Near Zero Emissions Oxy-combustion Flue Gas Purification

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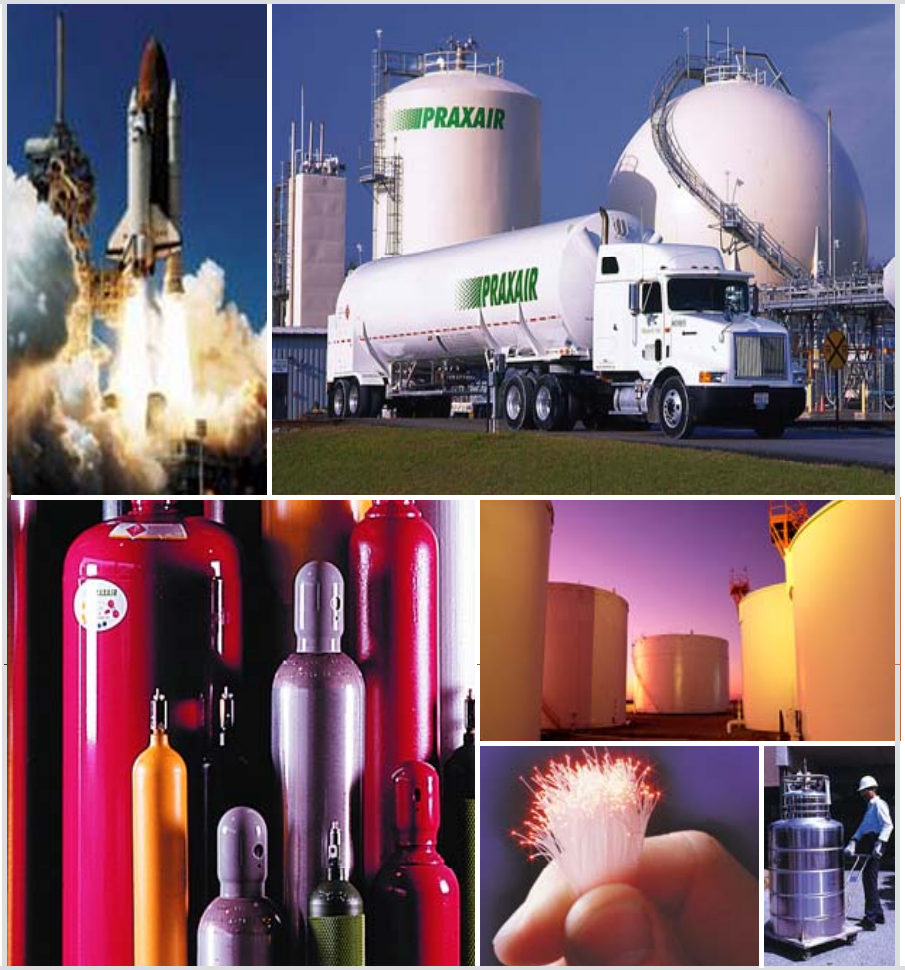

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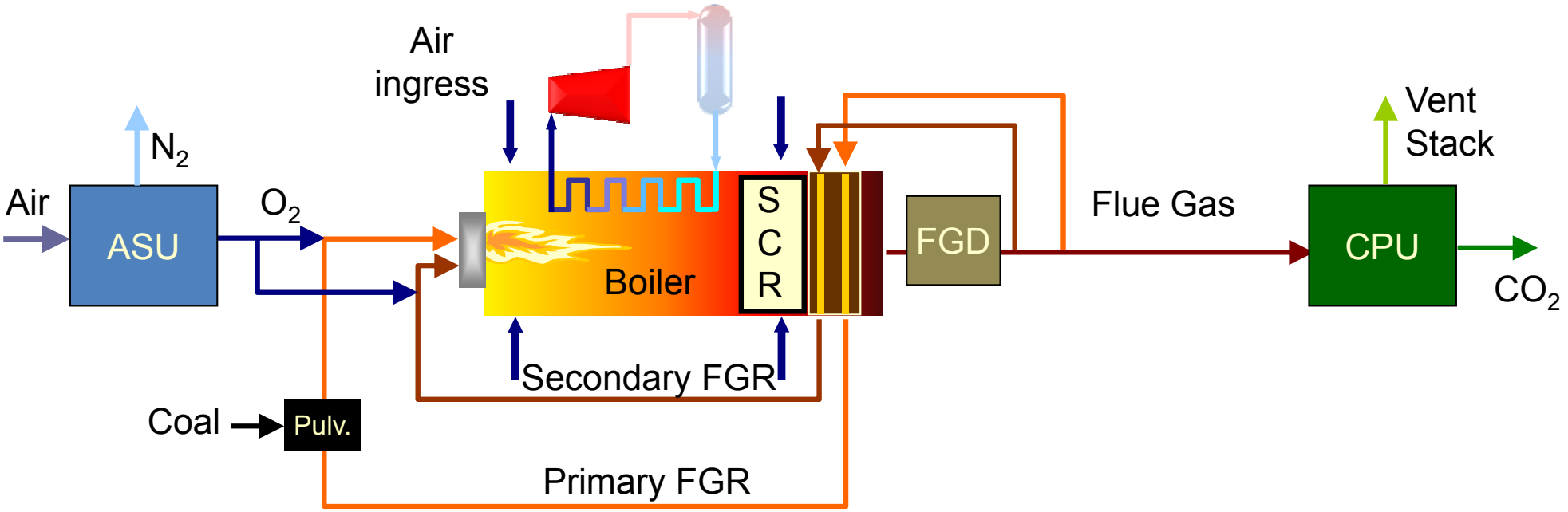
Praxair At A Glance

- **A Fortune 300 company with 2010 sales of $10 Billion**
- **One of the largest industrial gases companies in the world and the largest in North and South America**
- **Markets served**
  - Aerospace, Chemicals, Electronics, Energy, Food and Beverage Healthcare, Manufacturing, and Metals
- **Major gas products**
  - Oxygen, nitrogen, rare gases (argon, xenon, krypton, neon)
  - Hydrogen, carbon dioxide, helium, acetylene
  - Specialty gases
- **Core technologies applicable to CCUS**
  - Cryogenic air separation
  - Hydrogen production and purification
  - Carbon dioxide capture and purification
  - 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 >99% of SOx/Hg and >90% NOx
- **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
  - WorleyParsons Canada

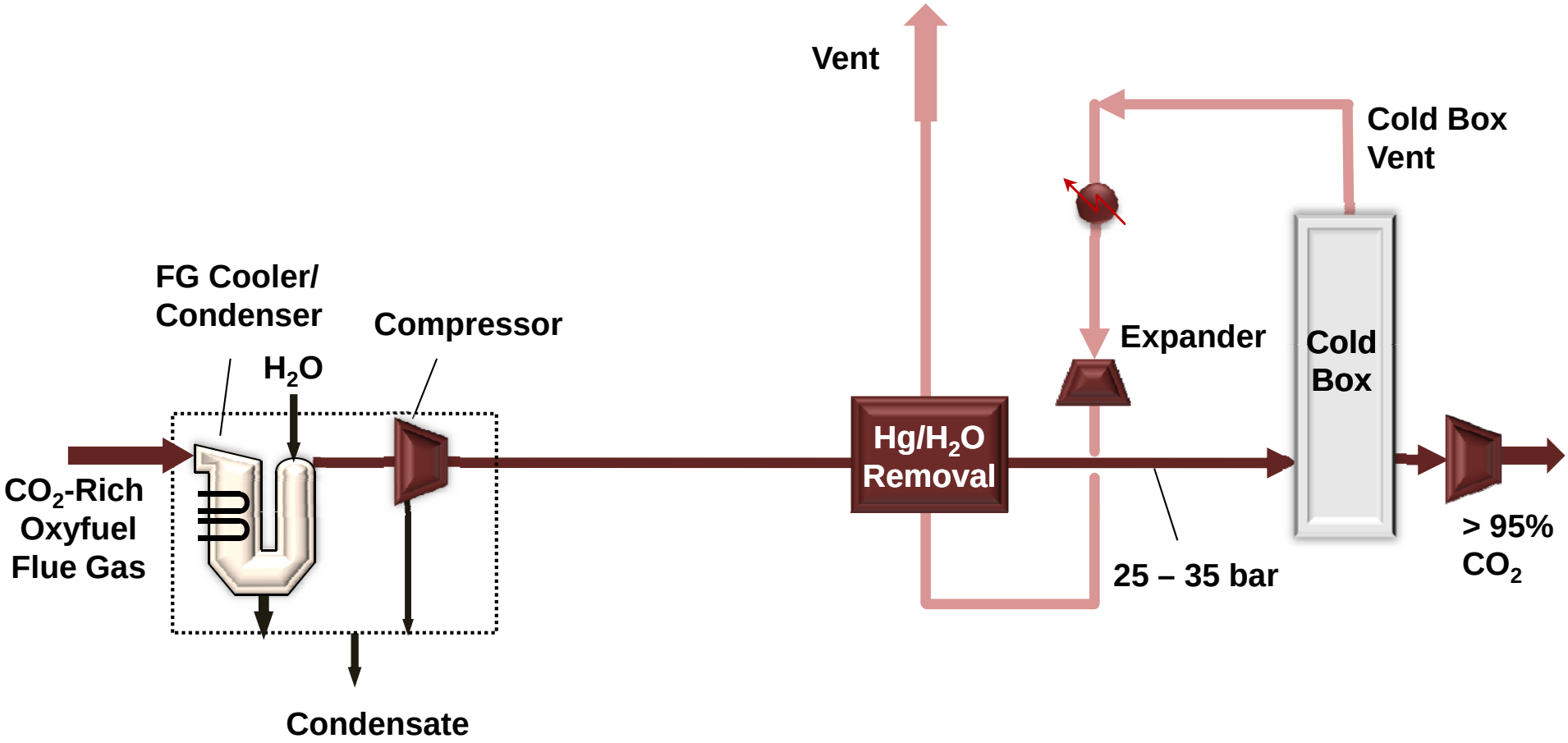
Problem Description



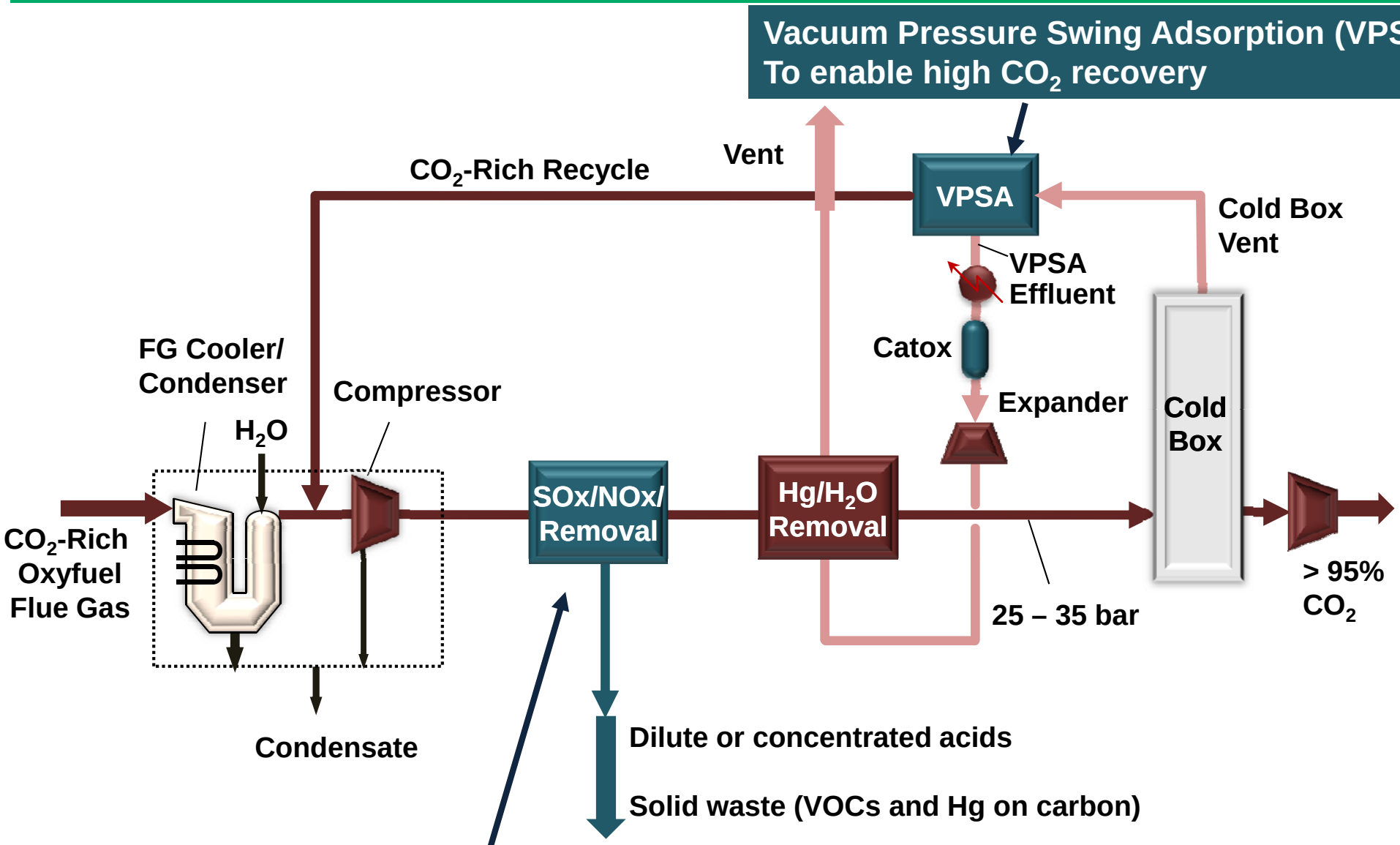
- **Existing plants could have high (10 – 15%) air ingress →Lower CO_2 concentration in flue gas → low CO_2 capture rate**

- **>50% of plants do not have FGD and SCR; to produce high purity CO_2**
  - Plants without FGD & SCR will require significant investment
  - Plants with FGD & SCR will still require additional polishing steps to remove SOx/NOx

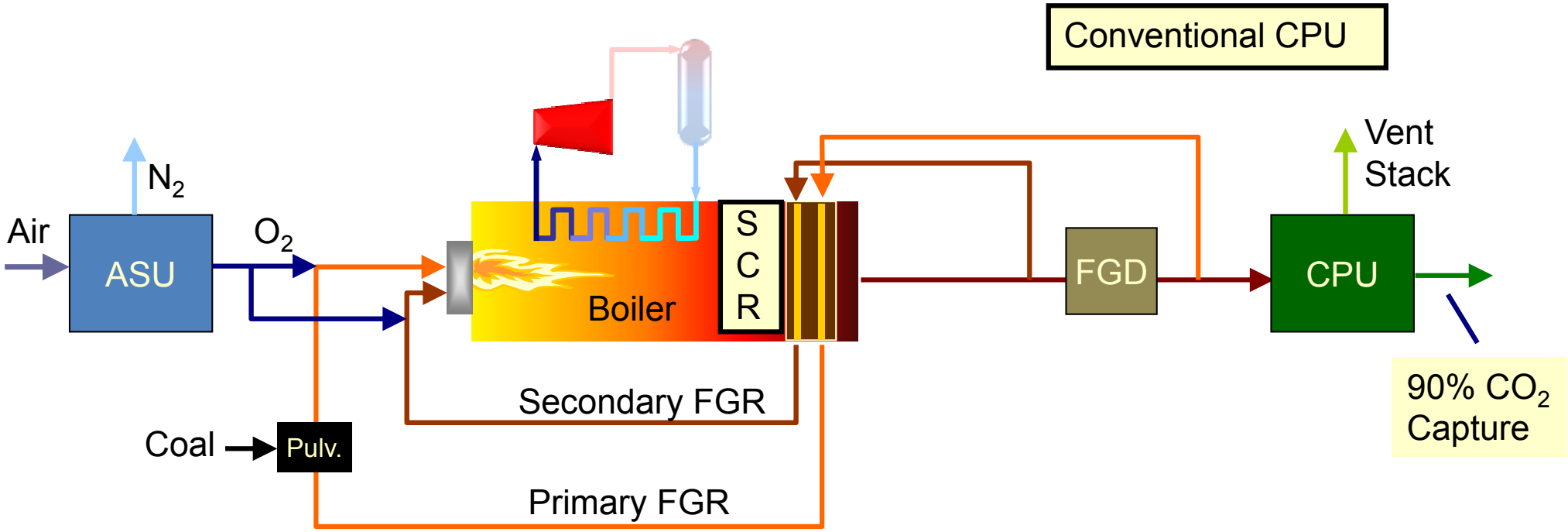
Technology Fundamentals
Conventional CO_2 Processing Unit (CPU)



Technology Fundamentals
Near Zero Emissions CO_2 Processing Unit (CPU)



Benefits of Praxair CPU in Comparison to Conventional CPU



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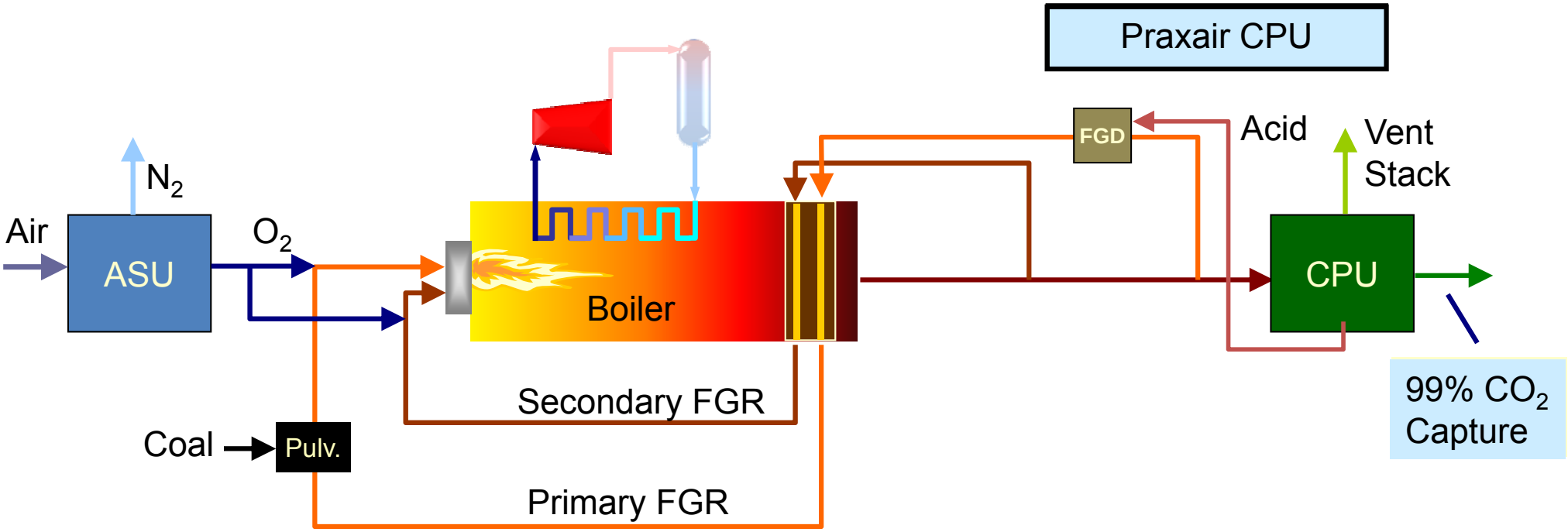
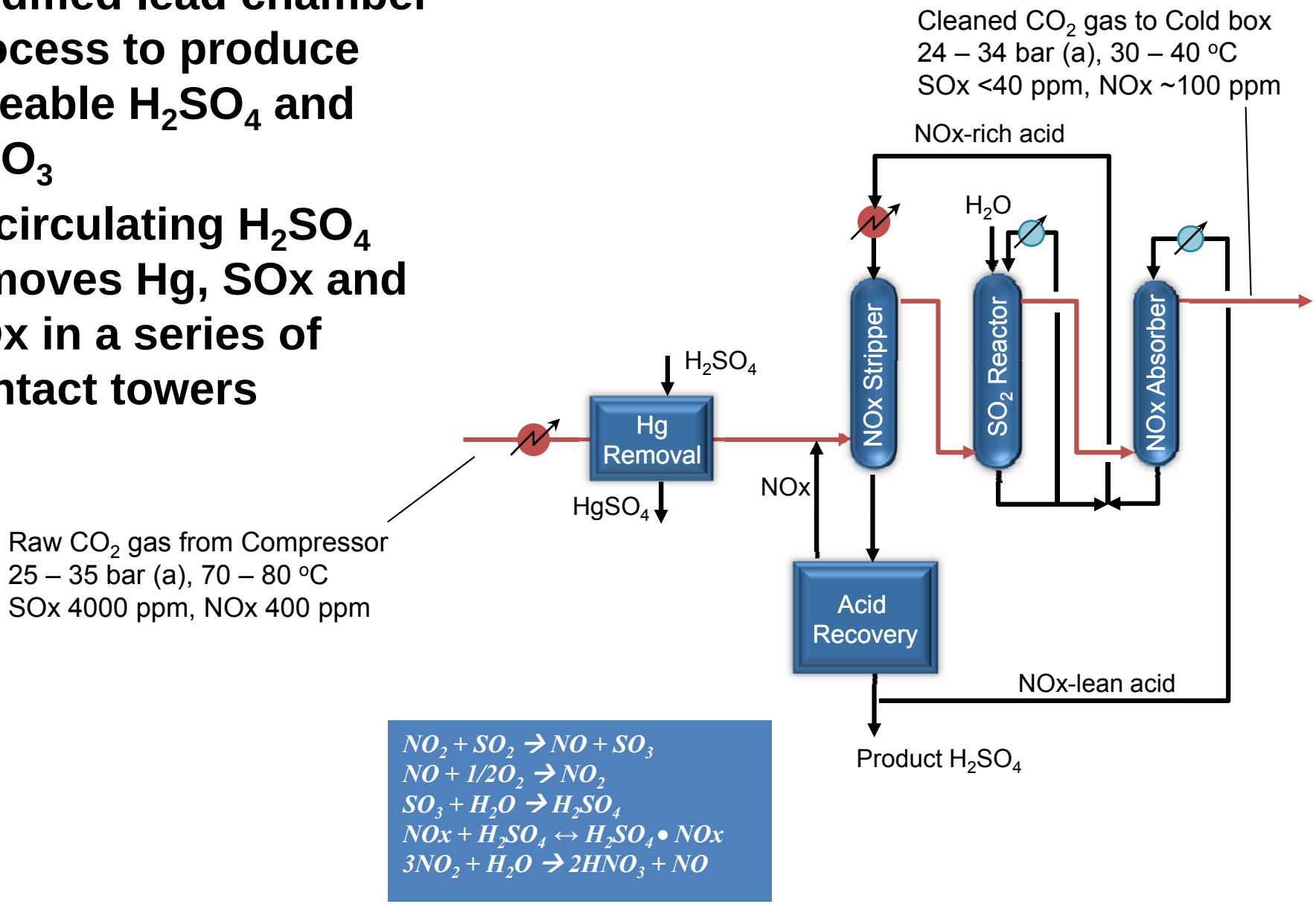


Benefits of Praxair CPU

- **Near zero stack emissions**
- **High CO_2 recovery**
  - >95% for old plants with 10% air ingress
  - >99% for new plants with 2% air ingress
- **High CO_2 purity**
- **Lower CAPEX for SOx/NOx removal**
  - Elimination of SCR and reduced size FGD in the boiler island
  - Much smaller vessel sizes in the CPU
- **Lower CO_2 capture costs; Benefit maximized when**
  - Existing plant does not have FGD/SCR and high purity CO_2 is desired → conventional process will require installation of FGD/SCR
  - FGD/SCR exists, but CO_2 purity spec for SOx/NOx is very stringent → conventional process will require a polishing unit
  - Existing plant has high air ingress → conventional process will have poor CO_2 recovery

Sulfuric Acid Process for SOx/NOx/Hg Removal Technology Fundamentals

- **Modified lead chamber process to produce saleable H_2SO_4 and HNO_3**
- **Recirculating H_2SO_4 removes Hg, SOx and NOx in a series of contact towers**



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

Sulfuric Acid Process
Current Status

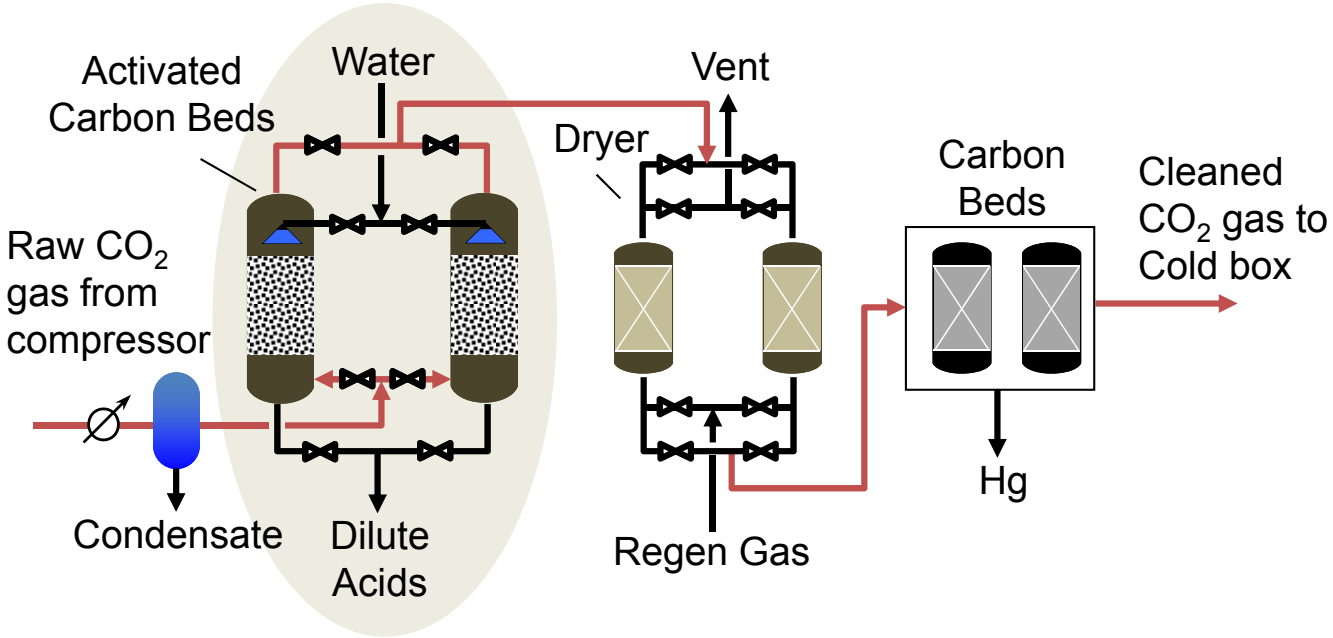
- **Bench-scale tests concluded in Q4 2010**
  - Single column (1' L, 1.5" ID) unit used to test various unit operations
  - Capacity – 0.06 tpd CO_2 in flue gas
  - Gas phase nitric oxide (NO) oxidation kinetics confirmed
  - NOx mass transfer in H_2SO_4 evaluated under the conditions of NOx absorber and NOx stripper
  - Effect of various process variables in SO_2 reactor investigated
    - Residence time, temperature, SOx and NOx levels in the feed, acid flow rate

Sulfuric Acid Process
Current Status and Future Plans

- **Process simulations used to predict process performance**
  - >99% SOx removal will be achieved by SO_2 reactor
  - >98% NOx removal will be achieved by NOx absorber;
  - NOx removal from 93% H_2SO_4 not achieved in NOx stripper
  - Accumulation of NOx in the loop limited overall NOx removal to ~75%
  - Residual NOx in flue gas present as NO_2; it can be removed by water wash
- **Commercial viability assessment**
  - CAPEX of H_2SO_4 process will be >90% lower than the full size FGD
  - However, 60% of the full size FGD is required in the boiler island
  - H_2SO_4 containing high level of NOx unlikely to be marketable
  - Therefore, produced H_2SO_4 must be neutralized and disposed off
- **Final report will be issued in Q4 2011**

No further development on this process is planned

Activated Carbon Process for SOx/NOx/Hg Removal Technology Fundamentals

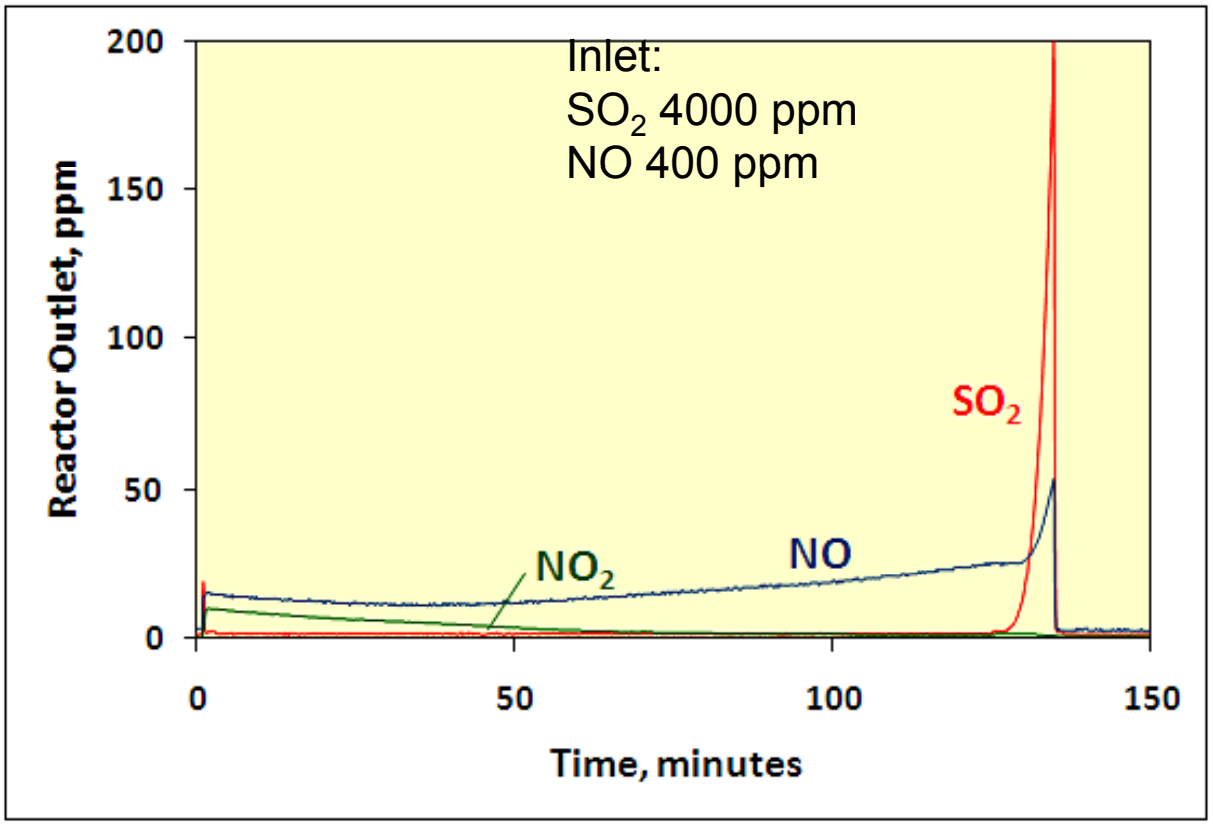


$SO_2 + 1/2O_2 \rightarrow SO_3$
$NO + 1/2O_2 \rightarrow NO_2$
$SO_3 + H_2O \rightarrow H_2SO_4$
$3NO_2 + H_2O \rightarrow 2HNO_3 + NO$

- **SO_2 and NO are oxidized and retained on activated carbon**
- **Carbon is regenerated by water wash followed by drying**
- **Dilute acid stream is produced**

Activated Carbon Process – Single Bed Unit Current Status

- **Bench-scale tests**
  - Single-bed batch unit (1' L, 1" ID)
  - Capacity – 0.02 tpd CO_2 in flue gas
  - Synthetic flue gas is fed until breakthrough of SOx or NOx



Activated Carbon Process – Single Bed Unit Current Status

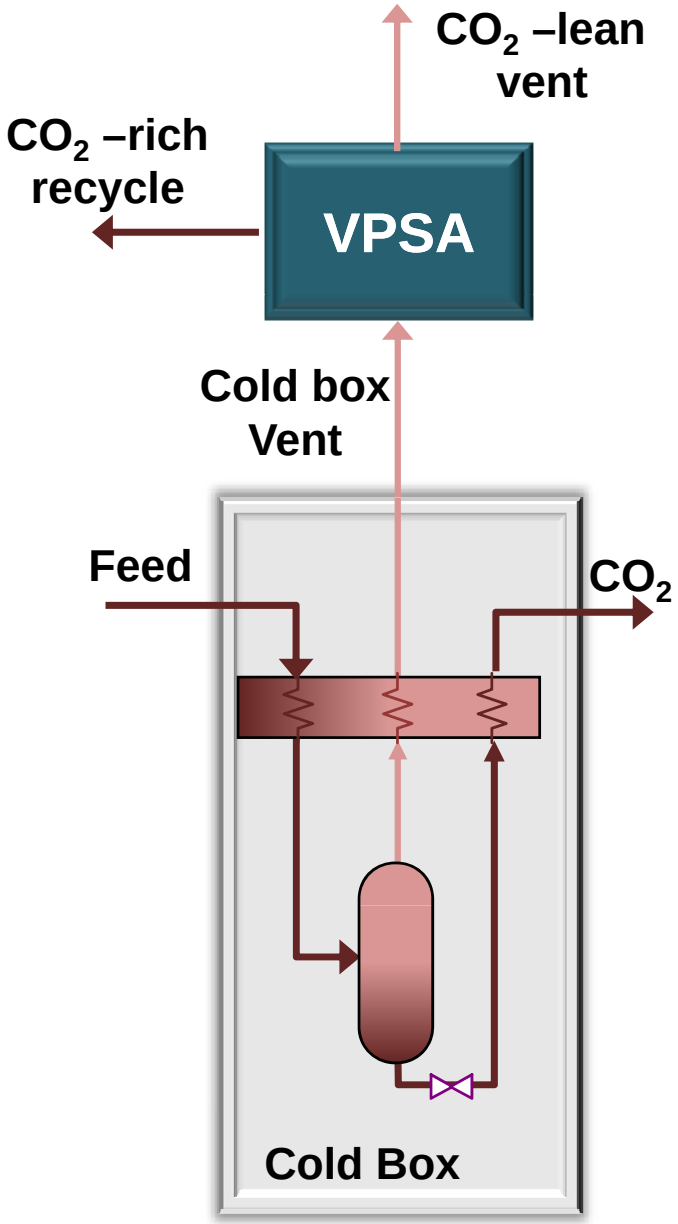
	Inlet ppm		Average Outlet ppm		Removal eff. %	
	SOx	NOx	SOx	NOx	SOx	NOx
Low Sulfur Coal	450	200	2.3	13.0	99.8	93.9
Intermediate S Coal	2000	750	1.6	17.1	>99.9	98.2
High Sulfur Coal	4000	400	1.5	22.8	>99.9	95.2

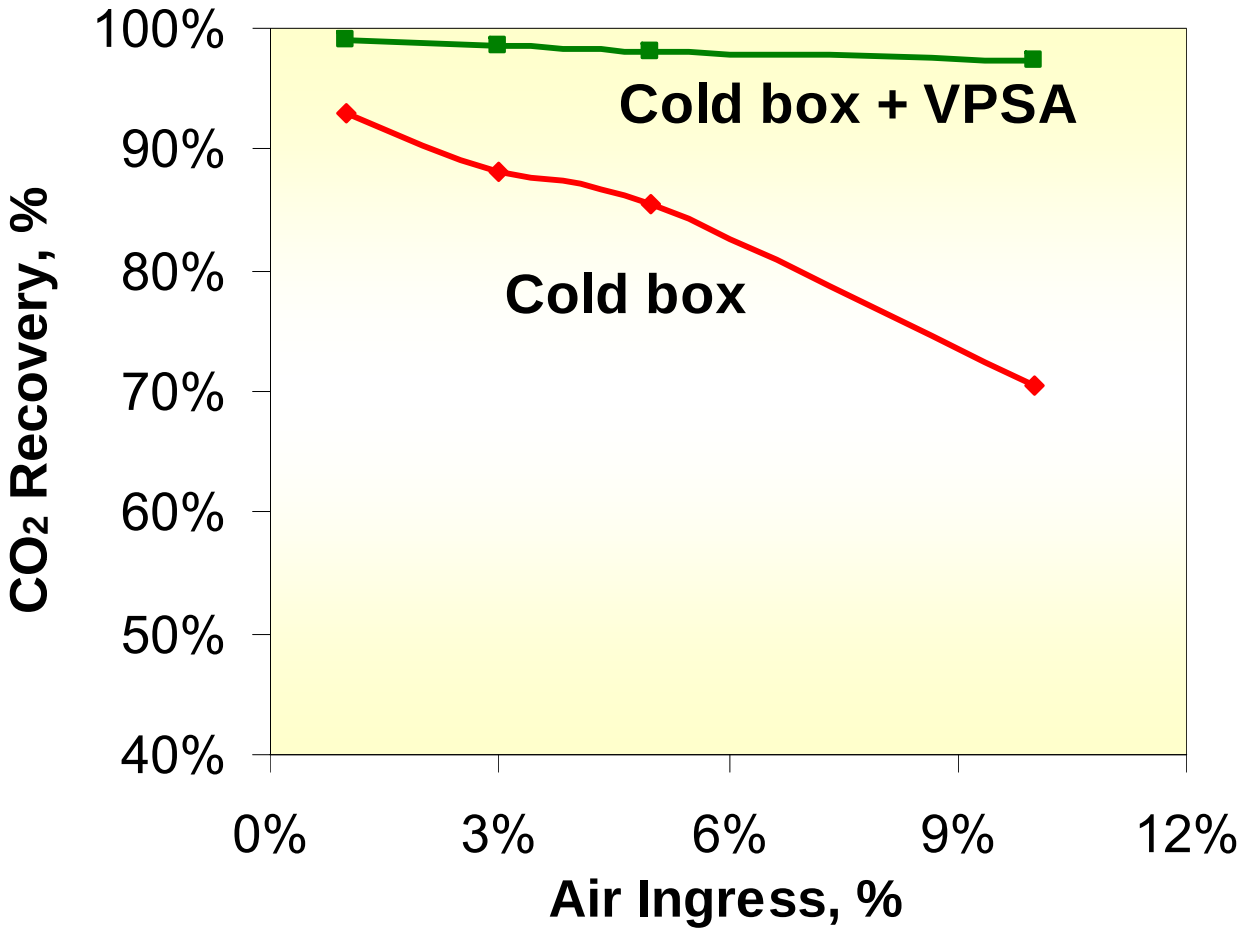
- **Excellent simultaneous SOx/NOx removal achieved**
  - SO_2 >99.9 % and NOx up to 98%
- **Preliminary longevity test results were favorable**
  - Performance could be maintained over 20 cycles
- **Technology also applicable for high sulfur coal flue gas**

Activated Carbon Process – Dual Bed Continuous Unit Current Status and Future Plans

- **Objectives**
  - Collect data for engineering design of a larger unit of 10 – 50 tpd capacity
  - Test longevity of activated carbon material
- **Design and construction are complete**
  - Reactor size – 2” D and 20” L; 0.125 tpd CO_2 capacity
  - Designed for automated continuous operation (24 hours x 5 days at a time)
- **Instruments check out and control system programming are in progress**
- **Commissioning is planned in September**
- **Complete longevity tests in Q4 2011**

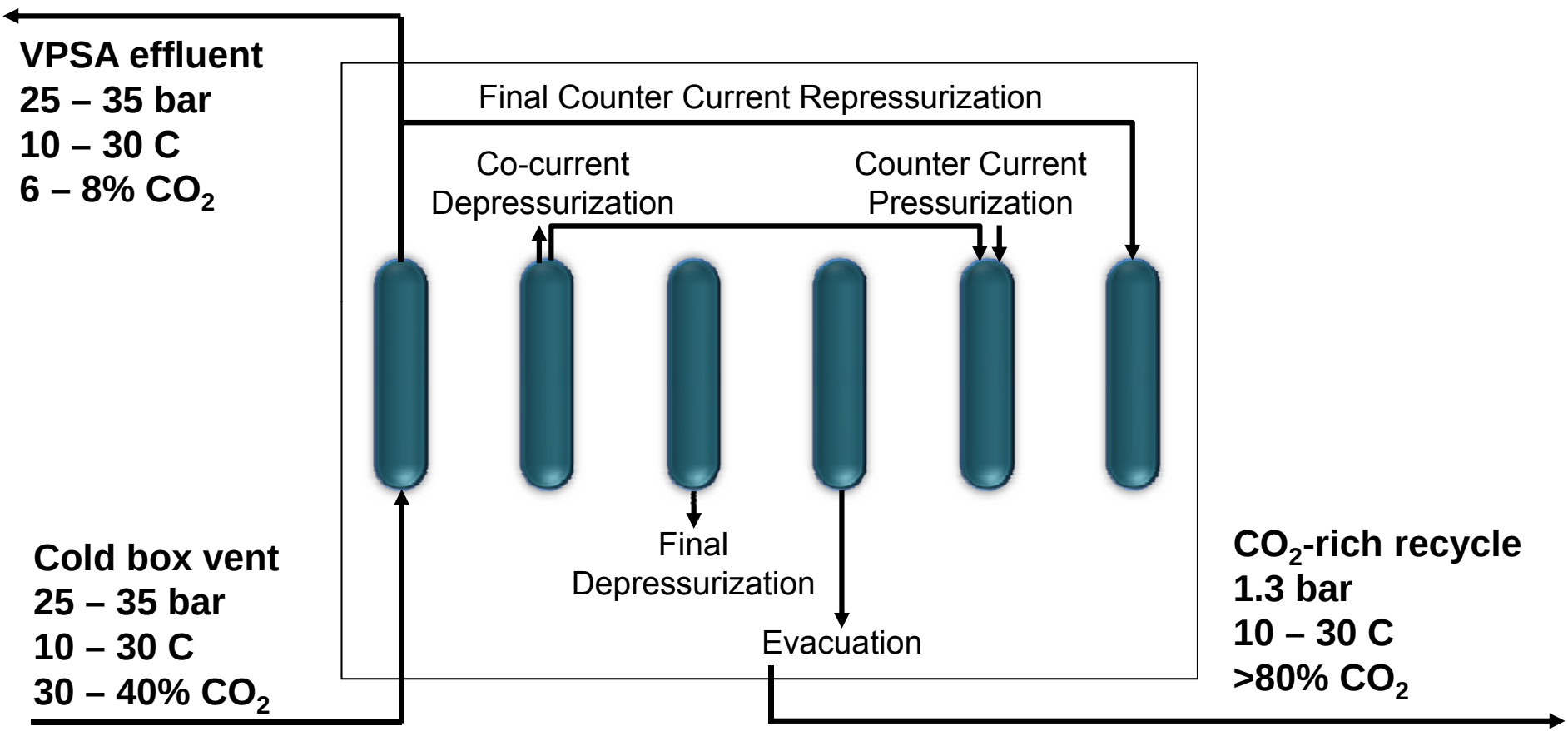
VPSA (Vacuum Pressure Swing Adsorption) Technology Fundamentals





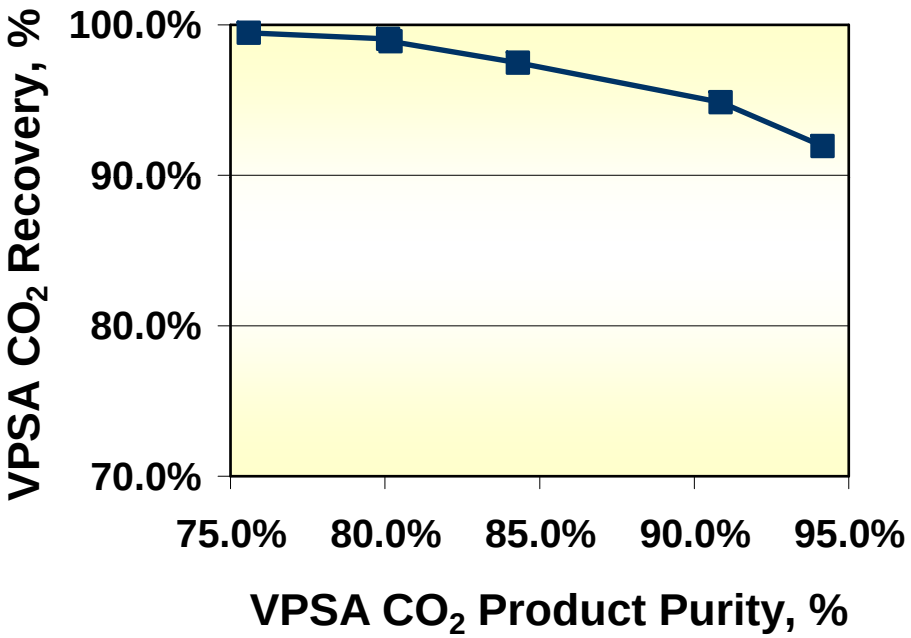
VPSA
Technology Fundamentals

- **Multi-bed unit for separating CO_2 from cold box vent stream**
- **Simple cycle with minimum rotating equipment**
- **Shallow evacuation level**



VPSA
Current Status and Future Plans

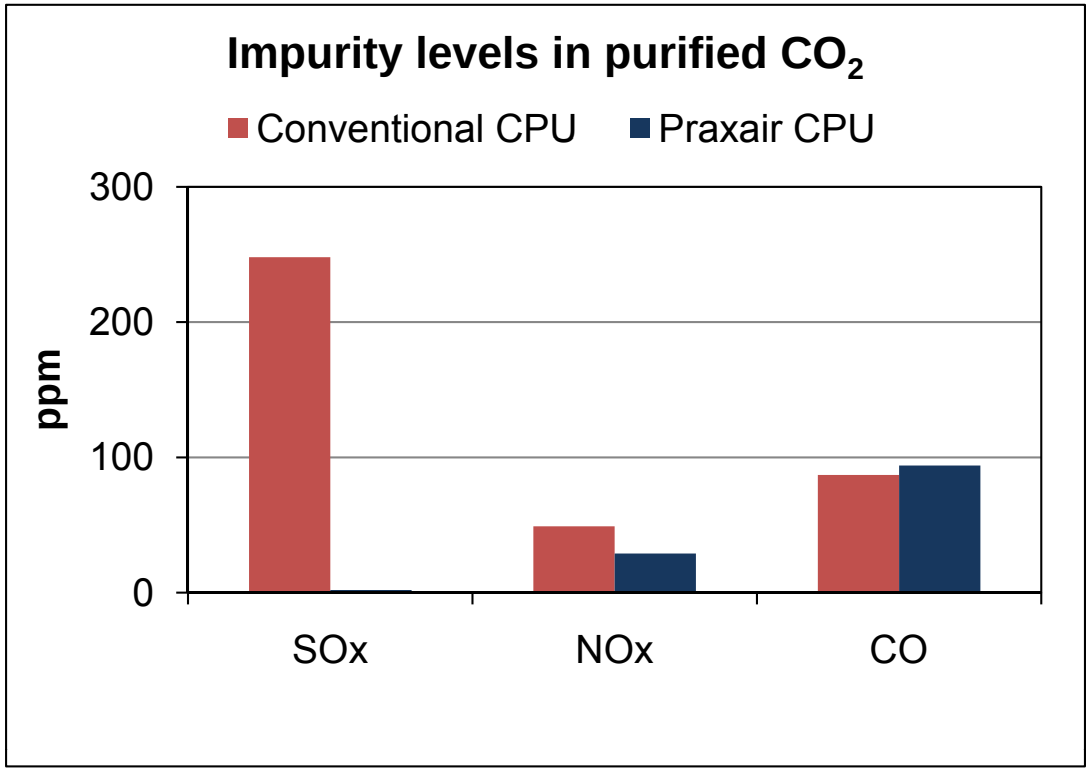
- **Pilot unit with 12 vessels (L ~ 11', ID ~ 2.5") built**
  - Capacity – cold box vent 0.3 tpd CO_2 (equiv. to 3 tpd CO_2 in FG)
- **VPSA performance targets exceeded**
  - > 80% CO_2 purity and > 90% CO_2 recovery with VPSA
  - > 99% capture rate with VPSA + cold box
- **Complete pilot tests (Q4 2011)**



Commercial Viability – Design Basis Current Status

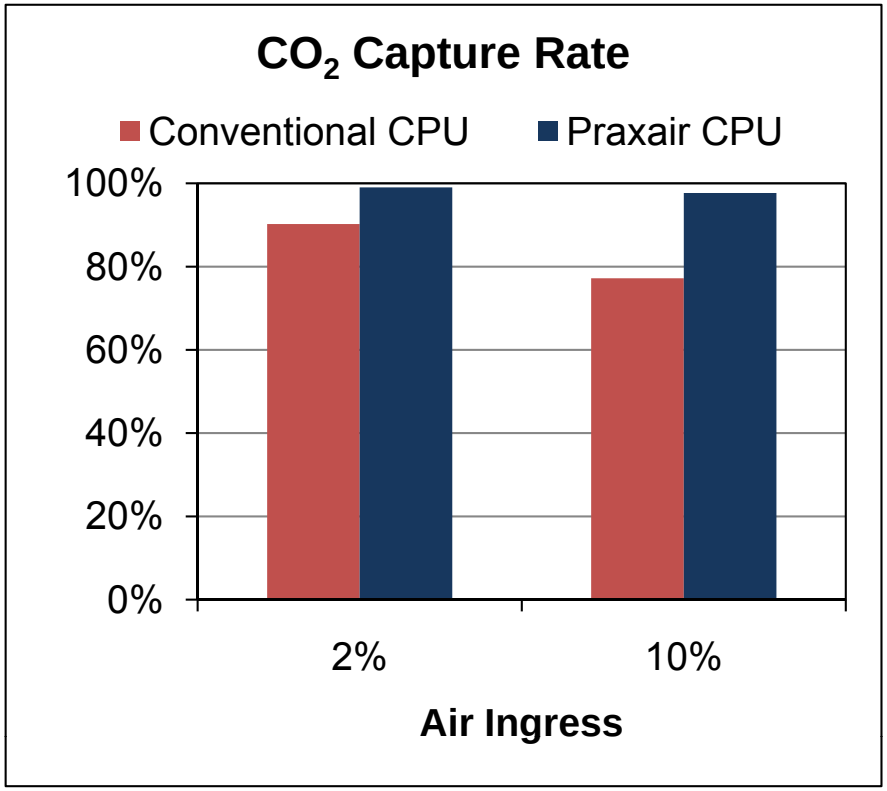
- **Subcritical power plant**
  - 550 MW (net) for both air and oxy-firing modes
  - Site ambient conditions: 14.7 psia, 59 F, 60% RH
  - PRB coal (low sulfur)
  - FGD and SCR are not included in air-fired power plant
- **Air separation unit (ASU)**
  - 97% O_2
- **CO_2 processing unit (CPU)**
  - CO_2 purified to >95% purity and compressed to 153 bar
- **Oxy-fired plant with conventional CPU**
  - FGD (for ~55% of flue gas) and SCR are installed
- **Oxy-fired plant with Praxair CPU**
  - FGD (for ~27% of flue gas) installed
  - Activated carbon process and VPSA included in Praxair CPU

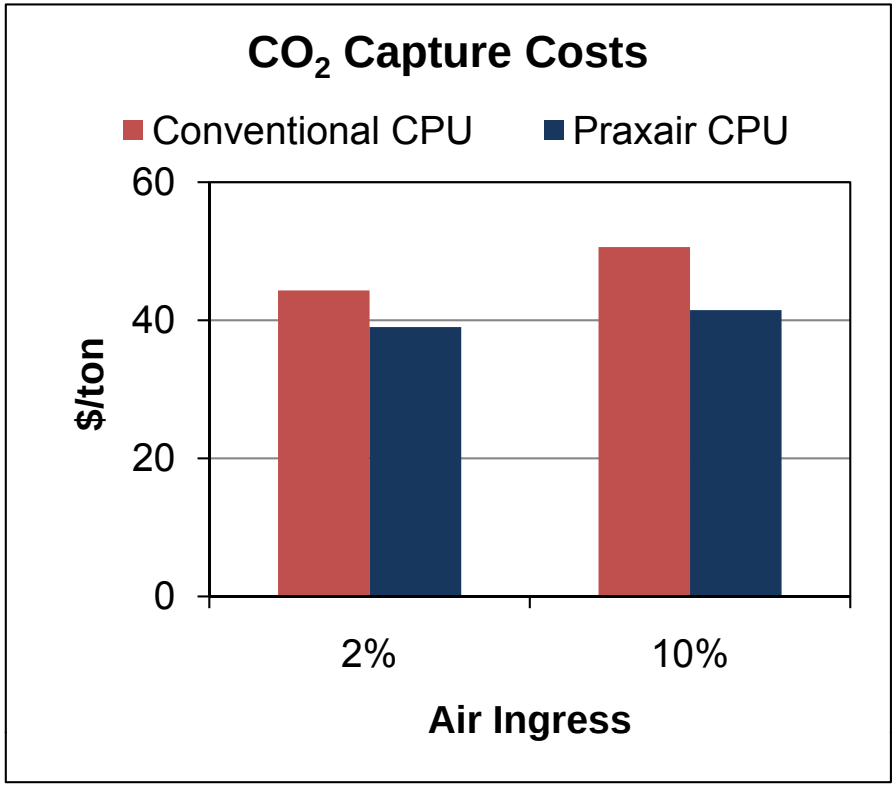
Commercial Viability
Current Status



Concentrations in CPU Vent		
Vol. % or ppm	**Conventional CPU**	**Praxair CPU**
CO_2, %	37%	7%
SOx, ppm	9	0
NOx, ppm	24	23
CO, ppm	1448	24

Commercial Viability
Current Status and Future Plans





- Cost analysis for various scenarios (Q4 2011)
  - Existing plants with FGD and SCR
  - High sulfur coal
  - Supercritical and ultra supercritical steam cycles

Commercialization

- **Technology is ready for 10 – 50 tpd demonstration**
- **Currently estimating costs of a 20 tpd CPU demonstration**
  - 2 MW_{th} oxy-coal boiler at U. of Utah
  - Near zero emissions CPU to produce ~20 tpd purified CO_2
  - CPU will include all the unit operations except final product compression
- **Proposed commercialization timeline**
  - 10 – 50 tpd CPU demo (2012 – 2014)
  - Design for larger CPU (for 250+ MW plants) to be available in 2015

Summary

- **Successful development of one near zero emissions technology option based on activated carbon and VPSA**
- **High CO_2 recovery, high purity CO_2 and near zero stack emissions while lowering capture costs**
- **Ready for 10 – 50 tpd CPU demonstration**

Acknowledgement & Disclaimer

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