubbing (Cansolv Technologies, Inc.), in which a proprietary amine is utilized.
- Amine-enriched sorbents (NETL)
- Amino acid salt solutions (Norwegian University of Science and Technology)



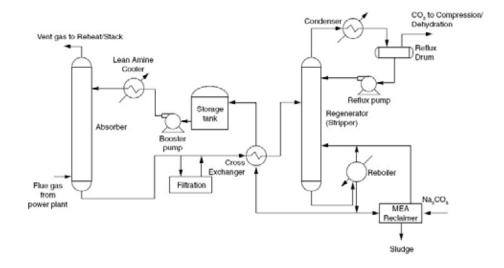
Mitsubishi Heavy Industries

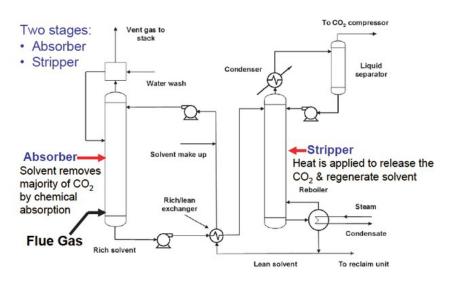
- KS-family of sterically hindered amines
- Advantages claimed
 - Enhance reactivity toward CO₂.
 - 1 mol of hindered amine is required to react with 1 mol CO₂ (compared with 2 mol MEA).
 - 90% less solvent degradation, 20% lower regeneration energy, 15% less power, 40% lower solvent recirculation rates due to higher net absorption capacity, lower regeneration temperature, less corrosion in the presence of dissolved oxygen, and lower chemical additive cost.



Ammonia Processes

Typical Amine Process





ALSTOM's Cold Ammonia Process









Powerspan ECO₂ Technology

- Selected by Basin Electric for 125-MW demonstration.
- Uses ammonia scrubbing joint research with DOE NETL.
- Higher CO₂ loading (kg CO₂ absorbed per kg sorbent) compared to MEA.
- Requires less energy to release CO₂ and regenerate sorbent.
- Minimal sorbent degradation by other flue gas constituents.
- Lower-cost reagent.
- Lower corrosion issues.
- No degradation, requiring less makeup.



Ammonia Process Chemistry (absorption)

- 2 NH₃ + CO₂ → NH₂COONH₄
- NH₂COONH₄ + CO₂ + 2 H₂O → 2 NH₄HCO₃
- $NH_2COONH_4 + H_2O \longrightarrow NH_4HCO_3 + NH_3$
- NH₃ + H₂O + CO₂ → NH₄HCO₃
- $2 \text{ NH}_3 + \text{H}_2\text{O} + \text{CO}_2 \longrightarrow (\text{NH}_4)_2\text{CO}_3$
- $(NH_4)_2CO_3 + CO_2 + H_2O \longrightarrow 2 NH_4HCO_3$



Ammonia Process Chemistry (regeneration)

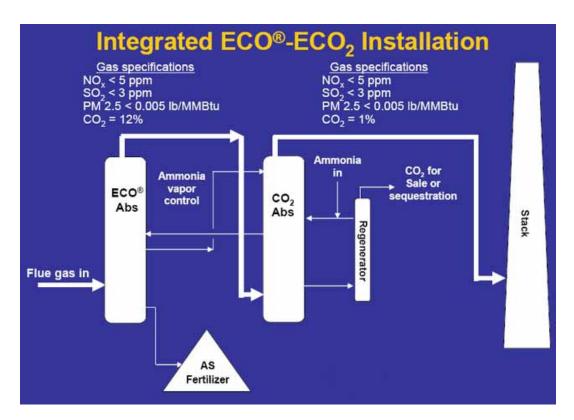
• 2 NH₄HCO₃(aq)
$$\longrightarrow$$
 (NH₄)₂CO₃(aq) + CO₂(g) + H₂O

•
$$NH_4HCO_3(aq) \longrightarrow NH_3(aq) + CO_2(g) + H_2O$$

•
$$(NH_4)_2CO_3(aq) \longrightarrow 2NH_3(aq) + CO_2(g) + H_2O$$



Powerspan ECO and ECO₂



The ECO₂ process is integrated after the ECO process, which provides NO_x , SO_x , and particulate control.



Powerspan Bench and Pilot Testing

- Bench testing Powerspan and DOE
 - 90% CO₂ removal with ammonium carbonate solutions.
 - Parametric testing under way absorption rates,
 ammonia vapor management, absorptive capacity.
- Pilot testing
 - Planned for FirstEnergy's R.E. Burger Plant.
 - 1-MW slipstream (20 ton/day).
 - Testing scheduled to begin in 2008.



Cansoly Process

- Core platform process is Cansolv SO₂ scrubbing selective amine scrubbing in an oxidative environment.
- The Cansolv breakthrough in operating costs:
 - Low salt formation
 - low amine degradation
 - low heat of regeneration
- R&D focus in 2000–2004 on developing highperformance solvents for NO_x, Hg, and CO₂ absorption.
- Commercialization focus in 2005–2007: heat integrating/optimizing processes:
 - $-CO_2-SO_2$
 - SO₂-NO_{xx}-mercury

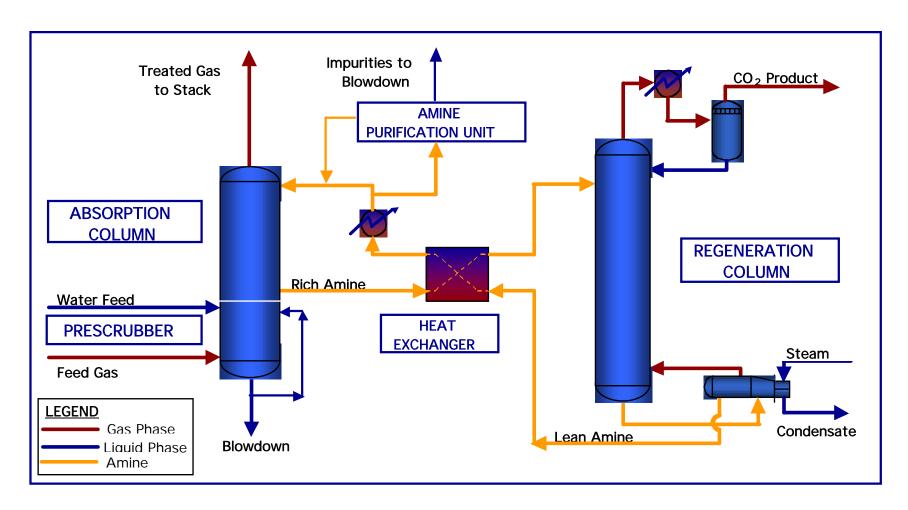


CO₂ Capture

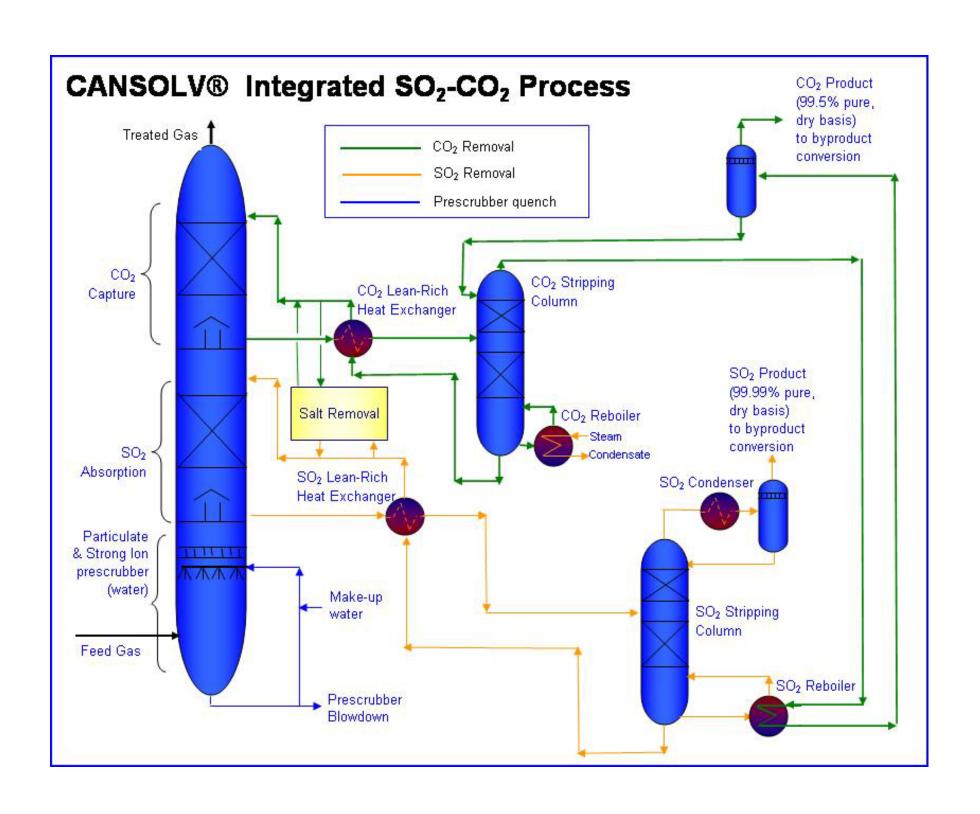
- Cansolv absorbents are designed to exhibit:
 - Fast kinetics similar to 1° amines.
 - Very low degradation similar to 3° amines.
 - High resistance against oxidation and free radical attack.
 - Lowest possible regeneration energy similar to formulated amines.



Cansolv CO₂ Capture Flow Sheet







Absorption

Physical



Physical Absorption

- Used primarily to remove CO₂ from gasification fuel or synthesis gas.
 - Selexol™ (glycol)
 - Rectisol® (methanol)

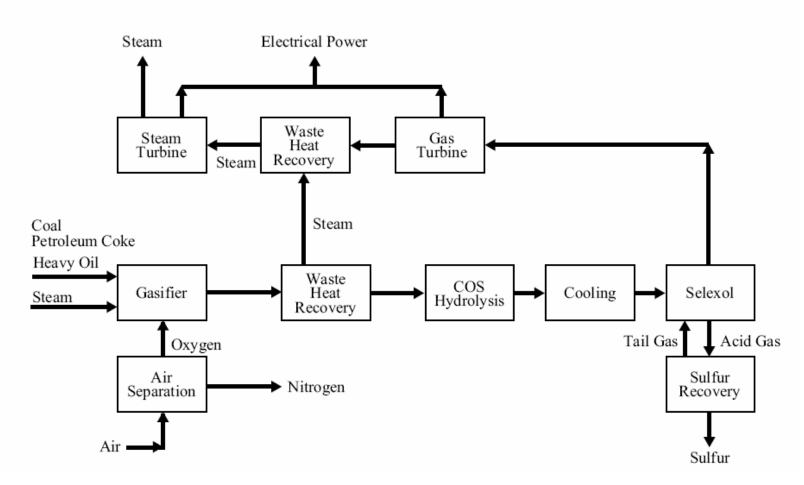


Selexol™

- Selexol[™] is a liquid physical solvent developed over 30 years ago and currently owned by UOP.
- The solvent removes H₂S, CO₂, and mercaptans and is for both hydrocarbon and water dew point control.
- The Selexol[™] solvent is a mixture of dimethyl ethers of polyethylene glycol, and has the formulation of CH₃ (CH₂CH₂0)nCH₃, where n is between 3 and 9.
- Selexol[™] solvents are true physical solvents and do not react chemically with the absorbed gases.
- The solvent has high selectivity for sulfur compounds over CO₂ and produces a highly enriched feed to the Claus unit. It also provides maximum CO₂ for any downstream process.

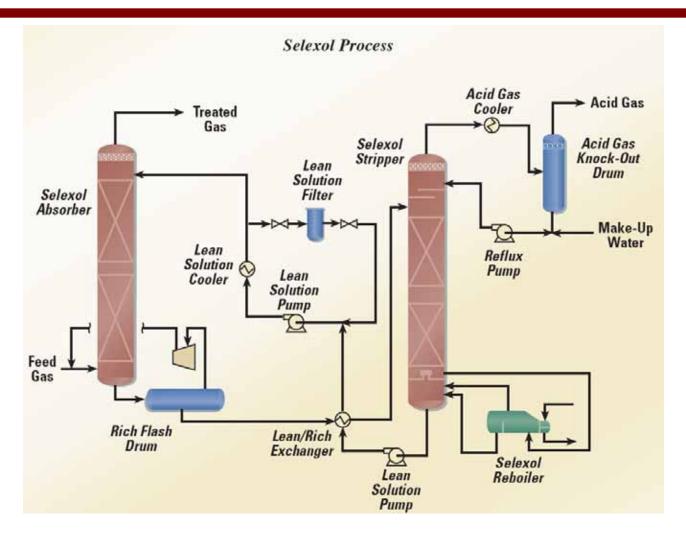


IGCC with Selexol™





Selexol™ Process Schematic

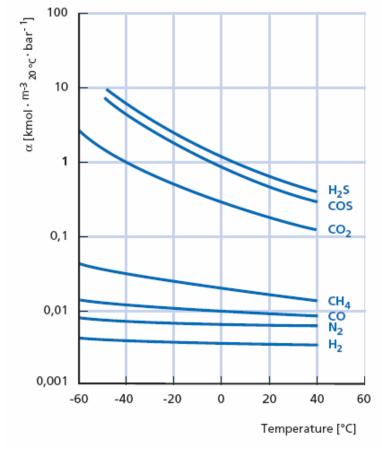




Rectisol

- Rectisol uses refrigerated methanol at -94°F as the solvent for physical absorption of CO₂ and H₂S.
- Removes all impurities and trace contaminants in one single absorption process.
- Ultrapure product gas: e.g., total sulfur <0.1 ppmv, CO₂ <2 ppmv.

Absorption Coefficients in Methanol





Other Technologies

- Dry, regenerable, solid sorbents are under development for postcombustion CO₂ capture.
 - Currently at bench scale.
 - Essentially pure CO₂ because of selective adsorption.
 - Dry system eliminates need to heat and cool large quantities of water.



Other Technologies

- Alkali carbonate system (Research Triangle Institute [RTI]).
- Warm-gas sodium-based solid sorbents (NETL) have been developed for pressure swing adsorption (PSA)/thermal swing adsorption (TSA) application for removal from integrated gasification combined cycle (IGCC) syngas streams. They rely on chemical reaction for CO₂ capture. Regeneration temperatures are currently too high at 1292°F.
- Ionic liquids (University of Notre Dame, Sachem Inc., Merck) can dissolve gaseous CO₂ and are stable at temperatures up to several hundred degrees Celsius. Little heat is required for CO₂ recovery.



Adsorption

Chemical/Physical



Adsorption

- Adsorbent beds typically comprise alumina, zeolite, or activated carbon.
- Regenerate by
 - PSA
 - Vacuum PSA (VPSA)
 - TSA
 - "Washing" of adsorbent bed by CO₂-free fluid
- Other adsorption techniques
 - Electrical swing adsorption (ESA)
 - Sorption-enhanced water–gas shift process
 - Metal organic frameworks (MOFs)



Other Adsorption Techniques

- ESA (Oak Ridge National Laboratory) uses carbon-bonded activated carbon fiber as adsorption material. Adsorbed gas is removed by a low-energy electric current.
- Sorption-enhanced water—gas shift process (Air Products), in which a water—gas shift catalyst is combined with CO₂-selective hydrotalcite adsorbent. Multiple adiabatic fixed beds are used for cyclic reaction/adsorption and regeneration.
- Metal organic frameworks (UOP, UCLA, University of Michigan, Northwestern University) consist of large molecules with engineered macromolecular cavities that can adsorb CO₂. A high storage density is possible, and low heat is required for CO₂ recovery.



C-Quest Technologies

- C-Quest is a chemical sorbent system designed to significantly reduce CO₂ emissions from utility and industrial boilers.
- The sorbent ingredients are widely available.
- The by-product is a safe, recyclable solid which can be safely disposed of (as opposed to a gas which may be difficult to dispose of).
- Laboratory testing at the EERC reflects CO₂ capture rates as high 90%.
- Capture rates are dependent on several factors including gas-to-sorbent ratios, temperatures, and retention times.
- The sorbent captures other pollutants as well. In the lab, capture rates as high as 99% SO₂, 90% mercury, and 15% NO_x have been observed concurrently with the CO₂ capture.
- Further testing is currently being performed to determine capture efficiencies and other information which will be required to determine ultimate cost per ton of CO₂ captured; however, current results are extremely promising.



Cryogenics



Cryogenics

CO₂ is separated from a mixed-gas stream by compressing it and removing the heat of compression and condensation. Three methods are as follows:

- Compress to ~1100 psia; water used for cooling.
- Compress to 250–350 psia at 10° to 70°F, dehydrate feed stream with activated alumina or silica gel dryer, distill condensate in a stripping column.
- Cool the mixed-gas stream to condense CO₂.



Membranes

Organic/Inorganic



Gas Separation Membranes

- Use partial pressure as the driving force for separation most effective at high CO₂ concentrations and pressure.
- Differences in physical or chemical interaction between the components present in a gas mixture with the membrane material cause one component to permeate through the membrane faster than the other component.
- The gas component dissolves into the membrane material and diffuses through it to the other side.
- The membrane divides the feed gas stream into the permeate stream and the retentate stream.



New Membrane System - I

- Enzymatic liquid membranes (Carbozyme) are enzyme-based systems that achieve CO₂ capture and release by mimicking the mammalian respiratory mechanism. Its fast kinetics can lower system size and cost.
- CO₂ selective membrane (Media and Process Technology, University of Southern California), a membrane reactor that combines water—gas shift with CO₂ removal. It employs a tubular ceramic membrane, permeable only to CO₂, inside a water—gas shift reactor.
- Membrane water—gas shift reactor (Eltron Research/SOFCo/Chevron Texaco) is a catalytic membrane reactor (CMR) that utilizes oxygen transport membrane technology to facilitate in situ partial oxidation reforming. Syngas passes to a dense metal alloy membrane reactor to facilitate selective permeation of H₂ and enhanced shift. H₂ permeabilities are one order of magnitude higher than palladium and two orders of magnitude less expensive. This process requires sweet syngas, however.



New Membrane System – II

- Hydrogen membrane reformer (Norsk Hydro, SINTEF, and UiO) is a two-reactor process that combines reforming, water—gas shift reaction, and H₂ separation. It utilizes a dense, mixed-conducting membrane (MCM). Since the transport process is based on ion diffusion, the selectivity of the membrane is infinite as long as the membrane is gas impervious (barring any defects).
- Palladium membrane reactor (NETL). This reactor system combines a palladium-based membrane with the water—gas shift reaction. The high temperature (1652°F) and pressure of operation and the catalytic effect of the membrane eliminate the need for a separate water—gas shift catalyst. A sulfur-tolerant membrane is possible.
- Hybrid alumina/organosilane membrane (NETL). In this system, organic molecules are grafted onto a substrate surface to attain higher selectivity toward CO₂ permeation.



New Membrane System – III

- Thermally optimized polymer membrane (LANL, INEEL, Pall Corporation, University of Colorado, Shell Oil Company), in which polymer-based membranes exhibit high selectivity because of size-based exclusion and solubility variances of molecules within the polymer matrix. Polymer membranes have been commercially successful for a number of industrial applications. The intent of additional research is to increase the temperature of application.
- Inorganic nanoporous membrane (ORNL) with pore sizes of less than 1 nm. Composite membranes made of a ~2-μm membrane (e.g., alumina) layer on a ~450-μm porous support structure can allow operation at temperatures up to 1852°F.
- Molecular gate membrane (Research Institute of Innovative Technology for the Earth [RITE]), a cardo polyimide membrane that is selective to CO₂ permeation.
- Kvaerner hybrid membrane absorption system (Kvaerner Process Systems), a gas—liquid membrane contactor that replaces a traditional absorber. CO₂ diffuses through a microporous, hydrophobic solid membrane into liquid flow. The solvent, rather than the membrane, provides the selectivity. Compared to a conventional absorber, it weighs 70% less and has a 65% smaller footprint.

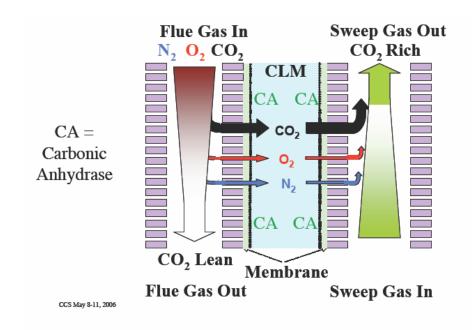


Carbozyme Technology



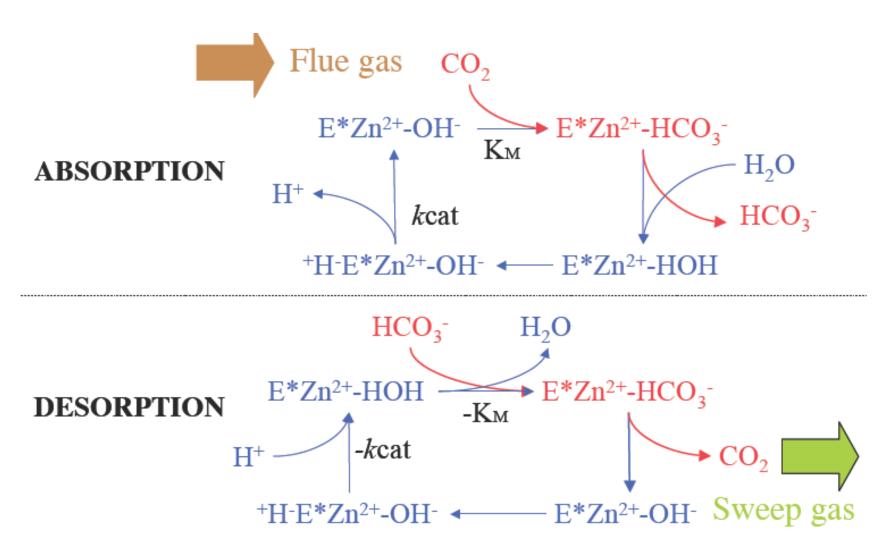
Carbozyme, Inc.

- Developing process to capture and separate CO₂
- Uses catalyzed liquid membrane reactor/separator
- Demonstrated at lab scale



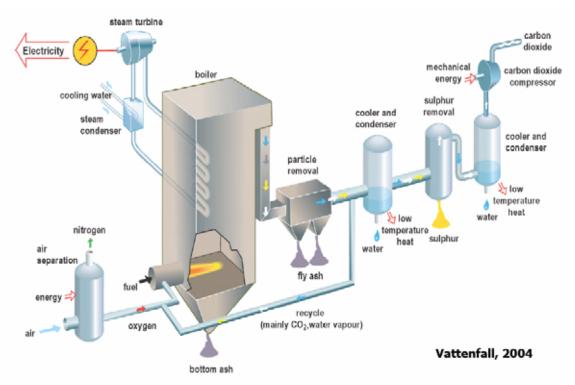


Carbozyme Chemistry



Oxycombustion

- Combustion in O₂/recycled flue gas.
- Produce high-CO₂-content (>80 vol%) flue gas.
- Shown to significantly reduce NO_x.
- Potential for zero emissions by sequestering all components in flue gas.
- Major cost component is air separation (cryogenics).





Oxygen Separation

 State-of-the-art cryogenic distillation air separation has little room for improvement or cost reduction.

Process	Status	Scale (tpd)	Purity % O ₂	LO _X and by-prod	Start-up ¹ (turndown)	Energy kWh/t	Integration options
Membrane	Commercial	<20	35-45	No	5 min		Low
					0-100%		
Adsorption	Commercial	<150	95	No	5 min		Med
					0-100%		
Chemical	Developing	?	>99	No	<1 min		Med
					0-100%		
Ion transport membrane (ITM)	Commercial	<10	+99	No	<1 min	~225	Med
					0-100%		
Catalytic autothermal reforming (CAR)	Lab/pilot	N/A	+90	No	<1 min	~225	Med
					0-100%		
Cryogenic (ASU)	Mature	20-3500	90-99.5	LOX, Ar, N ₂	8 hours	250-400	High
					65-100%		

¹ From 0% capacity, but assumes that reactors/beds etc are hot.

Oxygen Separation (cont.)

- Current development activities are centered on ion transport membranes.
 - These are complex crystalline structures with oxygen ion vacancies onto which oxygen adsorbs and decomposes into ions. The ions are transported through the membrane by sequential occupation of oxygen ion vacancies with the ion transport balanced by the counterflow of electrons. Oxygen partial pressure provides the driving force, which requires highpressure air at temperatures above 1292°F. Barring the presence of defects, the membrane is selective to oxygen transport only.



Oxygen Separation (cont.)

- The ion transport membranes can theoretically integrate high-temperature oxygen separation from air with the combustion process, leading to a significant reduction in parasitic power as well as lower cost for O₂ production.
- Development issues include materials of construction, integration with or into the boiler, control of wall temperature (as a consequence of combustion reaction), and carbon formation.
- Developers and systems include Praxair and Alstom Power (oxygen transport membrane [OTM]) and Air Products (ion transport membrane [ITM]).



Other Capture Methods

- Regenerative carbonate process
- Chemical looping gasification
- Chemical looping combustion
- ZEC technology
- Unmixed fuel processor
- CO₂ hydrate formation
- CO₂ hybrid process
- Water cycle
- Graz cycle
- MATIANT cycle



Capture Technology Commercial Demonstrations

North America

- ABB Lummus scrubber with MEA Shady Point Power Plant, OK, and Warrior Run Power Plant, Cumberland, MD
- Fluor Econamine FG[™] –
 Cogeneration Facility, Bellingham,
 MA
- Rectisol® Great Plains Synfuels Plant, Beulah, ND
- Solvent Absorption (unspecified) Trona, CA
- Precombustion Capture, BP Carson Refinery, CA

South America

 MEA-based scrubber – Prosint Methanol Production Plant, Rio de Janiero, Brazil

Africa

Unspecified capture technology –
 In Salah Project, Algeria

Europe

- Solid sorbents Hammerfest, Norway
- Unspecified RWE IGCC Power Plant, Germany
- Unspecified Tjeldbergodden and offshore, Norway
- Precombustion Peterhead
 Power Station, Aberdeen,
 Scotland, and Miller field offshore
 UK, North Sea



Capture Technology Commercial Demonstrations (cont.)

Asia

- Fluor Econamine FGSM –
 Sumitomo Chemicals Plant,
 Chiba, Japan; The Indo Gulf
 Fertilizer Company,
 Jagdishpur, Uttar Pradesh,
 India; Luzhou Natural Gas
 Chemicals, Luzhou City,
 China
- Novel Amine Solvent
 Absorption Petronas
 Fertilizer Company, Malaysia,
 Malaysia

Australia

ZeroGen Precombustion
 Capture – Stanwell IGCC,
 Queensland, Australia



CO₂ Capture R&D Projects

Many CO₂ capture R&D projects are under way:

- North America 22
- Europe 15
- Asia one
- Australia one

Technologies being investigated run the gamut:

- Regenerable sorbents
- Vortex tubes
- Membranes
- Oxyfuel combustion
- Postcombustion using potassium carbonate
- Photosynthesis of microalgae



Summary

- Commercial technologies for CO₂ capture are available.
- Work is continuing to enhance performance.
- Limited data on the impact of impurities on cost and performance of CO₂ capture strategies.
- CO₂ management is a critical part of the future for many industries worldwide.

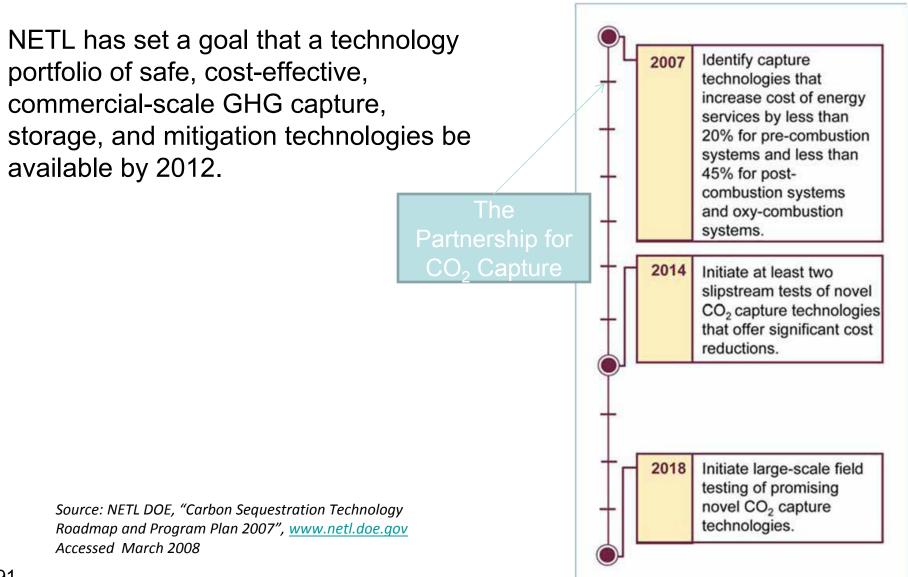


CO₂ Capture Challenges

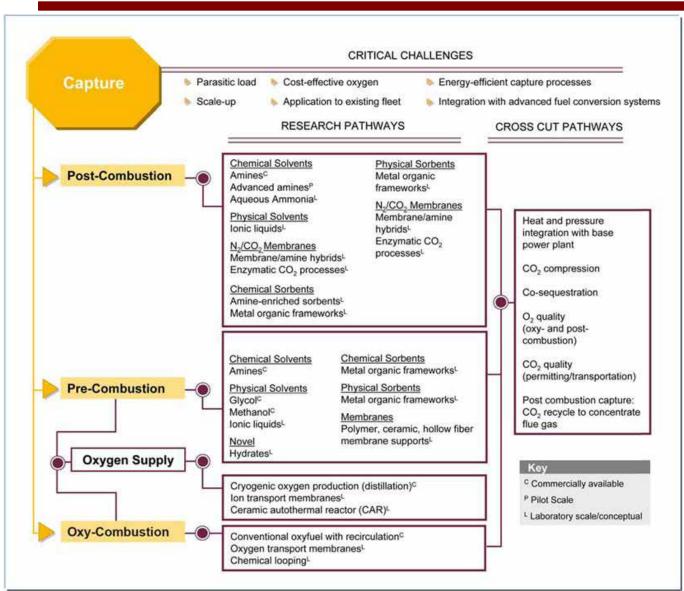
Brandon Pavlish



Time Lines



DOE NETL Identified Challenges



Source: NETL DOE, "Carbon Sequestration Technology Roadmap and Program Plan 2007", <u>www.netl.doe.gov</u> Accessed March 2008



Challenges

- Solvent Systems
 - Impurities in flue gas streams
 - Integration and energy penalty
 - Footprint
 - Solvent availability
 - Waste management/new product streams
 - Unintended consequences
 - Environmental
 - Health and safety
- Oxy-firing
 - Air separation unit (ASU)
 - Footprint
 - Energy consumption
 - · Equipment availability
 - Retrofit and new plant issues
 - · Fouling and slagging
 - Flame stability
 - Heat transfer
 - Corrosion
 - Pollution control equipment

- Unknowns
- Product stream
- Costs



Solvent System Challenges



Impurities in Flue Gas







Capture Technology Flue Gas Requirements

- Ultralow SO_x and NO_x (especially SO₃ and NO) levels
 - Less than 10 ppm SO_x
 - Less than 20 ppm NO₂

Solvent Degradation

- Low particulate loading
 - Condensed phase
 - Aerosols

System plugging – increased pressure drop

O&M Costs

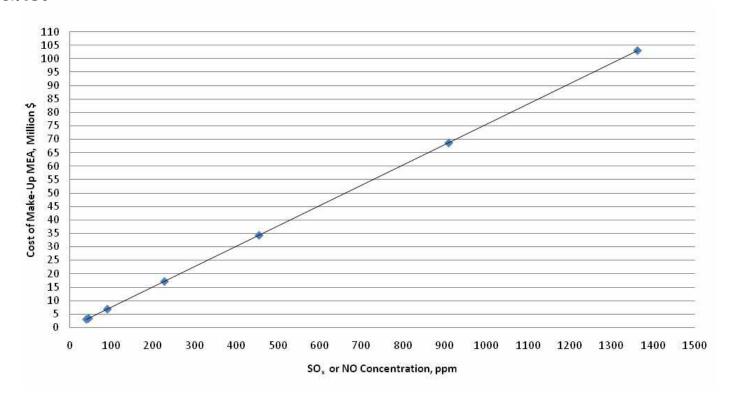
Low HF, HCl, HBr, and Hg²⁺ levels

Solvent degradation, contamination, and decreased absorption efficiency



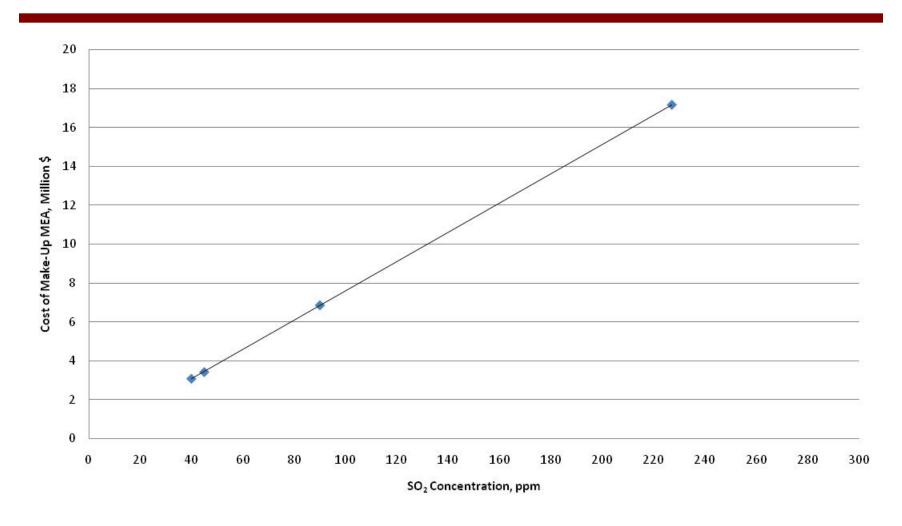
Solvent Degradation

- Conventional wet and dry scrubber outlets have 40–60 ppm SO₂.
- 1 mole of SO₂/NO₂ consumes 2 moles of solvent to form heat-stable salts.





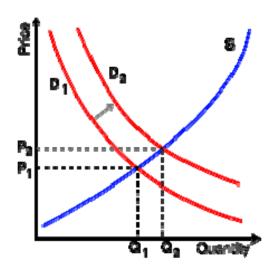
Effect of SO_x





Solvent Availability

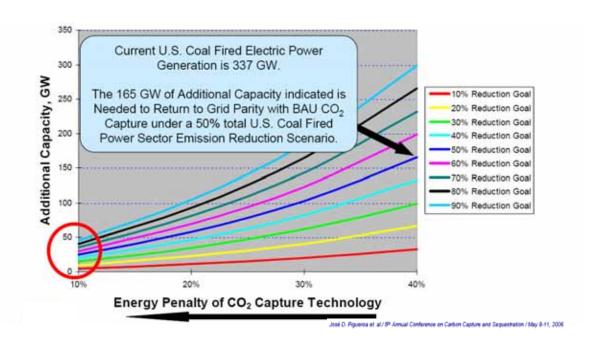
- A significant amount of solvent will be required.
- Reliability from vendors.
- Cost
 - Ammonia produced from natural gas
 - Current cost ~ \$300–\$400 per ton.
 - Cost could become highly variable based on natural gas prices.
 - Amines produced from ammonia
 - Current cost ~ \$1500 per ton.
 - Cost could become highly variable based on ammonia prices.
 - Supply vs. demand





Energy Penalties

- The energy penalty for a typical MEA system is 30% to 50% of plant load for a retrofit.
- Example of energy penalty for ammonia systems.
 - Alstom's Chilled Ammonia 30% to 40%
 - Powerspan?
- Others?



Energy Penalties

A technology and economic analysis was performed by NETL comparing MEA and the chilled ammonia process:

550-MW Base Plant

Property	Base-no CO ₂ capture	MEA	Chilled Ammonia	
Electric load, MW	37.3	121	164	
Lost generating capacity (due to steam consumption), MW		187	101	
Total Energy Penalty, MW		271	228	
Additional Capital Investment (millions)		\$236	\$276	
HHV efficiency, i.e., energy fuel in – power output	39.5%	27.0%	28.4%	
Cost of electricity, per kWh	\$0.0510	\$0.0808	\$0.0808	
CO ₂ captured (tons/hr)		636	603	
CO ₂ capture efficiency		95%	90%	
Contura aget nor ton CO	Avoided	\$33.87	\$33.54	
Capture cost, per ton CO ₂	Removed	\$25.77	\$27.13	

A 550-MW base plant is derated to a 279-MW plant for MEA or a 322-MW plant for chilled ammonia.



CO₂ Capture Retrofit Challenges Using Solvents

- Sufficient space (usually at least 2 to 6 acres) must be available within and around the plant for the chosen capture technology (footprint).
- Balance-of-plant equipment must be (re)sized to meet the requirements of not only the power block but the capture plant as well (larger sulfur removal equipment or new equipment).
- Waste and wastewater treatment needs will increase.
 - HSS, hazardous wastes, cooling water, process water
- Parasitic power load must be taken into account.
 - Replacement power requirements



Footprint

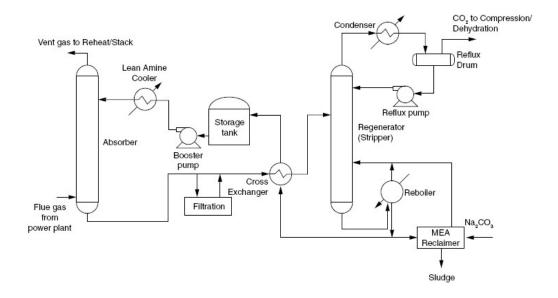


Fluor Daniel Econamine FGSM Retrofit at a gas-processing plant.



New Streams Due to CO₂ Removal

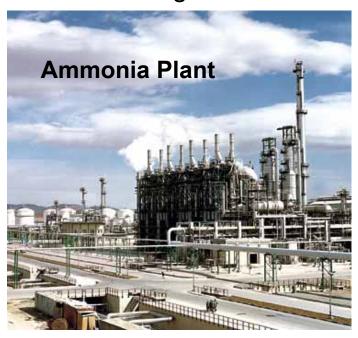
- Insoluble salts (amines = waste, ammonia = fertilizer). The production of fertilizer from one 500-MW plant would consume 13% to 27% of the present U.S. consumption of ammonium sulfate (fertilizer).
- Increased waste from further reductions in SO_x, NO_x, and particulate matter (PM).
- Large quantities of solvents on-site (MEA, ammonia, others)
- Others: wastewater, etc.



Unintended Consequences

- Effluent streams vapors, slip, characteristics??
- Production of solvents produce CO₂ (1.65 ton CO₂/ton ammonia)
- By-products hazardous waste potential from reclaiming HSS







What Does It All Mean?

- Impurities in the flue gas
 - Increased solvent use through degradation
 - Increased O&M
 - Decreased absorption efficiency
- Solvent availability
 - Increased cost
 - Decreased reliability
- Energy penalties
 - Increased cost
 - Increased replacement power needs
- Footprint
 - Retrofit applicability
 - Larger space requirements for new plants



What Does It All Mean? (cont.)

- New streams
 - Increased waste
 - Increased safety hazards
 - Increased water needs

Increased Cost

- Unintended consequences
 - Other environmental impacts
 - Large solvent use requires more energy and increased
 CO₂ emissions from chemical processes



Solvent Technology Status: Pros and Cons



MEA Challenges

- Significant amount of power to operate pumps and blowers for gas and solvent circulation.
- The largest parasitic load to the power cycle is associated with the steam used for solvent regeneration. Energy consumption as steam can be as high as 3.6 to 4.5 million Btu/ton CO₂ recovered.
- Additional issues:
 - Corrosion
 - Solvent degradation caused by the presence of dissolved O₂ and other impurities
 - Solvent reactions with SO₂, SO₃, and NO_x to produce nonregenerable, heat-stable salts
 - Requires SO₂ levels below 10 ppm, NO₂ levels below 20 ppm, and NO_x below 400 ppm.



Tailored Amines/Designer Amines

Pros

- Lower heat of regeneration over MEA
- Lower corrosion issues over MEA
- Higher CO₂ absorption loading in some designer amines

- Still require large amounts of regeneration energy
- Solvent degradation remains an issue
- Solvent availability (less produced) and greater cost
- Unknowns



Pros and Cons of Ammonia Processes

Pros

- Lower heat of regeneration than MEA
- Higher net CO₂ transfer capacity than MEA
- Lower stripping steam requirement
- Offers multipollutant control

- Ammonium bicarbonate decomposes at 140°F, so temperatures in the absorber must be lower.
- Ammonia is more volatile than MEA and often produces an ammonia slip into the exit gas.
- Ammonia is consumed through the irreversible formation of ammonium sulfates and nitrates as well as removal of HCl and HF.
- Considerable energy required for chilled ammonia.
- Unknowns.









Activated Hot Potassium Carbonate Processes: Gasification (precombustion)

Pros

- Absorbs CO₂ at a relatively high temperature.
- Solvent regeneration is accomplished through pressure reduction with some heating.

- Solvent stream must be split before entering the absorber, with a portion cooled to increase CO₂ solubility.
- The CO₂ partial pressure should be at least 30 to 50 psi.



Pros and Cons of Physical Absorbents: Gasification (precombustion)

Pros

- Low utility consumption.
- Rectisol[®] uses inexpensive, readily available methanol.
- Selexol[™] has a higher capacity to absorb gases than amines.
- Selexol[™] can remove H₂S and organic sulfur compounds.
- Both provide simultaneous dehydration of the gas stream.

- Rectisol refrigeration costs can be high.
- Hydrocarbons are coabsorbed in Selexol[™], resulting in reduced product revenue and often requiring recycle compression.
- Refrigeration is often required for the lean Selexol[™] solution.
- More economical at high pressures.



Oxygen-Fired Combustion Challenges



Oxyfuel Combustion Challenges

- Air separation unit
 - Footprint
 - Energy consumption
 - Oxygen purity
 - Equipment availability
- Retrofit and new plant issues
 - Fouling and slagging
 - Existing pollution control devices
 - Air leaks
 - Thermal properties change
 - Corrosion



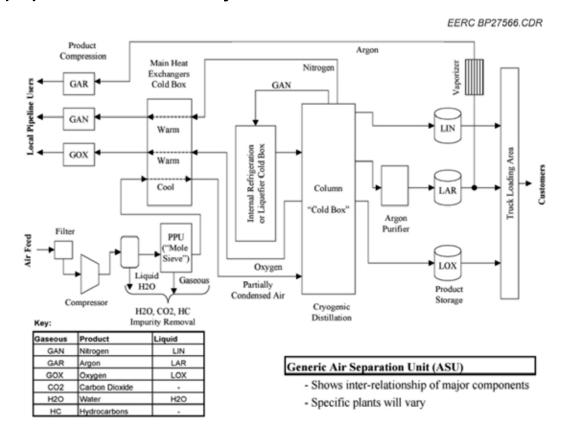
Air Separation Unit

- A 500-MW oxy-fired plant would consume 9000 ton/day of O₂.
- A cryogenic ASU of this size would require 5 to 6 acres of space.
- Cryogenic ASUs require between 250 and 450 kWh of electricity per ton of O₂.
- The ASU alone will consume 15% to 20% of the plants generation, with compression 25% to 30%.



Air Separation Unit (cont.)

- Operating flexibility: requires liquid oxygen storage.
- Unit scale: the current scale of cryogenics is around 4000 ton/day.
- Nitrogen contamination.
- Equipment availability.





Oxyfuel Retrofit Issues

- Fouling and slagging differences.
- Existing pollution control equipment:
 - Will be oversized.
- Air leaks:
 - Systems will need to be sealed in order to prevent nitrogen contamination.
- Thermal properties will change which may affect steam cycle.



Oxyfuel Retrofit Issues (cont.)

- Flue gas recycle
 - Elevated concentrations of SO₂/SO₃ (corrosion).
 - Reliability.
 - High moisture concentrations (corrosion).
- Altered ash (oxy-firing)
 - Ash chemistry may change, making ash no longer salable.



Combustion and Ash Behavior During O₂/CO₂ Firing of Coal

- Flame radiation intensity increases up to 30% for the gas-fired O₂/CO₂ as compared to air-fired conditions due to gas emissivity and possible soot formation for gas-fired tests (Andersson, K.; Johnsson, F. *Fuel* **2007**, *86*, 656–668).
- Radiative heat transfer has been shown to increase but literature is limited.
- Unknowns:
 - Impact on partitioning of inorganic impurities (vapors, liquids, solids), slag flow behavior, ash deposition, corrosion and erosion is unknown.



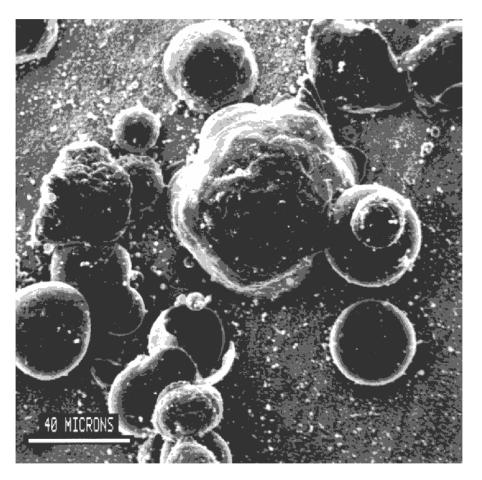
Key Issues – Impacts of Oxy-Firing

- Formation of intermediate ash species
 - Inorganic gases, liquids, and solids
 - Particle-size and composition evolution
- Deposit sticking and growth
 - Steel characteristics (oxide layer–deposit interface)
 - Liquid-phase formation (initial particle stickiness and captive surface)
- Deposit strength development
 - Sintering with a low-viscosity liquid phase (reactive and nonreactive)
- These issues depend on coal composition, system design, and operating conditions (temperature, oxygen concentration, and gas-cooling rate)



Ash Particle Impact and Bonding

- Substrate is stainless steel.
- Note flattened appearance of ash, indicative of being in a molten state on impact.





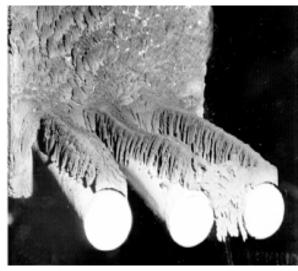
High-Temperature Ash-Fouling Probe Test Results Sinter Deposit at 1200°C (2200°F)

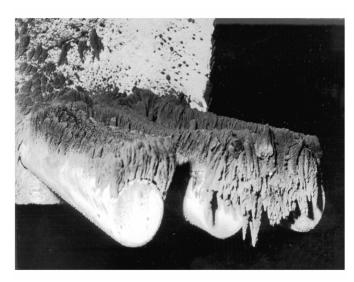
Bailey



Antelope









Product Stream



Product Stream Composition Targets

CO ₂	95%	Min.	MMP concern
Nitrogen	4%	Max.	MMP concern
Hydrocarbons	5%	Max.	MMP concern
Water	30 lbs/MMcf*	Max.	Corrosion
Oxygen	10 ppm	Max.	Corrosion
H ₂ S	10–200 ppm	Max.	Safety
Glycol	0.3 gal/MMcf	Max.	Operations
Temperature	120°F	Max.	Materials

Kinder Morgan pipeline requirements for EOR applications

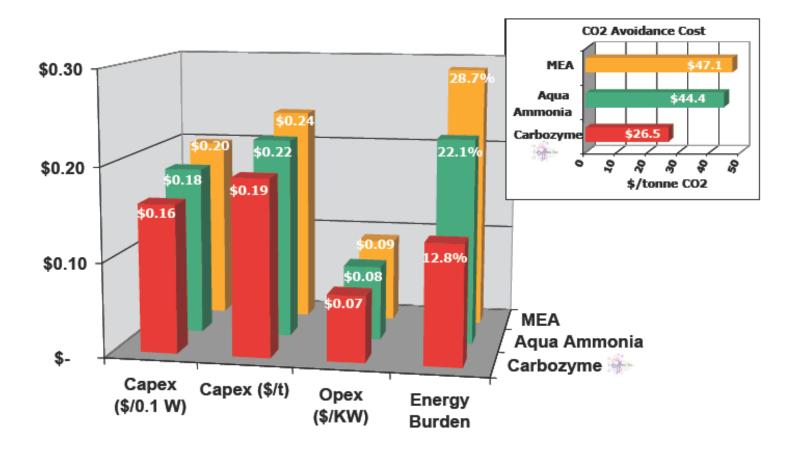


^{*} MMcf = million cubic feet at 1 atm and 60°F.

Costs



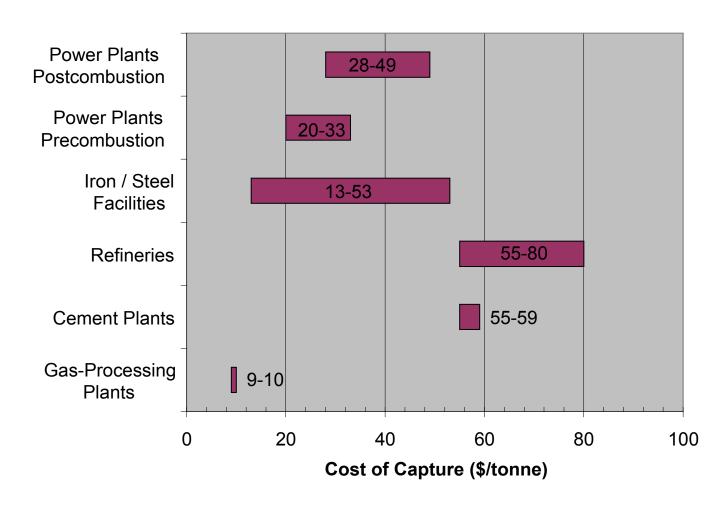
Cost Comparisons – Carbozyme Reports



Based on EPRI, 2000



Cost of Capture Technologies (as of 2005)



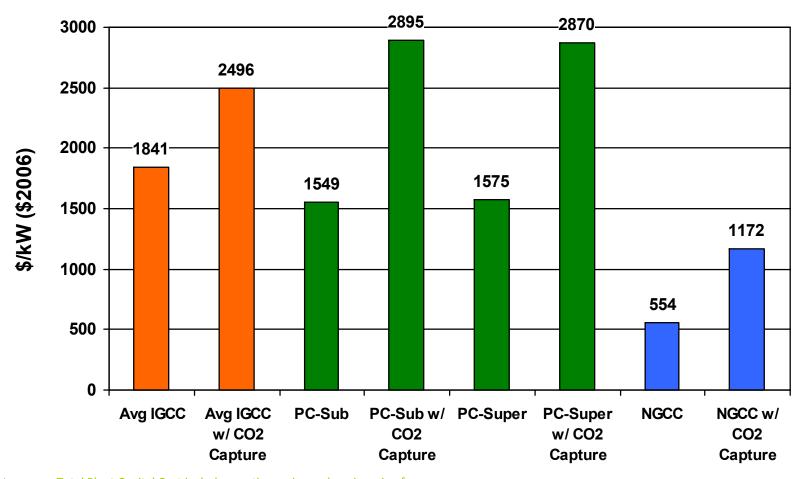








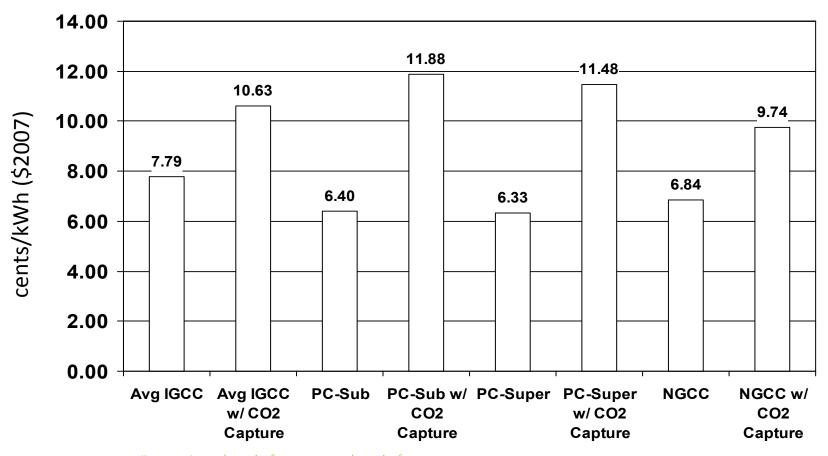
Total Plant Cost Comparison



Total Plant Capital Cost includes contingencies and engineering fees



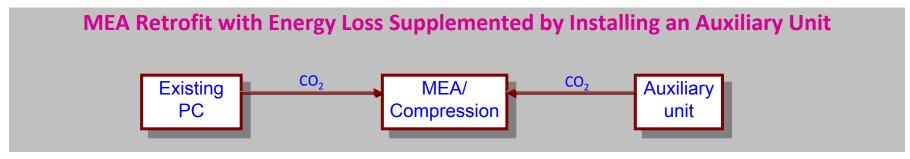
Cost of Electricity (COE) Comparison

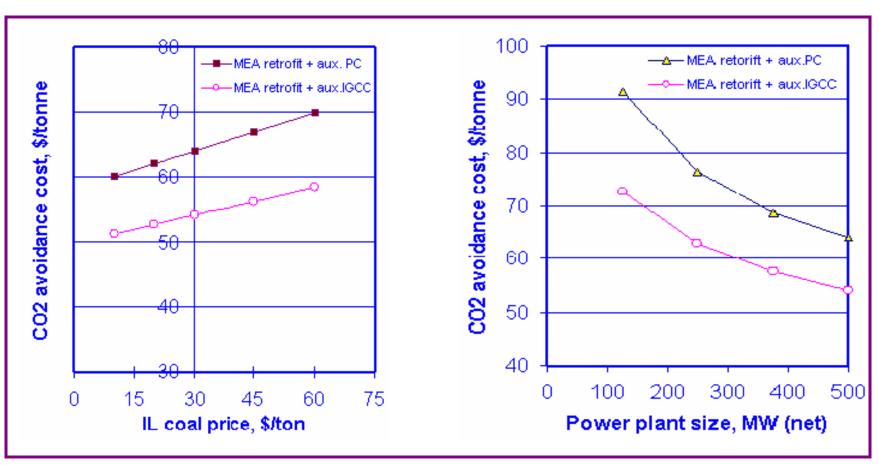


January 2007 Dollars, Coal cost \$1.80/106Btu. Gas cost \$6.75/106Btu

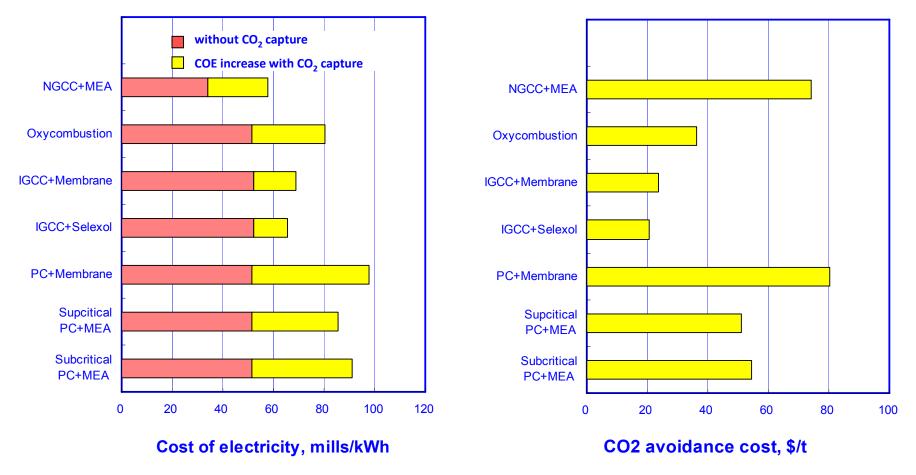








Source: Assessment of Carbon Capture Options for Power Plants. Illinois By Massoud Rostam-Abadi, Shiaoquo Chen, and Yonqiqi Lu



(All data in 2000 dollar; PC+ Membrane: 80% CO₂ recovery and 68% purity)

Data sources:

- 1. Hendriks C., Carbon Dioxide Removal from Coal-fired Power Plants, Kluwer Academic Publishers, The Netherlands, 1994.
- 2. Parsons Energy and Chemicals Group Inc., Evaluation of Innovative Fossil Fuel Power Plants with CO₂ Removal, DOE Interim Report 1000316, 2002
- 3. Chen S.G., Lu Y. and Rostam-Abadi M., Assessment of Geological Carbon Sequestration Options in the Illinois Basin Task 2: Assess Carbon Capture Options for Illinois Basin Carbon Dioxide Sources, DE-FC26-03NT41994, March 2005.
- 4. Assessment of Carbon Capture Options for Power Plants. By Massoud Rostam-Abadi, Shiaoguo Chen, and Yongqi Lu

Results Highlights: COE

- 20-year levelized COE: pc lowest cost generator
 - pc: 64 mills/kWh (average)
 - NGCC: 68 mills/kWh
 - IGCC: 78 mills/kWh (average)
- With CCS: IGCC lowest coal-based option
 - NGCC: 96 mills/kWh
 - IGCC: 105 mills/kWh (average)
 - pc: 116 mills/kWh (average)
- Breakeven LCOE* when natural gas price is:
 - No capture IGCC: \$7.99/MMBtu pc: \$6.15/MMBtu
 - With capture IGCC: \$7.73/MMBtu pc: \$8.87/MMBtu
 - * At baseline coal cost of \$1.80/MMBtu



Costs

- Very hard to find comparative cost estimates all on the same basis for other technologies:
 - Powerspan
 - Cansolv
 - MHI
 - Alstom's Chilled Ammonia
 - Others
 - Solid sorbents
 - Membranes
 - Etc.



Challenges

- Several challenges have been identified.
- Larger demonstrations have been initiated and are critical to reaching the targets set by DOE and others.
- Smaller-scale studies will continue to enhance the performance of larger demonstrations leading to more cost effect and efficient strategies for CO₂ capture.
 - Minimize key challenges
 - Increase energy efficiencies
 - Decrease costs



The Partnership for CO₂ Capture Overview

Brandon Pavlish



The Partnership for CO₂ Capture

- Time line
- Project goals
- Project objectives
- Project tasks
 - Task 1: Postcombustion Capture System Design and Construction
 - Task 2: Oxygen-Fired Retrofit(s)
 - Task 3: Shakedown and Testing
 - Task 4: System Engineering Studies
 - Task 5: Deliverables, Schedule, and Management



Time Line

ID	Task Name	Q2 08			Q3 08		Q4 08		Q1 09			Q2 09			Q3 09					
		Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct
1	Task 1-Post Combustion Capture system Design and Construction																			
2	Task 2-Oxygen Fired Retrofit																			
3	Task 3-Initial Shakedown and Testing																			
4	Task 4-Systems Engineering																			
5	Task 5-Management and Reporting																			



The Partnership for CO₂ Capture: Goals

The overall goal of this program is to demonstrate a wide range of CO₂ capture technologies to identify the key challenges associated with each in order to develop strategies for cost-effective and efficient implementation at the commercial scale.



The Partnership for CO₂ Capture: Objectives

- Gain a thorough understanding of the state of CO₂ capture technologies in order to move toward the development of strategies to enhance efficiencies and decrease costs.
 - Identify the key issues involved with several CO₂ capture technologies.
 - Test a wide range of back-end configurations (electrostatic precipitator [ESP], baghouse, selective catalytic reduction [SCR], wet flue gas desulfurization [WFGD], etc.) to mimic several CO₂ capture applications.
 - Determine effects of various fuel types and flue gas components on CO₂ capture efficiencies.
 - Begin to develop strategies to minimize or eliminate key issues.
 - Perform an overall technical and economic study on several CO₂ capture technologies to form a base to compare and improve upon the state of the technology.



The Partnership for CO₂ Capture: Tasks

- Modifications of pilot-scale and slipstream systems for postcombustion testing.
 - Flexible postcombustion CO₂ capture system(s)
 - Flexible flue gas cleanup and conditioning system(s)
- Oxygen-fired retrofit of existing EERC pilot systems.
- Conduct initial shakedown and testing of selected fuels, system configurations, and CO₂ capture technologies.
- Perform systems engineering analysis of selected systems (for multiple CO₂ technologies).
- Conduct overall project management and reporting.



Questions?



Task 1: Postcombustion Test Systems

Scott Tolbert



Postcombustion Test Systems

Bridging the gap between models, commercial designs, and challenging implementations

- Task 1: Postcombustion systems
 - Flexible CO₂ capture system
 - Flexible flue gas cleanup and conditioning system
 - Design ideas
 - Implementation
- Schedule
 - Critical path analysis

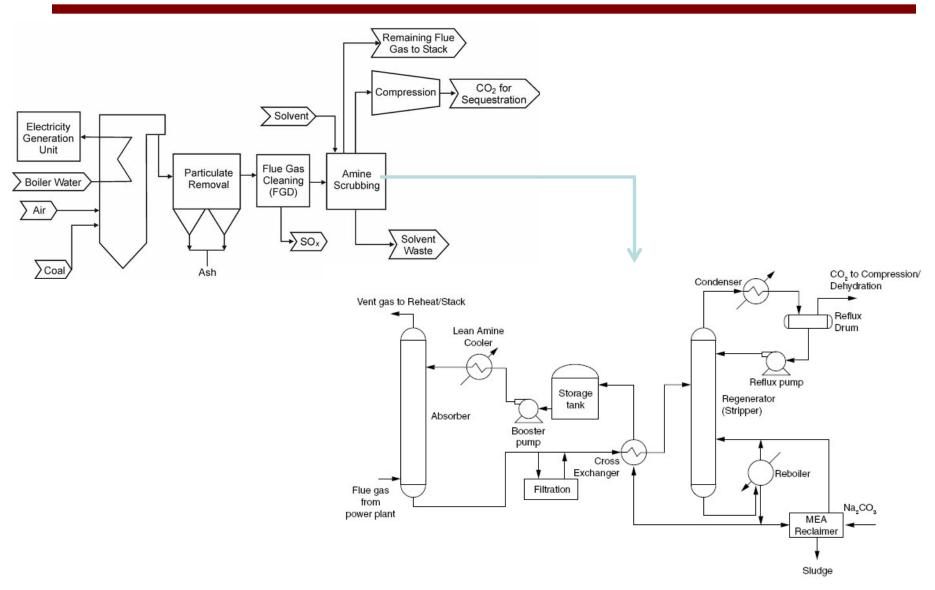


Flexible CO₂ Capture System

- Designed to be a postcombustion absorption CO₂ capture system.
- Will be able to mimic typical solvent systems.
- Design will be as flexible as possible to allow for easy scaleup and for several design modifications.
- Design will allow for the unit to be portable to test on different test systems:
 - Combustion test furnace (CTF)
 - Slagging furnace system (SFS)
 - Others (potential to trailer mount)

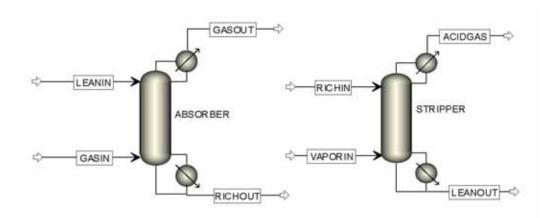


Flexible CO₂ Capture System (cont.)



Equipment Design

- Specific equipment will be designed with the help of Aspen.
 - Pumps
 - Heat exchangers
 - Columns
 - Absorber
 - Stripper
 - Tanks
- Where Aspen is not available, engineering design equations and firsthand experience will be used.





Flexible CO₂ Capture System

- Special design considerations for adequate measurements to determine:
 - Heat of regeneration
 - Solvent flows
 - Temperatures
 - Energy consumption
 - Flue gas components
 - Final CO₂ purity
 - Others to be determined
- Columns will be designed in sections to be able to change out internals easily.
 - Spray nozzles/spray sections
 - Internal packing



Flexible Flue Gas-Conditioning System

- The flue gas-conditioning system will be design to enable the control of the incoming flue gas conditions to the absorption system.
 - Particulate loading
 - HF, HCl, and Hg²⁺ levels
 - Temperatures
 - Flow rates
 - Concentrations of SO_x
 - Concentrations of NO_x
 - Moisture levels



Flexible Flue Gas-Conditioning System (cont.)

- Equipment may include, but is not limited to:
 - Heat exchangers
 - Flow control loops
 - SO_x polishing equipment
 - Wet ESP
 - NO_x control system (other than existing SCR)
 - Others to be determined



Pilot-Scale Testing Units

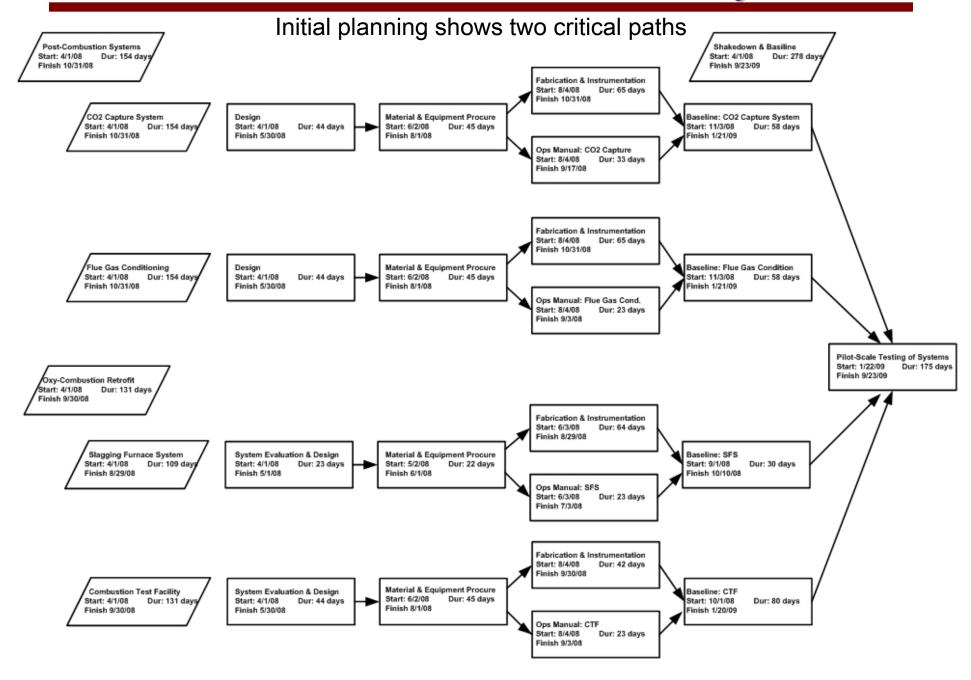
		Combustion Test Facility	Slagging Furnace System	Particulate Test Combustor
COMBUSTION MODE DATA	mBtu/hr	0.55	2.50	0.55
	Exhaust Flow (scfm)	130	530	130
	Exhaust Temperature (°F)	2500	2800	1800
	Air Fired	Х	Х	Х
	Flue Gas Recycle	R\$	Х	R\$
	O ₂ Fired	R\$	X	R\$
	Air Separation Unit	R\$	R \$\$\$	R\$
	Staged Combustion	Х	R \$\$\$	R\$
	Low NOx Burner	Х	Х	Х
	Daily Operational Cost	\$	\$\$\$	\$
FUELS	Bituminous	х	Х	х
	Subbituminous	Х	Х	Х
	Lignite	Х	Х	Х
	Petroleum Coke	Х	R \$\$\$	R\$
	Coal Slurry	Х	R \$\$\$	R\$
	Municiple Solid Waste	Х	R \$\$\$	R\$
	Municiple Sludge	Х	R \$\$\$	R\$
	Biomass	Х	R \$\$\$	R\$
	Fuel Oil	X	R \$\$\$	R\$
	Residual Oil	Х	R \$\$\$	R\$
	Crude Oil	Х	R \$\$\$	R\$
	Natural Gas	Х	Х	Х
	Other	Х		

		Combustion Test Facility	Slagging Furnace System	Particulate Test Combustor
STUDIES	Ash Fouling	Х	Х	
	Heat Flux	х	Х	R\$
	Flame Stability Tests	x	Χ	Х
EXHAUST CLEANUP	Multi-Port Sorbent Injection	Х	R	
	Cyclone	х	Х	Х
	Wet ESP	R\$	R \$\$\$	R\$
	Hot ESP	Х	R \$\$\$	R\$
	Cold ESP	Х	R \$\$\$	Х
	Baghouse	Х	Χ	Х
	Spray Dryer Adsorber	х	R \$\$\$	Х
	Dry Flue Gas Desulfurization	R \$ Slip stream	R \$\$\$	R \$ Slip stream
	Wet Flue Gas Desulfurization	х	Χ	R\$
	Selective Catalytic Reduction	Х	R \$\$\$	Х
	Ammonia CO ₂ Scrubber	R\$	R \$\$\$	R\$
	MEA CO ₂ Scrubber	R\$	R \$\$\$	R\$
INSTRUMENTATION	so _x	х	Х	Х
	NO _x	х	Х	Х
	со	Х	Х	Х
	CO ₂	х	Х	Х
	O_2	х	Х	Х
	Hg	Х	Х	Х

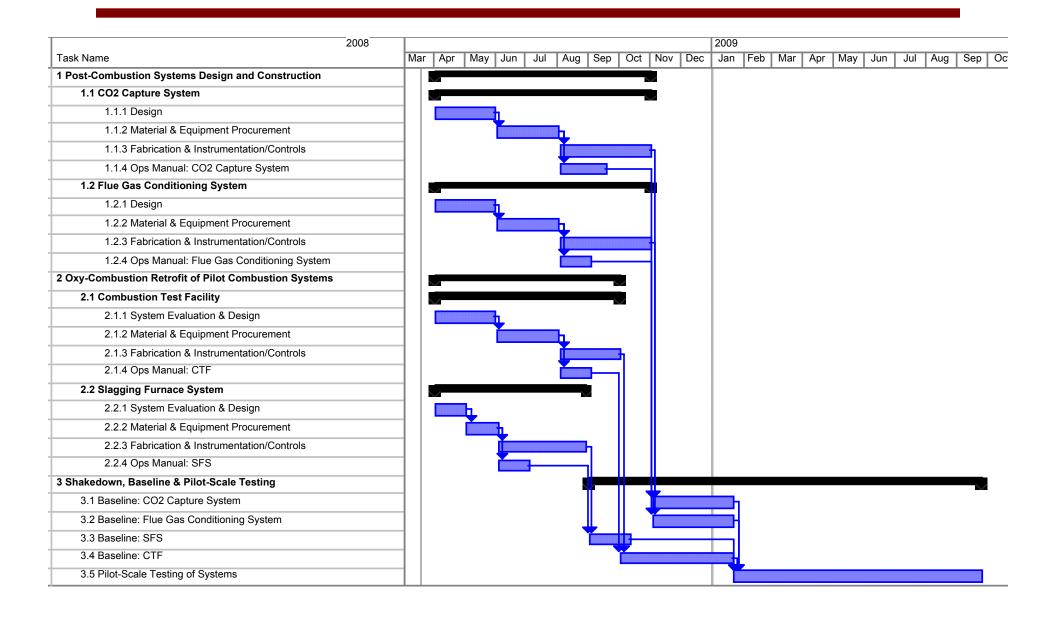
- X Presently capable
- R Retrofit possible
- \$ Relative costs for operation and retrofits



Tasks 1 and 2: Critical Path Analysis



Tasks 1–3: Schedule



Task 2: Oxygen-Fired Retrofit(s)

Jason Laumb



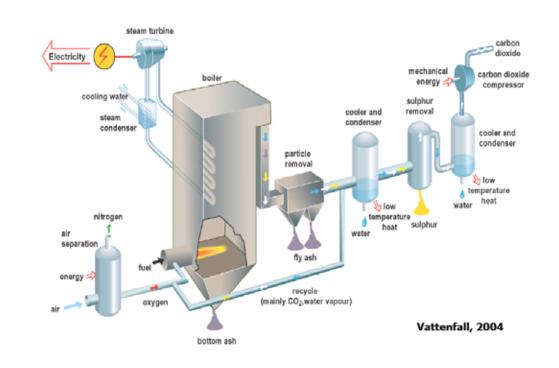
Oxygen-Fired Retrofit(s)

Rationale

- Reduced footprint.
- Maturity of technology.
- Reduced NO_x emissions.
- SO_x, particulate, mercury
- Sodium
- Challenges
 - Fouling/slagging
 - Materials
 - Flue gas recycle
 - ASU

Pilot-Scale Units:

- CTF
- SFS





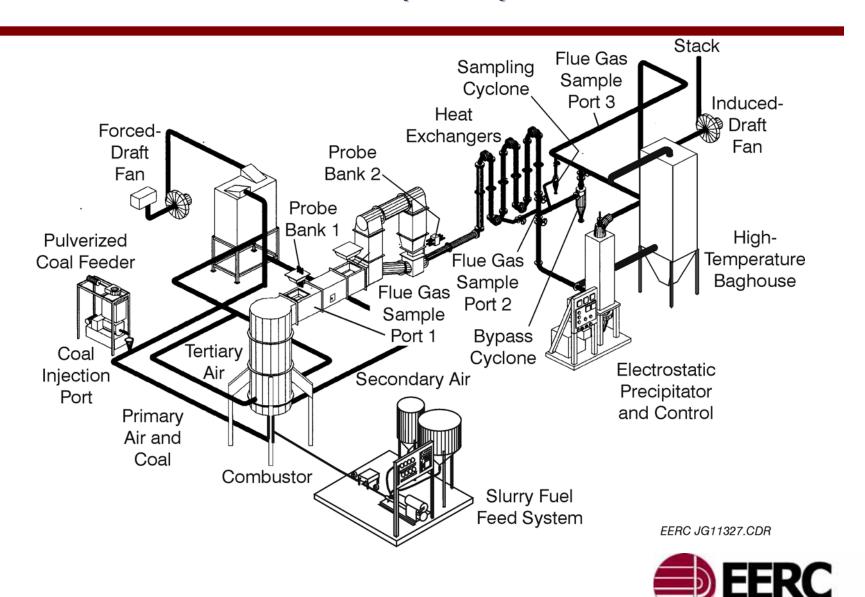
Combustion Test Facility







CTF (cont.)



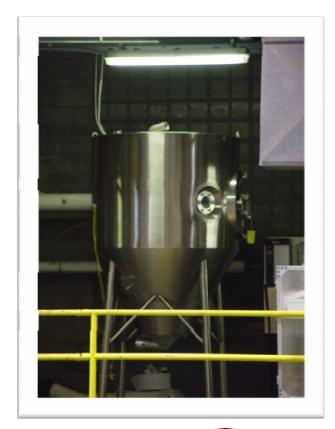
CTF (cont.)

- A 550,000-Btu/hr pulverized fuel pilot plant test furnace
- Furnace exit gas temperature as high as 2500°F
- Research applications:
 - Determine ash-fouling rates and the strength, composition, and structure of fouling deposits for coals of all rank.
 - Apply sophisticated analytical methods to characterize input coal, ash, and deposits.
 - Evaluate the combustion characteristics of coal—water fuels, biomass fuels, municipal solid waste, and petroleum coke.
 - Determine fly ash collection properties of various fuels by electrostatic precipitation or fabric filtration using a pulse-jet baghouse, including hightemperature applications.
 - Perform flame stability tests for comparing a particular fuel at full load and under turndown conditions.
 - Evaluate sorbent injection for SO_x and Hg control and assess integrated particulate and SO_x–NO_x control.
 - Furnace heat flux measurement



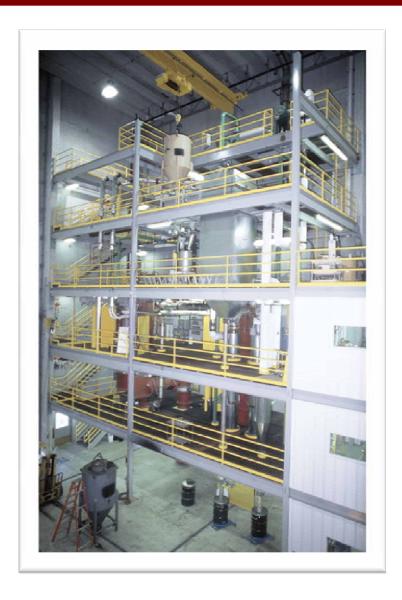
CTF (cont.)

- The CTF is fully instrumented for SO_x, NO_x, CO₂, CO, O₂, Hg, temperatures, pressures, and flow rates.
- Flue gas cleanup equipment:
 - SCR
 - CESP
 - HESP
 - Baghouse
 - Cyclone
 - SDA
 - WFGD



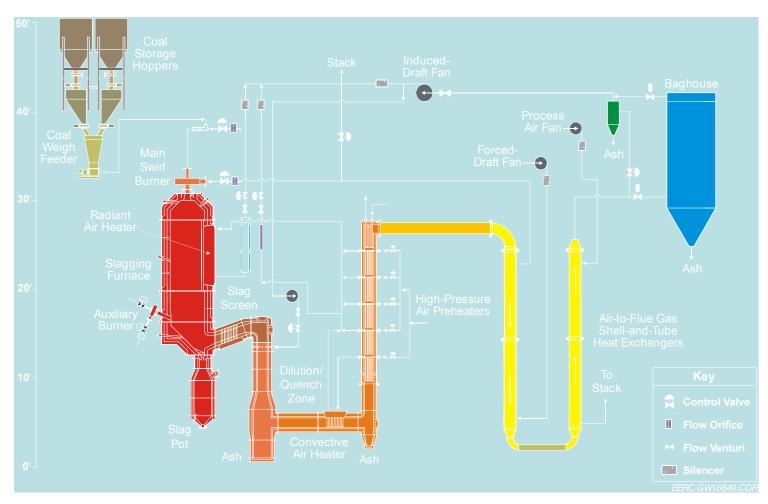


Slagging Furnace System





SFS (cont.)





SFS (cont.)

- The SFS is a slagging design intended to be as fuelflexible as possible.
- Maximum furnace exit temperature of 2900°F, but is typically run at 2800°F.
- The SFS has a nominal firing rate of 2.5 million Btu/hr and a range of 2.0 to 3.0 million Btu/hr using a single burner.
- Resulting flue gas flow rates range from roughly 425 to 640 scfm, with a nominal value of 530 scfm based on 20% excess air.



SFS (cont.)

- Has been run in an oxygen-fired mode.
- Contains the necessary flue gas recycle loop.
- Flue gas cleanup equipment:
 - Baghouse
 - ESP
 - WFGD
 - Wet ESP



Past Experience with Oxy-Firing

- SFS system operated in oxy-firing mode.
 - Flue gas recycle (20% primary, 80% secondary).
 - Automated oxygen injection system.
 - Oxygen levels up to 35% in secondary air.



Proposed Oxycombustion Work

- Determine proper scale for retrofit.
- Enhance current oxy-firing capability:
 - Flue gas recycle
 - Control systems
- Determine fouling/slagging issues associated with oxy-firing.
- Work with exotic metal alloys.



Task 3: Initial Shakedown and Testing

John Kay



Initial Shakedown and Testing





Initial Shakedown

- CO₂ postcombustion system, flue gas pretreatment/conditioning system, and oxy-fired retrofits
 - Develop proper start-up and shutdown procedures
 - Operational parameters verified and optimization of systems
 - Temperatures, pressures, flow rates, etc.
- Expected shakedown length of 1–2 weeks



Baseline Testing – CO₂ Postcombustion System

- MEA
- Intended as standard for comparison
 - Determine regeneration energy required
 - Solvent degradation
 - Effects of flue gas constituents (SO_x, NO_x, Hg, particulate)
 - System optimization
 - CO₂ capture rate and purity
 - Energy penalty
- Utilize flue gas pretreatment/conditioning system
 - Vary the concentrations of SO_x, NO_x and other gas constituents to determine their effects
- Baseline testing of 1–2 weeks



Baseline Testing – Oxy-Fired

- CTF
- SFS
- Baseline will be used to identify potential challenges:
 - Flame stability
 - Heat-transfer issues
 - Fouling and slagging
 - Effects of Hg capture
- Baseline testing of 1–2 weeks



Beyond Baseline

- Develop detailed test plan
 - Content finalized by input from DOE and cost-share partners
- Possible technologies postcombustion
 - MDEA
 - Ammonia
 - Tailored amines
 - Potassium bicarbonate
 - Other



Beyond Baseline – Oxy-Fired

- Additional parameters
 - Effects on Hg control
 - Fabric filter performance
 - ESP performance
 - WFGD performance
 - SDA performance
 - SCR performance
 - Other



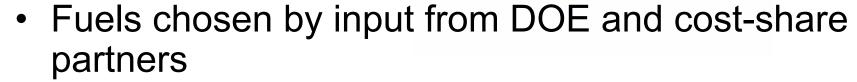
Beyond Baseline – Small-Scale Slipstreams

- Carbozyme
- Solid sorbents (Zeolytes, MOFs, solid amines)
- Other membranes
- Other
- Test parameters
 - Determined on a technology basis
 - CO₂ capture rates and CO₂ purity
 - Energy penalty
 - Technology robustness
 - Other



Potential Fuel Types

- Biomass
- Lignite
- Subbituminous
- Bituminous
- Petcoke
- Blends







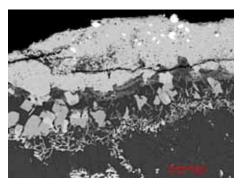
Analytical Toolbox

The EERC has more than 50 years of analytical experience.

Analytical tools provide key information in the characterization of fuels, deposits, slags, ashes, alloy corrosion, and mechanical components.

Advanced techniques provide that information quickly.









Advanced Analysis

- Scanning electron microscopy and x-ray microanalysis
 - Coal mineral typing and sizing
 - Ash deposits and slag
 - Morphological examination
- Electron backscattered diffraction
 - Crystalline phases and composition
- Heated-stage x-ray diffraction
 - Changes of crystalline phases with time and/or temperature



Scanning Electron Microscopy

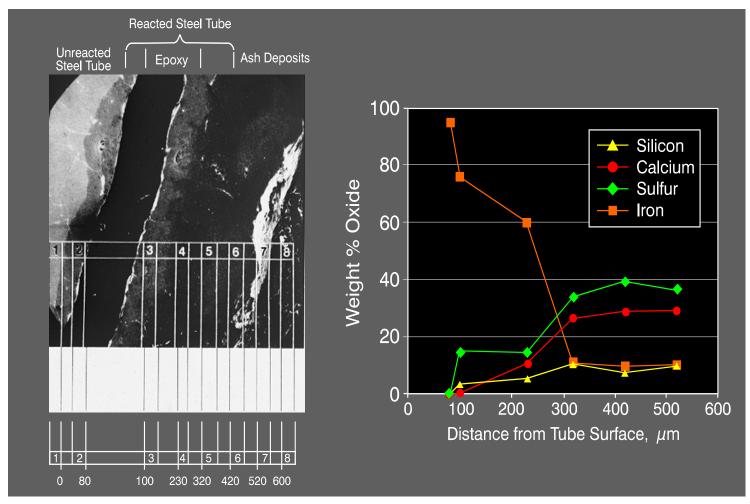




- Morphological analysis
- Fuel impurity analysis— size, shape, and chemistry of several thousands of particles per sample.
- Slag and ash deposit liquidphase identification and physical properties.
- X-ray elemental mapping.

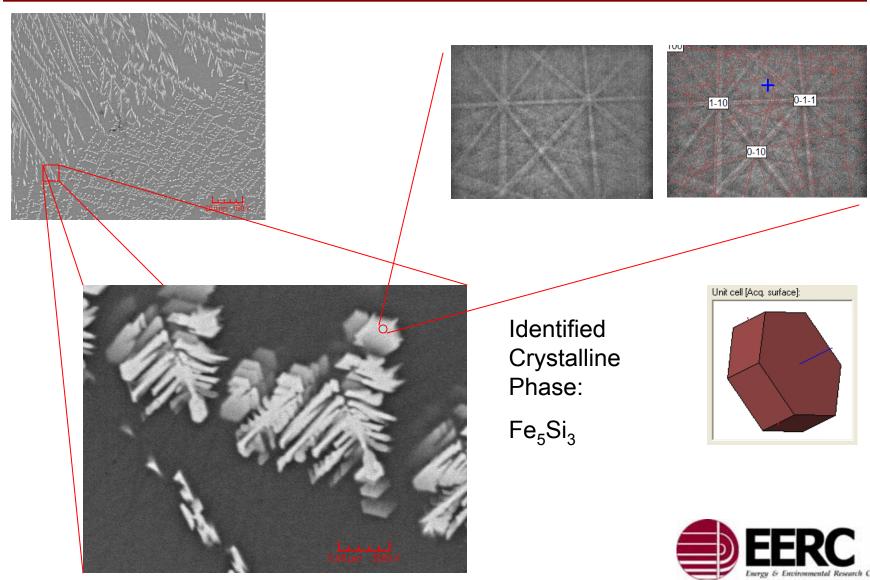


Relationship Between Corrosion and Deposit Adhesion

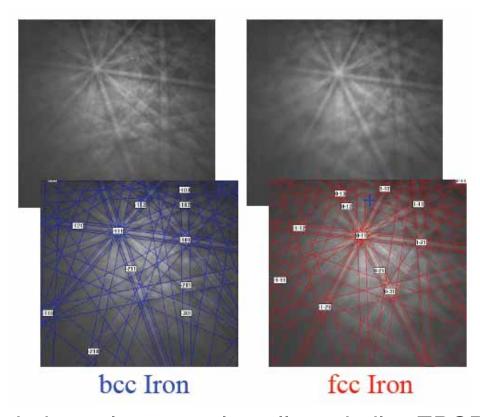




Electron Backscattered Diffraction (EBSD)



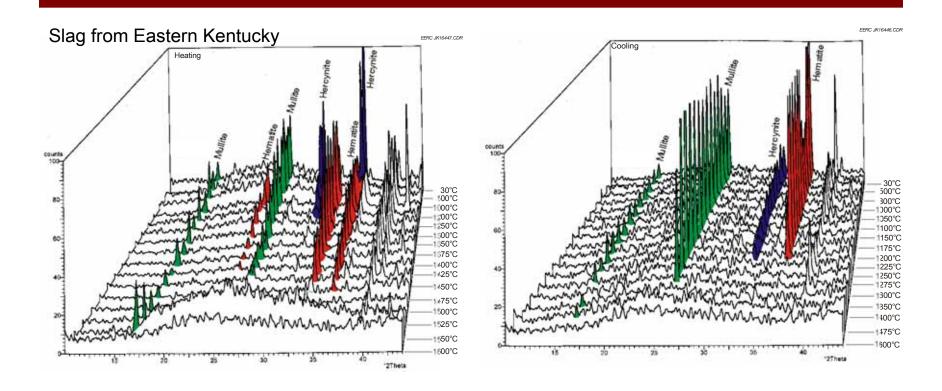
Phase Discrimination



Differences in interplanar angles allow similar EBSD patterns to be discriminately identified.



X-Ray Diffraction of Slags



Differences in crystallization can be detected and identified.



Summary of Task 3

- Shakedown and baseline testing of post-CO₂ combustion, flue gas pretreatment/conditioning system, and oxy-fired retrofits.
- Additional testing based on sponsor input.
- Utilization of EERC analytical experience and toolbox to provide vital information on fuel characterization, ash and deposit analysis, corrosion, and slagging/fouling mechanisms.



Task 4: Systems Engineering Studies

Josh Stanislowski



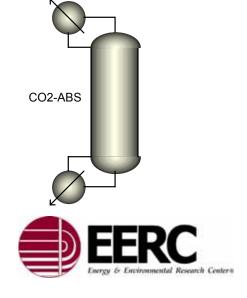
Systems Engineering Studies Overview

- Task 4 will utilize Aspen Plus process-modeling software to aid in design and evaluation of CO₂ capture systems.
 - Aspen Plus will be the design tool for pilot-scale equipment additions and upgrades in Tasks 1 and 2.
 - Develop postcombustion CO₂ capture models (retrofit technologies).
 - Gasification modeling with and without CO₂ capture (precombustion).
 - Economic studies and comparisons of CO₂ capture technologies.

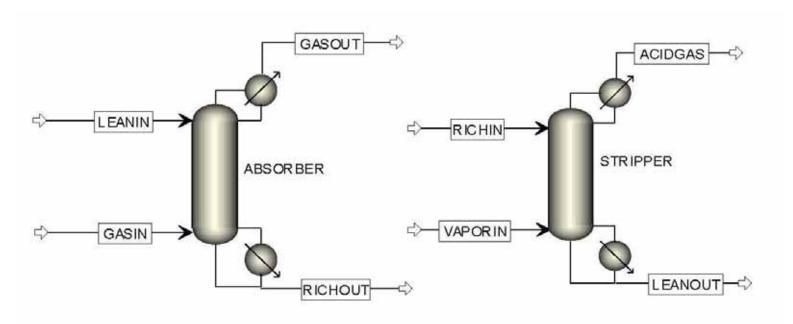


Systems Engineering with Aspen Plus®

- Aspen Plus[®] is a very versatile model for gasification systems engineering:
 - Heat and energy balances
 - Equipment sizing
 - Solids-handling capabilities
 - Accepts proximate—ultimate analysis to determine coal properties
 - Models for coal ash properties
 - Fluegas/syngas composition predictions
 - Particle-size modeling
 - Absorber-stripper modeling capabilities
 - NIST Chemical Properties Database



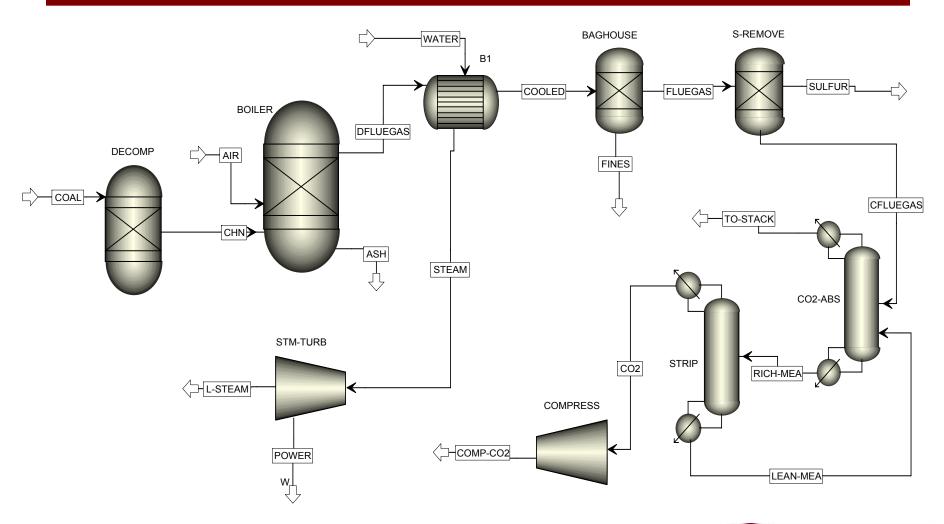
Aspen-Based CO₂ Capture Model



- Base model for various absorption and stripping column designs.
- Model details are contained within the modules:
 - Kinetics
 - Mass transfer
 - Chemical reaction and phase equilibrium
- User-specified models can be incorporated.

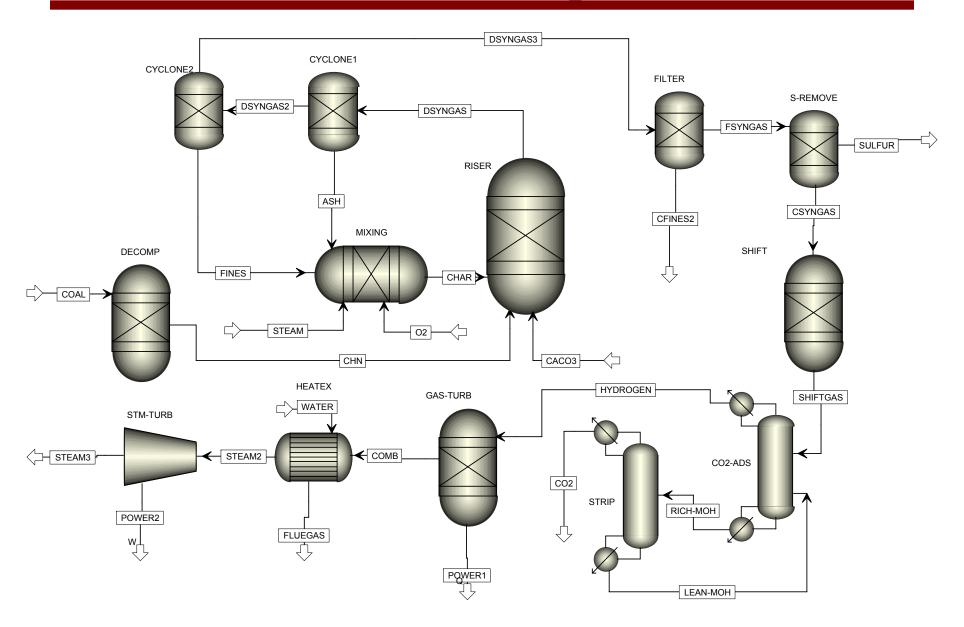


Postcombustion CO₂ Capture Model





Precombustion CO₂ Capture



Aspen Modeling Results Sample

		BIOMASS	C-FINES	CHN	DSYNGAS	DSYNGAS2	DSYNGAS3	O2	QSYNGAS	QSYNGAS2	SLAG	STEAM	WATER-Q	
From			CYCLONE	DECOMP	RGIBBS	SLAGTAP	CYCLONE		QUENCH	QUENCHE	SLAGTAP			
То		DECOMP		RGIBBS	QUENCH	CYCLONE		RGIBBS	QUENCHE	SLAGTAP		RGIBBS	QUENCH	
Substream	: ALL													
Mass Flow	LB/HR	100	0.36	100	165.7	220.82	220.47	45.7	229.82	229.82	9	20	64.12	
Mass Enth	BTU/HR	-615601	169.68	-63755.11	-248945.8	-788214.7	-788384.3	-237.93	-688885.7	-788798.7	-584.09	-107770.9	-439939.9	
Substream	: MIXED													
Phase:			Missing	Mixed	Vapor	Vapor	Vapor	Vapor	Vapor	Vapor	Missing	Vapor	Liquid	
Componen	Component Mole Flow													
H2O	LBMOL/HF		0	0.56	1.68	4.26			5.24		0	1.11	3.56	
N2	LBMOL/HF	0	0	0.16		0.16	0.16		00	0.16	0	0	0	
02	LBMOL/HF		0	0.76		0		1.43	0	0	0	0	0	
S	LBMOL/HF		0	0.08	0	0		0	0	0	0	0	0	
NH3	LBMOL/HF	0	0	0	0	0			0	Ţ	0	0	0	
С	LBMOL/HF		0	0	•	0				0	0	·	·	
H2	LBMOL/HF		0	2.23	2.14	1.58			2.14	1.58	0	0	0	
CO	LBMOL/HF		0	0	0.00	0.56					0	0	0	
CO2	LBMOL/HF	0	0	0		2.39	2.39	0		2.39	0	0	0	
	LBMOL/HF	0	0	0	0.01	0	_		0.01	0	0	0	0	
	LBMOL/HF	0	Ŭ	0	0	0.76	0.76			0.76	0	·		
	LBMOL/HF		0	0		0	Ū	ů		0	0	0	0	
H2S	LBMOL/HF	0	0	0	0.08	0.08	0.08	0	0.08	0.08	0	0	0	
Component Mole Fraction														
H2O		0	0	0.15		0.43				0.43	0	1	1	
N2		0	Ŭ	0.04		0.02	0.02			0.02	0	·	Ŭ	
O2		0	ŭ	0.2	0	0		-	0	0	0	·	Ŭ	
S		0	ŭ	0.02	0	0			ŭ	0	0	·	Ū	
NH3		0	0	0		0					0	·		
С		0	<u> </u>	•	•	0	·	•		•	0	·	·	
H2		0	_			0.16								
CO		0	<u> </u>	0		0.06				0.06				
CO2		0	<u> </u>	0		0.24					0	·		
COS		0	<u> </u>	0		0	·	•	-	-	ŭ			
CH4		0	<u> </u>	0		0.08				0.00	0			
CL2		0	<u> </u>			0				0				
H2S		0	0	0	0.01	0.01	0.01	0	0.01	0.01	0	0	0	

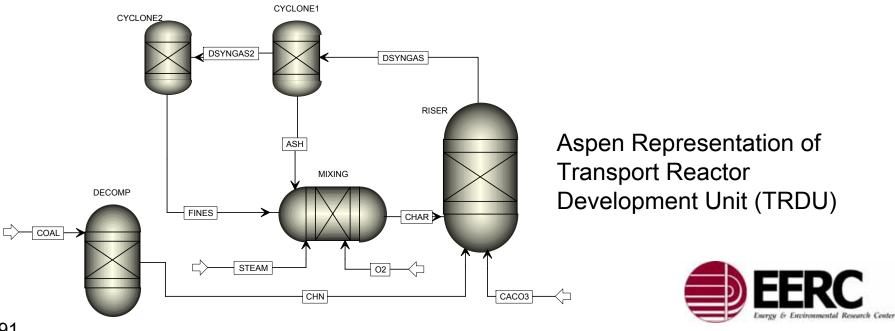
Postcombustion Models – Calibration and Validation

- Performance data from Task 3 will be used to calibrate and validate the Aspen capture models.
 - Combine existing Aspen CO₂ capture models and pilot-scale data to build upon and improve capture models.
 - Run modeling scenarios and provide results to consortium.
 - Use models as a scale-up tool from pilot- to full-scale systems.
 - Evaluate other variables not tested including other feedstocks and boiler operating conditions.
 - Models can be tuned to closely simulate input flue gas conditions.



Gasification Studies

- Task 4 will evaluate CO₂ capture technologies with gasification systems.
- Data will be used to compare cost and performance to combustion systems.



Economic Analysis

- Aspen Icarus Process Evaluator (IPE)
 - Vast database of costing information that is updated on a regular basis by receiving updates from Aspentech.
 - Costing information is customizable.
 - NETL CO₂ capture economic guidelines will be used to enhance comparability.

QA/QC

 The results obtained from IPE will be compared to current literature and to other models, where applicable, including the Integrated Environmental Control Model (IECM).



Task 5: Deliverables, Schedule, and Management

Brandon Pavlish

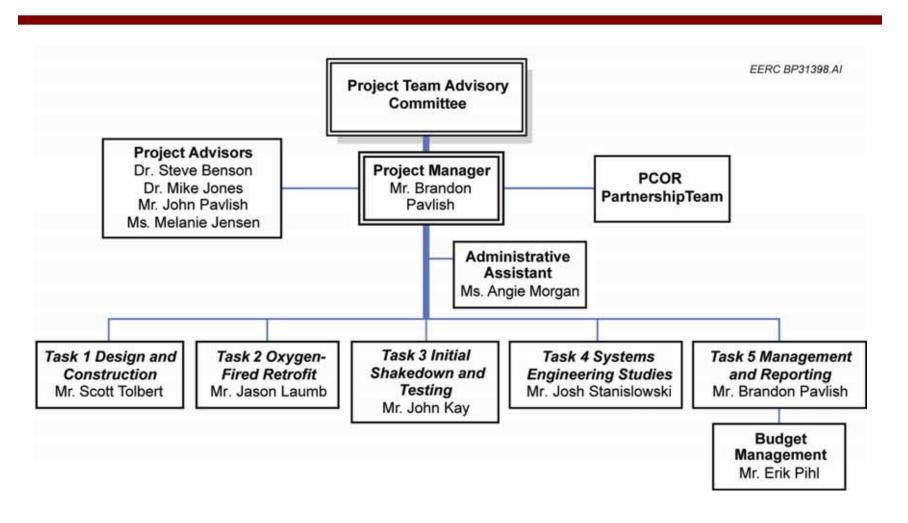


Management and Reporting

- The project team will work in close cooperation with the project steering group, which will include the committed project sponsors and the U.S. Department of Energy.
- Regular updates of the overall project progress and results will be provided through quarterly and annual reports to the sponsors.
- Project information of a proprietary nature will be conveyed to the individual sponsors separately.
- A detailed final report that will include the following:
 - Results from testing the CO₂ capture system
 - Results from testing the pre-gas cleanup system
 - Results of testing the oxyfuel system retrofit
 - Advanced model simulations
 - CO₂ capture feasibility studies
 - CO₂ capture economic sensitivity analysis

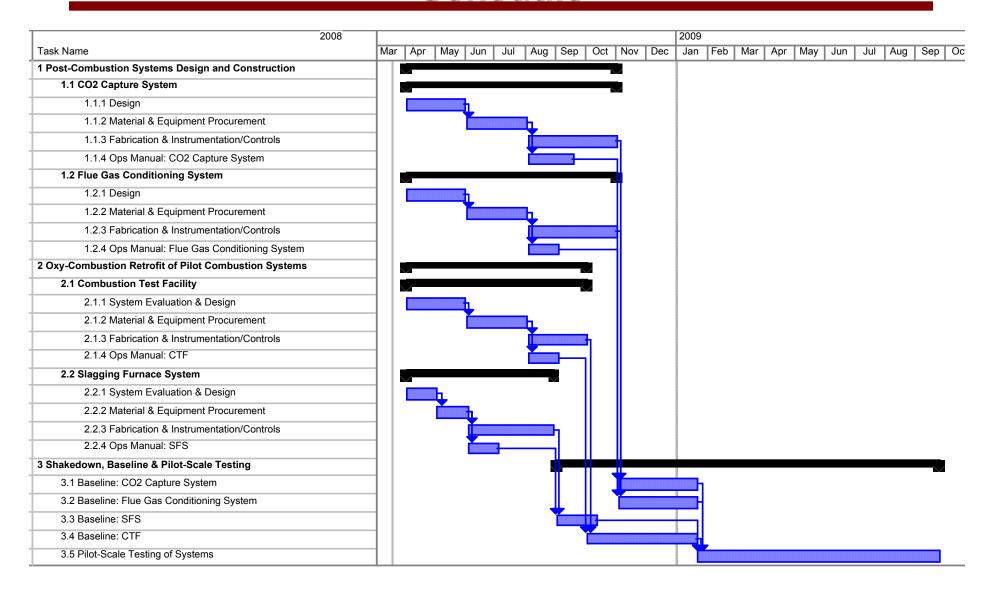


Management Structure





Schedule



Schedule (cont.)

ID	Task Name	Start	Finish	Duration	Q2 08	Q3 08	Q4 08	Q1 09	Q2 09	Q3 09
	radicivalino				Apr May Jun	Jul Aug Sep	Oct Nov Dec	Jan Feb Mar	Apr May Jun	Jul Aug Sep
1	Task 4 – Systems Engineering Studies	4/1/2008	2/27/2009	239d						
2	Sub-Task 4.1 Modeling of CO2 Capture Systems	4/1/2008	2/27/2009	239d						
3	Sub-Task 4.2 Economic Evaluation of CO2 Capture Systems	11/17/2008	2/27/2009	75d						
4	Task 6 Reporting	4/1/2008	10/1/2009	393d						
5	Sub-Task 6.1 Quarterly Reports	4/1/2008	4/1/2009	262d					1	
6	6.1.1 DOE Quarterly	4/1/2008	7/31/2008	88d						
7	6.1.2 DOE Quarterly	6/2/2008	9/29/2008	86d						
8	6.1.3 DOE Quarterly	9/1/2008	1/30/2009	110d						
9	6.1.4 DOE Quarterly	1/1/2009	4/2/2009	66d]	
10	Sub-Task 6.2 Final Report DOE	4/1/2008	10/1/2009	393d						
11	Sub-Task 6.3 Final Report Industrial	4/1/2008	10/1/2009	393d						



Benefits of Sponsorship

- Membership on the project's Advisory Committee.
- Information on mechanisms of CO₂ capture and interactions with fly ash and flue gas components.
- Detailed fuel characterization information.
- Results of CO₂ emissions and capture potential for various capture technologies.
- Performance and cost data for various CO₂ capture technologies to assist in developing an overall capture strategy. Data available will be directly applicable to coals and plants that are part of this project.



Benefits of Sponsorship (cont.)

- Collaborative research between stakeholders with an interest in developing cost-effective CO₂ capture technologies.
- Cost-effective research at a fraction of the cost available to a single company.
- Effective transfer of information and data through consultation with EERC staff and sponsor personnel.
- Interaction with other sponsors and with personnel interested in CO₂ capture problems and potential solutions.



Test Plan Development

- Questionnaire
 - Fuel types
 - Capture technologies
 - Critical test parameters
 - Unit configurations
 - Modeling efforts



Questionnaire

- Task 1: Postcombustion Test Systems
 - Design considerations
 - Scale
 - Temperature capabilities
 - Parameters of importance
 - Measurement capabilities
- Task 2: Oxygen-Fired Retrofit(s)
 - Design considerations
 - Scale
 - Measurement capabilities
 - Others



Questionnaire (cont.)

- Task 3: Initial Shakedown and Testing
 - Fuel types
 - Capture technologies
 - Parameters of interest
 - Suggested tests to consider
 - Others
- Task 4: Systems Engineering Studies
 - Systems to model
 - Parameters of interest
 - Others



Questionnaire (cont.)

- Task 5: Management and Reporting
 - Meeting(s)/conference calls to discuss work plans, results, accomplishments, and directions:
 - Frequency
 - Every 6 months
 - Every 3 months
 - Every other month
 - Other
 - Location preference
 - EERC for all meetings
 - EERC once per year of project and off-site at sponsors' suggested location



Contact Information

Energy & Environmental Research Center
University of North Dakota
15 North 23rd Street, Stop 9018
Grand Forks, North Dakota 58202-9018

World Wide Web: www.undeerc.org
Telephone No. (701) 777-5000
Fax No. (701) 777-5181

