Near-Zero Emissions Oxy-Combustion Flue Gas Purification

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Existing Plants R&D Meeting
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Praxair At A Glance

- A Fortune 300 company with 2008 sales of $10.8 Bn
- One of the largest industrial gases companies in the world
- Markets served
  - Metals, Energy, Chemicals, Healthcare, Electronics, Manufacturing, Food and Beverage, Aerospace and various other markets
- Major gas products
  - Atmospheric gases (O_2, N_2, rare gases (Ar, Xe, Kr, Ne))
  - Process Gases (H_2, CO_2, He acetylene)
  - Specialty Gases
- Experience with several technologies applicable to CCS
  - Cryogenic and non-cryogenic air separation
  - Hydrogen production
  - Carbon dioxide purification and liquefaction
  - Oxy-fuel combustion

Project Overview

- Goal: Develop a near-zero emissions oxy-combustion flue gas purification technology
  - >95% CO_2 capture for existing plants with high air ingress
  - Produce high purity CO_2 by removing >90% of SOx/NOx/Hg
- Total cost: $5.4MM
  - DOE $3.24 MM
  - Praxair $2.16 MM
- DOE Project # NT0005341
  - DOE Program manager – Mike Mosser
- Project performance dates: 1/1/09 – 12/31/11
- Project participants
  - Praxair
  - Foster Wheeler
  - AES
  - Colt Engineering

Problem Definition

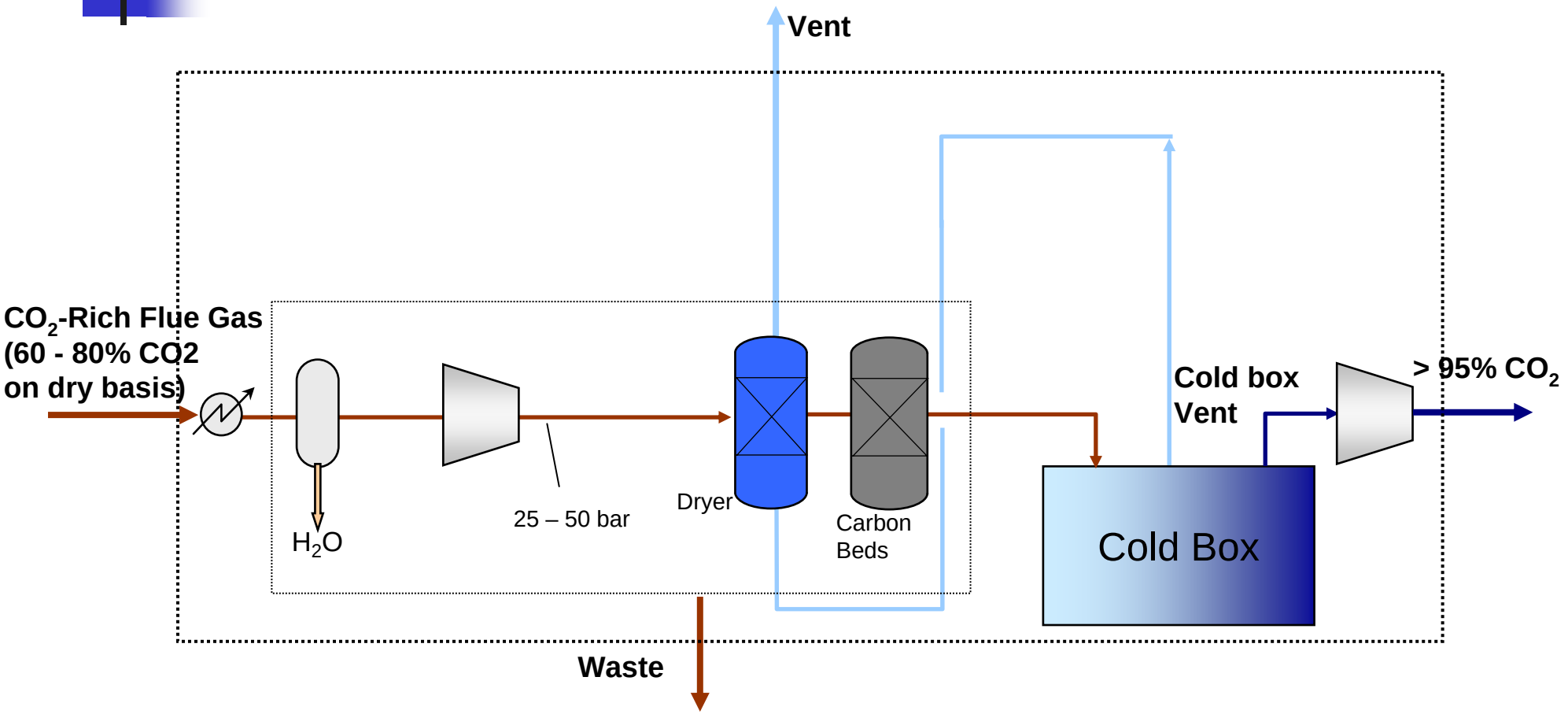
- DOE Objectives for CO_2 purification in the oxy-combustion option
  - Make progress towards goal of <35% COE increase for CCS plant
  - Achieve >90% CO_2 recovery
  - Reduce levels of SOx/NOx/Hg in CO_2

- Characteristics of existing plants
  - 30 – 36% HHV efficiency (average for the fleet 32% HHV)
  - Plants burning high sulfur coal have FGDs for SOx compliance
  - Many plants switched to low sulfur coal in 1990s
  - Air infiltration could be as high as 10%

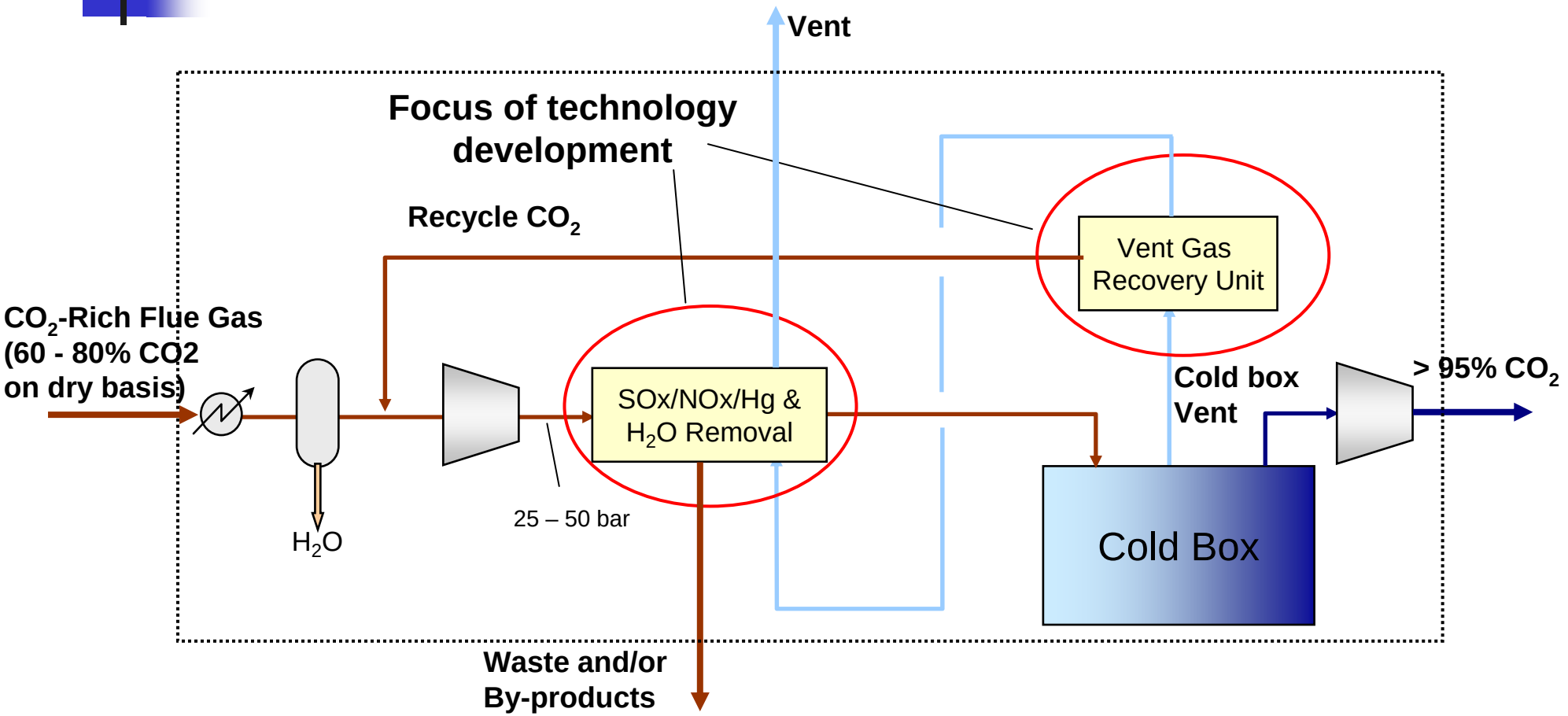
- Retrofit challenges
  - Plants burning high sulfur coal will require additional polishing step
  - Plants burning low sulfur coal will require investment in FGD
  - CO_2 recovery from conventional oxyfuel flue gas purification 60 – 80%

Technology

Conventional CO_2 Purification



Near Zero Emissions Technology



- SOx/NOx/Hg removal for high sulfur coal
- SOx/NOx/Hg removal for low sulfur coal
- High CO_2 recovery (>95%) by recovering CO_2 in cold box vent

Process for High Sulfur Coal

- Modified lead chamber process for SOx/NOx removal

$$NO_2 + SO_2 \rightarrow NO + SO_3$$
$$NO + 1/2O_2 \rightarrow NO_2$$
$$SO_3 + H_2O \rightarrow H_2SO_4$$
$$NOx + H_2SO_4 \leftrightarrow H_2SO_4 \bullet NOx$$
$$3NO_2 + H_2O \rightarrow 2HNO_3 + NO$$

  - Multiple unit operations in a 50 – 160 C temperature range
  - Produce saleable sulfuric acid
  - >99% SOx removal and > 90% NOx removal

- Incorporation of Outokumpu process for mercury removal
  - Concentrated H_2SO_4 generated in the process is used for Hg removal

Process for Low Sulfur Coal

- Praxair studied activated carbon for SOx/NOx removal in 1990s

$$SO_2 + 1/2O_2 \rightarrow SO_3$$
$$NO + 1/2O_2 \rightarrow NO_2$$
$$SO_3 + H_2O \rightarrow H_2SO_4$$
$$3NO_2 + H_2O \rightarrow 2HNO_3 + NO$$

  - Direct oxidation of SOx and NOx with solid catalyst
  - Dilute acid stream produced as waste stream
  - >95% removal of SOx demonstrated

- The concept adapted for oxycombustion flue gas purification
  - Performance at high pressure unknown
  - Regeneration of activated carbon a key for effective SOx/NOx removal

- Mercury removal in a separate carbon bed

Cold Box Vent CO_2 Recovery Unit

- Technology
  - Vacuum pressure swing adsorption (VPSA)
  - Multiple adsorption beds undergo different cycle steps
  - Each bed under cyclic stead state while VPSA as a unit at steady state
  - CO_2 recovery from VPSA 90%; enables overall recovery of 99%

- Cold box vent stream
  - 350 to 450 psia and ambient temperature
  - CO_2 concentration will be > 30%

- Recycle CO_2 stream
  - Ambient pressure
  - CO_2 concentration will be 80 – 95%

- Vent stream
  - Contains mainly atmospheric gases

Benefits of Proposed Technologies

- SOx/NOx/Hg Removal process for high sulfur coal
  - Lower operating costs
  - Shutdown FGD/SCR and generate revenue from by-products
  - Produce higher purity CO_2

- SOx/NOx/Hg Removal process for low sulfur coal
  - Lower investment costs compared to FGD/SCR
  - Produce high purity CO_2

- High CO_2 recovery using VPSA
  - Achieve >95% CO_2 recovery even for plants with high air ingress

Preliminary Cost Estimate – Old Plant

	Oxyfuel technology	Conventional	Proposed SOx/NOx process	Proposed SOx/NOx process + VPSA
Low Sulfur Coal Process	% COE increase	105%	66%	86%
	CO_2 recovery, %	62%	62%	96%
	CO_2 capture cost $/ton	$54	$34	$27
High Sulfur Coal Process	FGD operational?	Yes	No	No
	% COE increase	94%	70%	85%
	CO_2 recovery%	62%	62%	96%
	CO_2 capture cost $/ton	$57	$42	$32

- Low sulfur coal process avoids expensive FGD/SCR systems
- High sulfur coal process reduces operating costs by shutting down conventional FGD operation
- VPSA reduces CO_2 capture costs

Preliminary Cost Estimate – New Plant

	Oxyfuel technology	Conventional	Proposed SOx/NOx process	Proposed SOx/NOx process + VPSA
Low Sulfur Coal Process	% COE increase	74%	61%	65%
	CO_2 recovery, %	90%	90%	98%
	CO_2 capture cost $/ton	$47.7	$40.1	$38.6
High Sulfur Coal Process	FGD/SCR?	Yes	No	No
	% COE increase	73%	52%	56%
	CO_2 recovery%	90%	90%	98%
	CO_2 capture cost $/ton	$48.0	$34.5	$33.8

- Low/high sulfur coal processes avoids expensive FGD/SCR systems
- High sulfur coal process also reduces operating costs
- VPSA reduces CO_2 capture costs

Key Challenges

- SOx/NOx/Hg removal by sulfuric acid process
  - Technical feasibility of recycling flue gas with high SOx
  - NOx removal efficiency
  - Material of construction
- SOx/NOx/Hg removal by activated carbon process
  - Effective regeneration of activated carbon
  - Durability of materials
  - NOx removal efficiency
- High CO_2 recovery using VPSA
  - Tolerance to residual SOx/NOx
  - Cost of recovering additional CO_2
- Commercial viability
  - Modifications required for retrofitting existing plants
  - Capital cost advantage compared to conventional technology
  - Adoption by power producers

Objectives

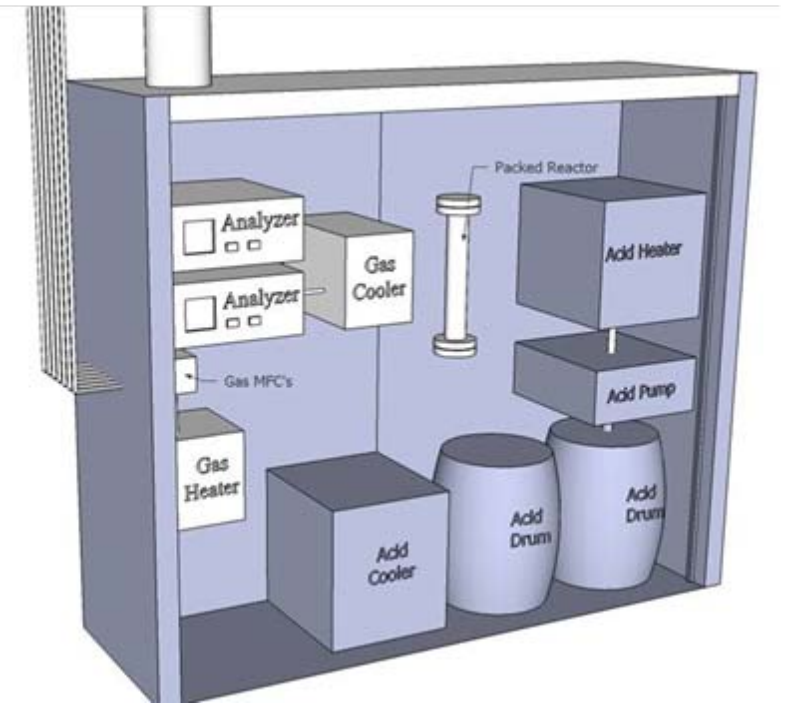
- Collect sufficient test data to enable process and system design
- SOx/NOx/Hg removal for high sulfur coal
  - Develop mass transfer and reaction kinetics data
  - Determine optimum process conditions for effective NOx removal
- SOx/NOx/Hg removal for low sulfur coal
  - Test materials for SOx/NOx removal efficiency and regenerability
  - Conduct bench-scale tests to determine optimum process conditions
  - Develop process concepts for high NOx removal efficiency
- VPSA Process
  - Identify adsorbents with tolerance to residual SOx/NOx
  - Conduct bench-scale and small pilot-scale tests to optimize process
- Assess commercial viability
  - Power plant performance for air & oxy firing modes (Foster Wheeler)
  - Technoeconomic feasibility (Praxair with input from Colt Eng)
  - Integration and operability assessment (AES)

Project Methodology

High Sulfur Coal Process – Experimental Plan

		2009				2010				2011			
		Q1	Q2	Q3	Q4	Q1	Q2	Q3	Q4	Q1	Q2	Q3	Q4
2	SOx/NOx/Hg Removal - High S Coal												
2.1	Bench-Scale Test Unit												
2.2	SOx/NOx Removal Tests												
2.3	NOx Reaction Tests												
2.4	By-Product Purification												
2.5	Mercury Removal Research												

- Bench-scale test unit in a walk-in hood
- Single gas/liquid contacting column
- Multiple unit operations
- Operating pressure up to 250 psia
- Operating temperature up to 300 F



Low Sulfur Coal Process – Experimental Plan

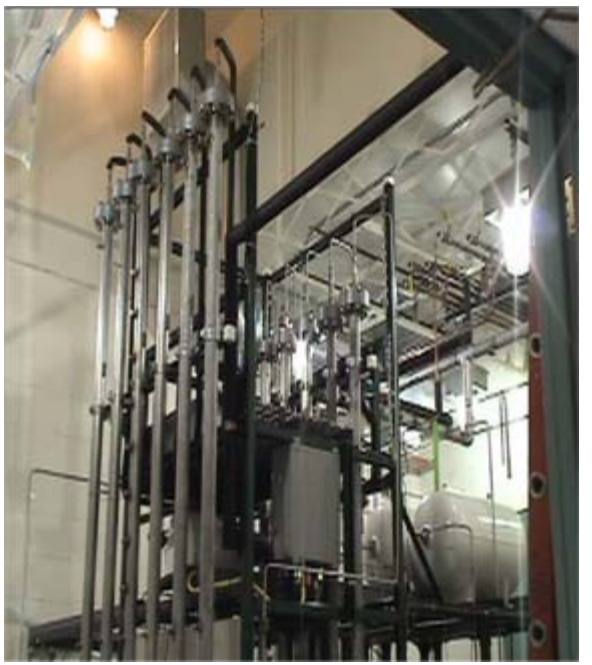
		2009				2010				2011			
		Q1	Q2	Q3	Q4	Q1	Q2	Q3	Q4	Q1	Q2	Q3	Q4
3	SOx/NOx/Hg Removal - Low S Coal												
3.1	SOx/NOx removal material selection												
3.2	Bench-Scale Test Unit												
3.3	SOx/NOx Removal Tests												
3.4	Hg and Residual NOx Removal Research												

- Lab-scale unit for material screening
- Bench-scale tests for performance assessment
- Single column unit (1” dia. 1.5’ long)
- Operating pressure up to 250 psia
- Operating temperature up to 200 F

VPSA – Experimental Plan

		2009				2010				2011			
		Q1	Q2	Q3	Q4	Q1	Q2	Q3	Q4	Q1	Q2	Q3	Q4
4	High CO2 Recovery												
4.1	Separation Agent Identification												
4.2	Simulation Tool												
4.3	Bench-Scale Tests												
4.4	Continuous Operation Tests												

- Bench-scale unit
  - Material and process cycle screening
  - Initial calibration of simulation tool
- Continuous operation unit
  - Mimic commercial system design
  - 1000 scfh
  - Design data for larger system



H_2 PSA Test Unit

Commercial Viability Assessment

- Technoeconomic evaluations
  - Existing power plant performance (Foster Wheeler)
  - Process simulations (Praxair)
  - Technoeconomic feasibility for H_2SO_4 process (Colt Engineering)
  - Economic feasibility including COE and cost of CO_2 capture (Praxair)
  - Integration and operability (AES)

		2009				2010				2011			
		Q1	Q2	Q3	Q4	Q1	Q2	Q3	Q4	Q1	Q2	Q3	Q4
5	Commercial Viability Assessment												
5.1	Process and Systems Engineering												
5.2	Power Plant Performance												
5.3	By-Product Commercial Viability												
5.4	Economic Feasibility												
5.5	Integration and Operability												
5.6	Plan for Pilot Demonstration												

Commercialization Pathway

- Near term opportunities likely for demonstration projects
- Praxair is developing a 50 MW oxy-coal demonstration project
  - Start-up date likely to be 2014
  - VPSA will be an integral part of the demonstration
  - Activated carbon process will be demonstrated on a slip stream
- Commercial opportunities will be driven by CO_2 regulations
- Smaller scale CO_2 capture opportunities for non-power applications
  - Could lead to a demonstration opportunity before 2015

Summary

- Near-zero emissions technology for power plants
- Unique combination of known unit operations to gain technical and economic benefits
- Technology applicable to existing and new plants

Acknowledgement & Disclaimer

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