Purification of oxy-combustion flue gas for SOx/NOx removal and high CO_2 recovery

Minish Shah, Nick Degenstein, Monica Zanfir, Rahul Solunke, Ravi Kumar, Jennifer Bugayong and Ken Burgers
Praxair, Inc.

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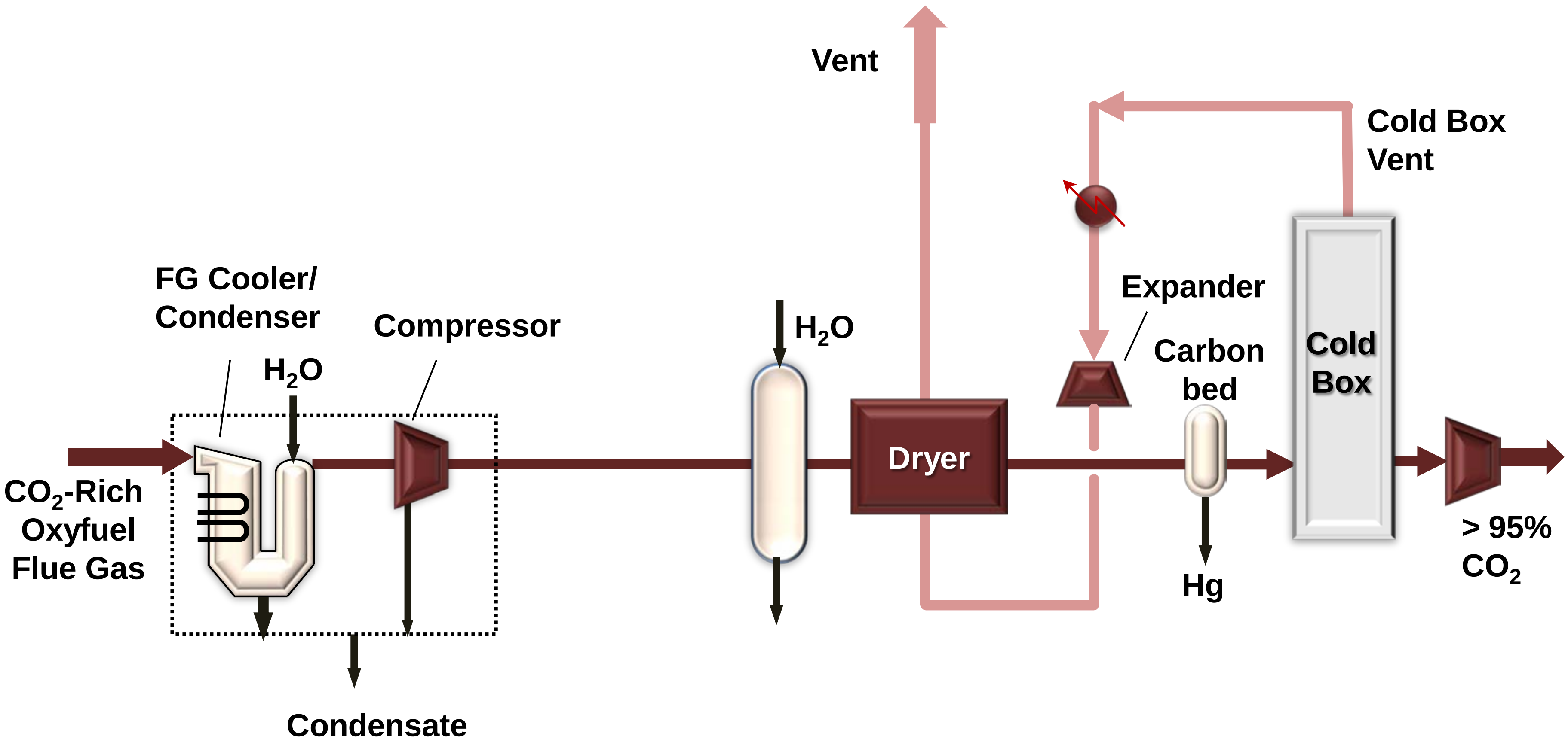
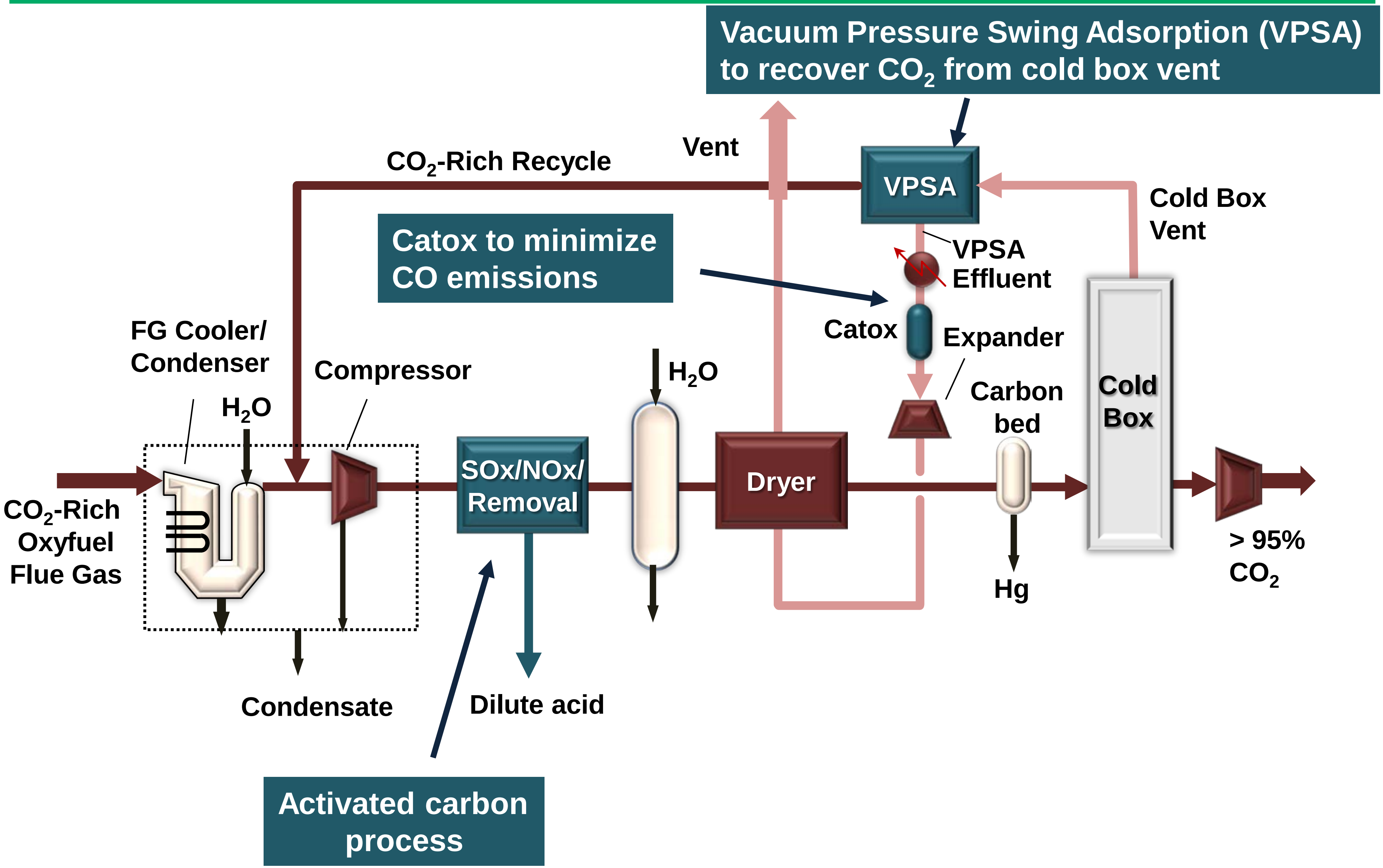
Outline

- Near Zero Emissions CPU Concept
- Activated Carbon Process for SOx/NOx Removal
- Sulfuric Acid Process for SOx/NOx Removal
- Autorefrigeration Process
- VPSA for CO_2 Recovery from Cold Box Vent
- Cost and Performance
- R&D Needs

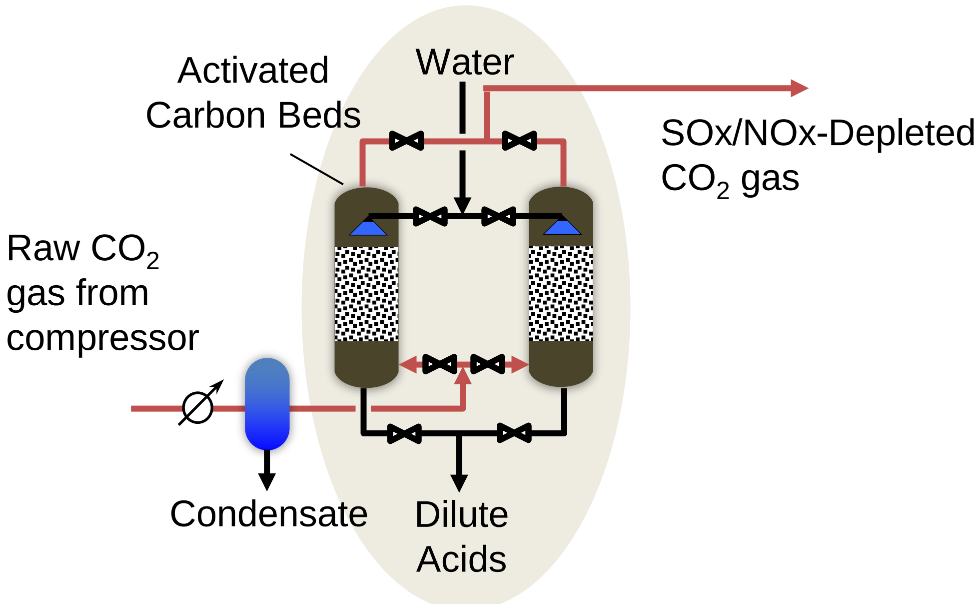
Conventional CO_2 Processing Unit (CPU)



Near Zero Emissions CPU



Activated Carbon Process Technology Concept

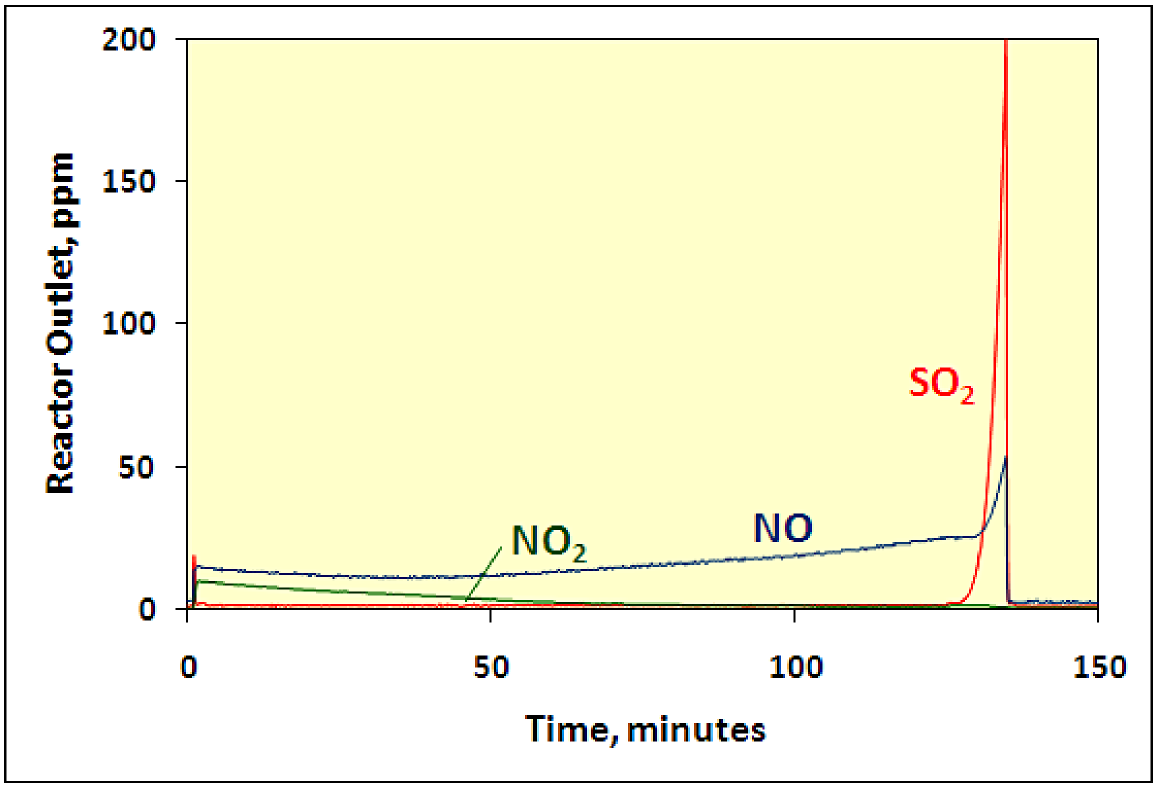


$SO_2 + 1/2O_2 \rightarrow SO_3$
$NO + 1/2O_2 \rightarrow NO_2$
$SO_3 + H_2O \rightarrow H_2SO_4$
$3NO_2 + H_2O \rightarrow 2HNO_3 + NO$

- 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
SOx/NOx Concentration Profiles in Reactor Outlet

- **Test system:**
  - Single bed unit operated in a batch mode
  - Synthetic flue gas mixture: ~85% CO_2, 4% O_2, SO_2 4000 ppm, NO 400 ppm, balance N_2, saturated with moisture
  - Temperature – 20 C; Pressure – 15 bar(a)



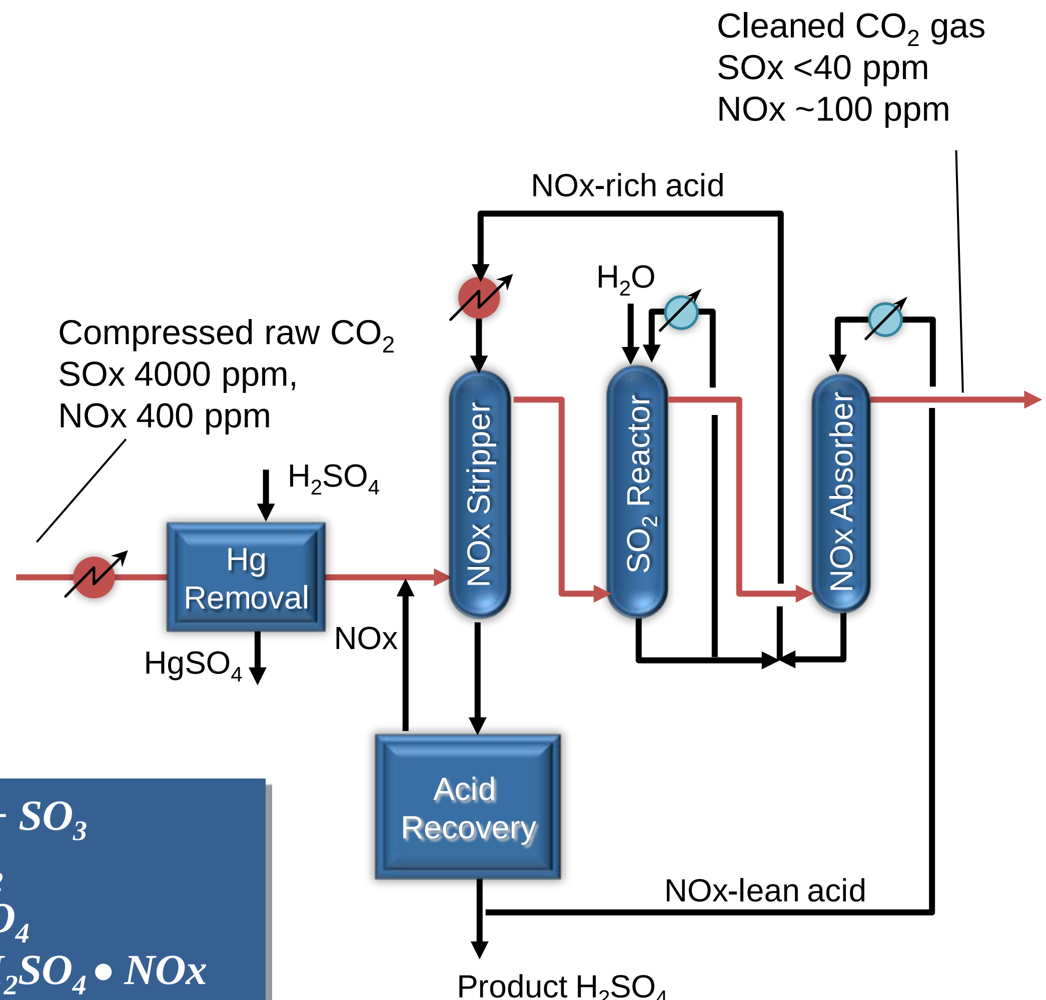
Activated Carbon Process Test Results

	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
Medium Sulfur 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
- **Currently building a dual bed continuous unit for long term tests**

Sulfuric Acid Process Technology Concept

- Recirculating H_2SO_4 removes Hg, SOx and NOx in a series of contact towers
- Produce saleable H_2SO_4 and HNO_3
- Eliminate limestone purchase and gypsum disposal costs



$NO_2 + SO_2 \rightarrow NO + SO_3$

$NO + 1/2O_2 \rightarrow NO_2$

$SO_3 + H_2O \rightarrow H_2SO_4$

$NOx + H_2SO_4 \bullet \quad H_2SO_4 \bullet NOx$

$3NO_2 + H_2O \rightarrow 2HNO_3 + NO$

Sulfuric Acid Process Technoeconomic Feasibility Results

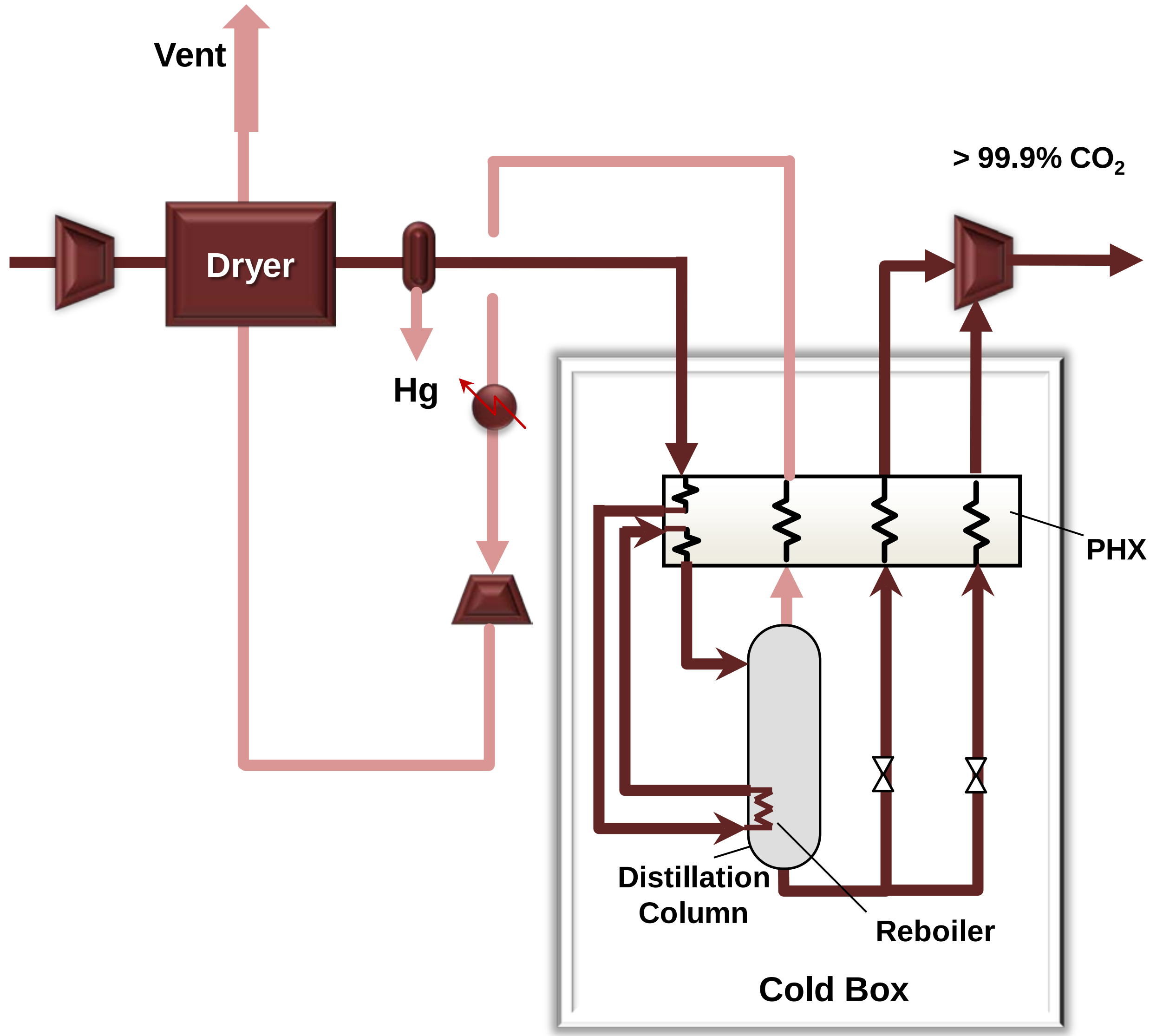
- **Bench scale tests and simulation results**
  - SO_2 reactor and NOx absorber projected to perform as expected, however, NOx stripper could not remove NOx from H_2SO_4
  - Process will achieve >99% SOx removal and ~75% NOx removal
  - Residual NOx present as NO_2 which can be removed by water wash
- **Economic feasibility 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 for high sulfur coal
  - H_2SO_4 containing high level of NOx unlikely to be marketable
  - Therefore, produced H_2SO_4 must be neutralized and disposed off
  - Value of technology similar to activated carbon process

Autorefrigeration Process

- J-T expansion of purified LCO_2 for refrigeration
- Raw CO_2 partially liquefied by boiling product

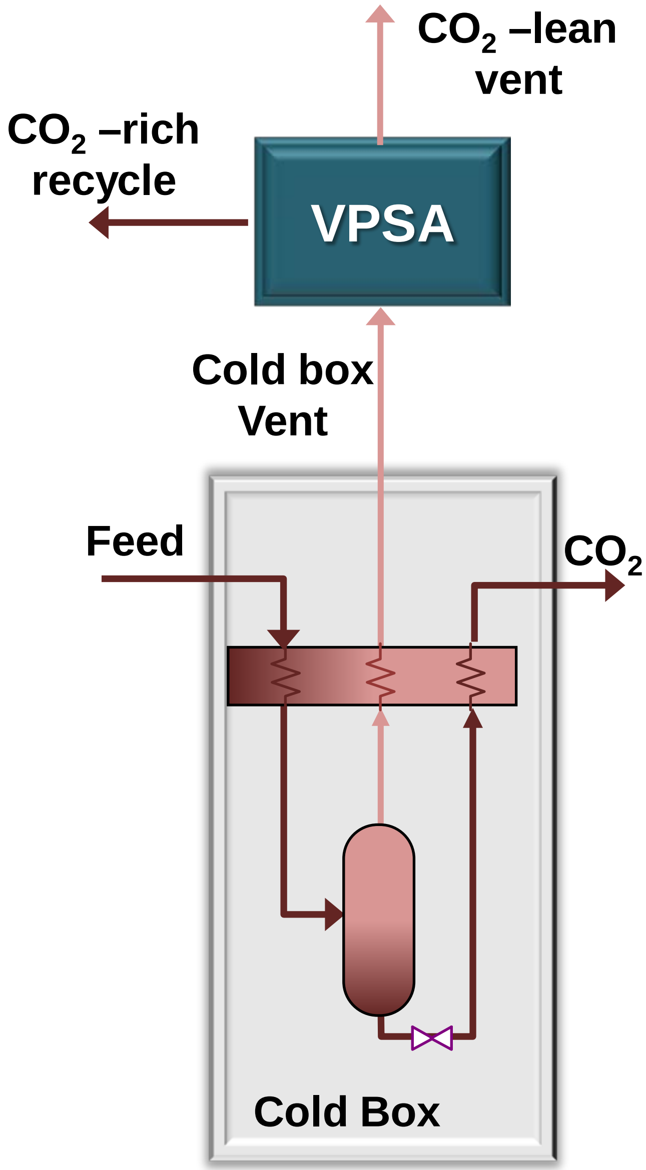
Compared to NH_3 refrigeration:

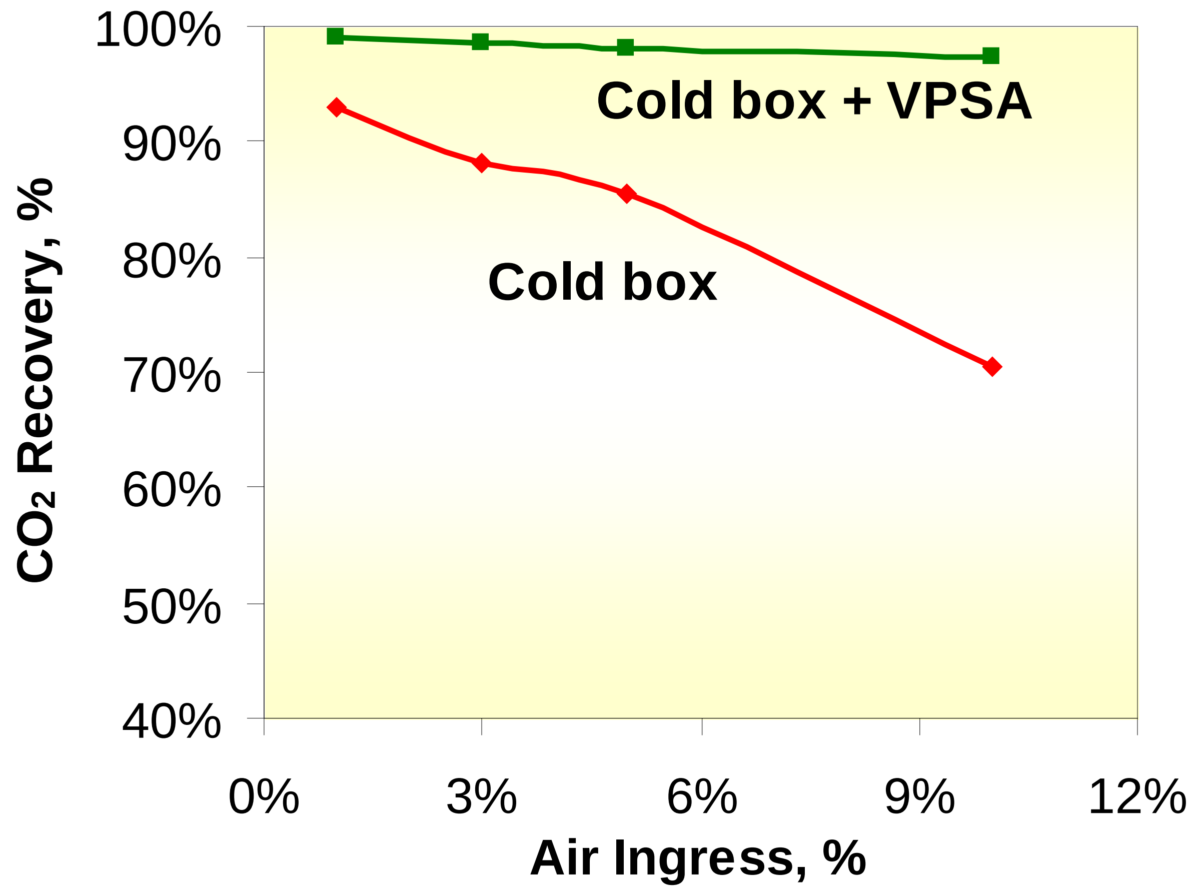
- Simpler process
- Lower CAPEX
- Higher CO_2 recovery
- Lower power



US Pat. 7,666,251

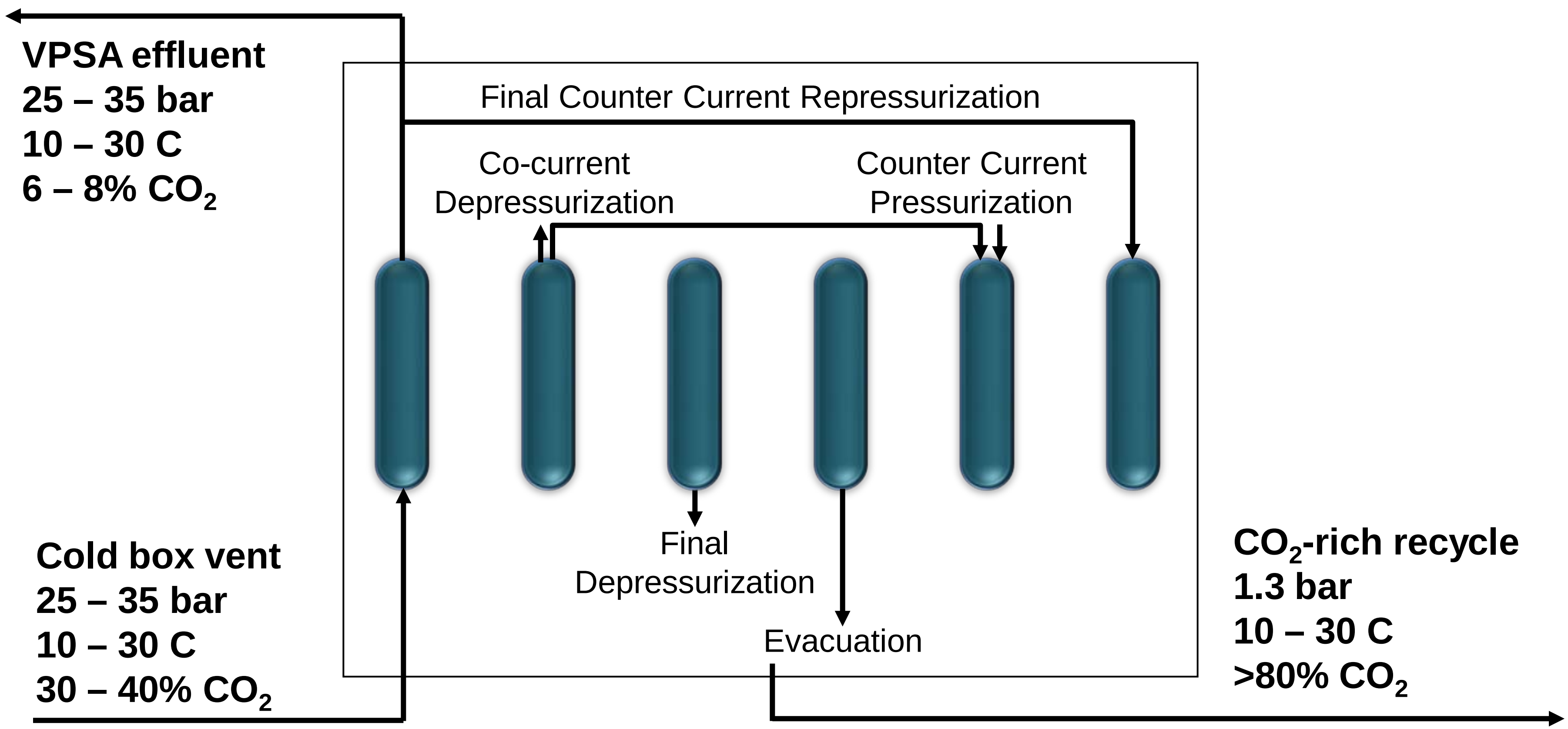
VPSA (Vacuum Pressure Swing Adsorption) for Recovering CO_2 from Cold Box Vent





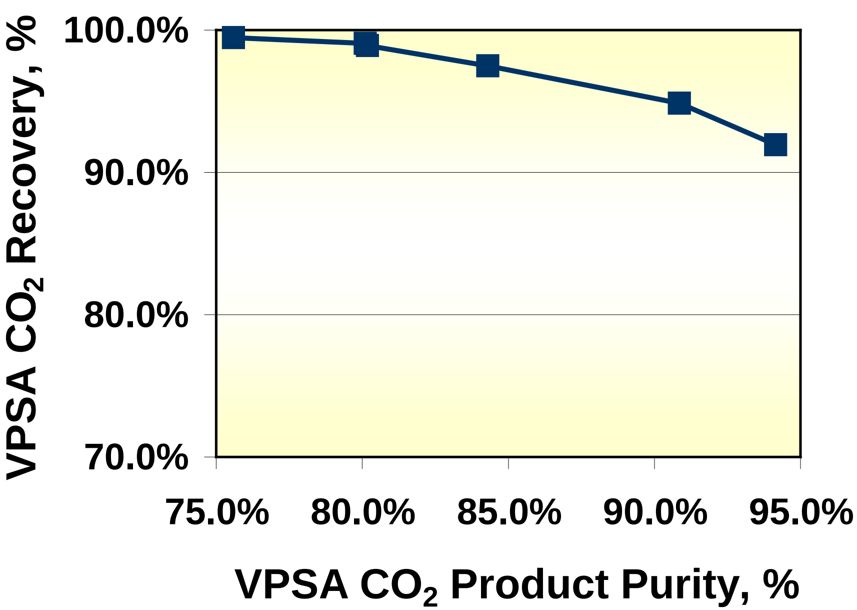
VPSA Process

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

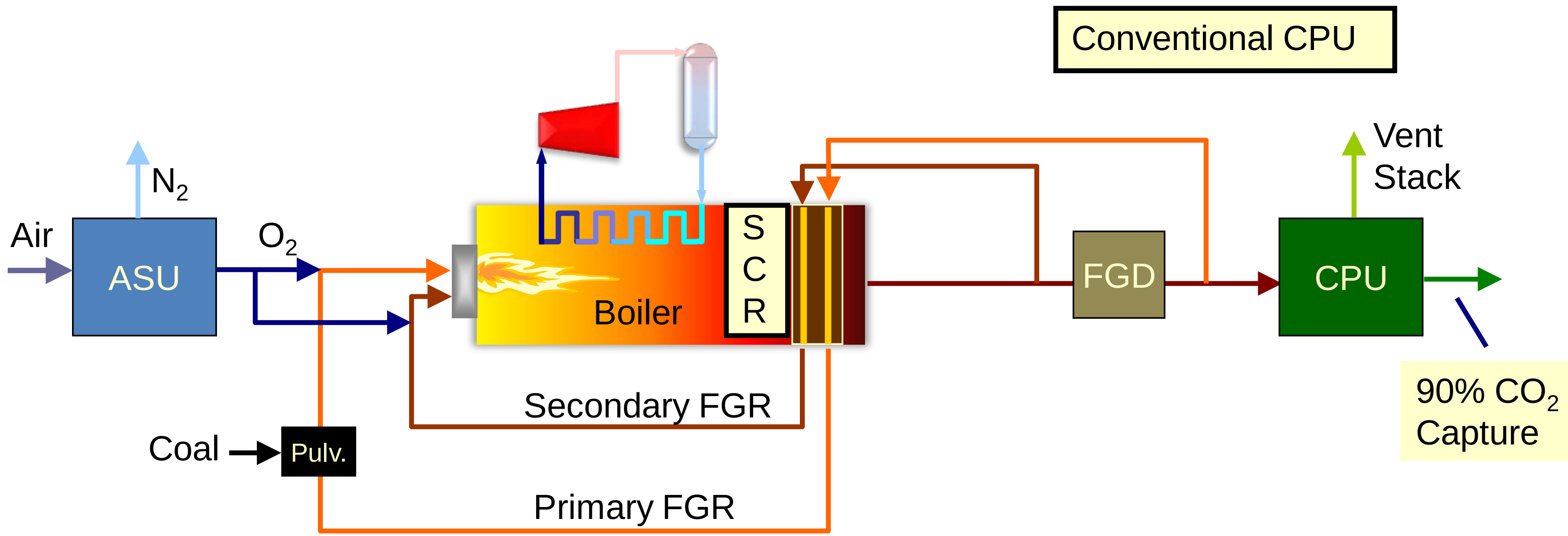


VPSA Pilot Test Results

- **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



Benefits of Praxair CPU in Comparison to Conventional CPU



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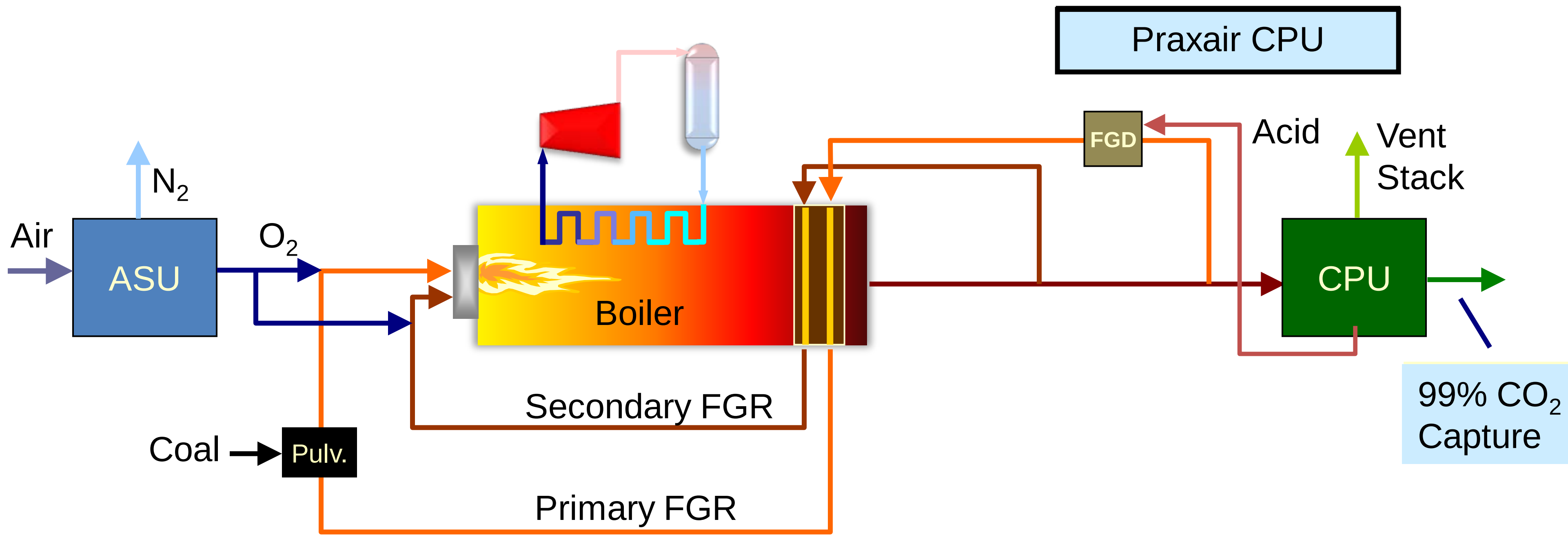

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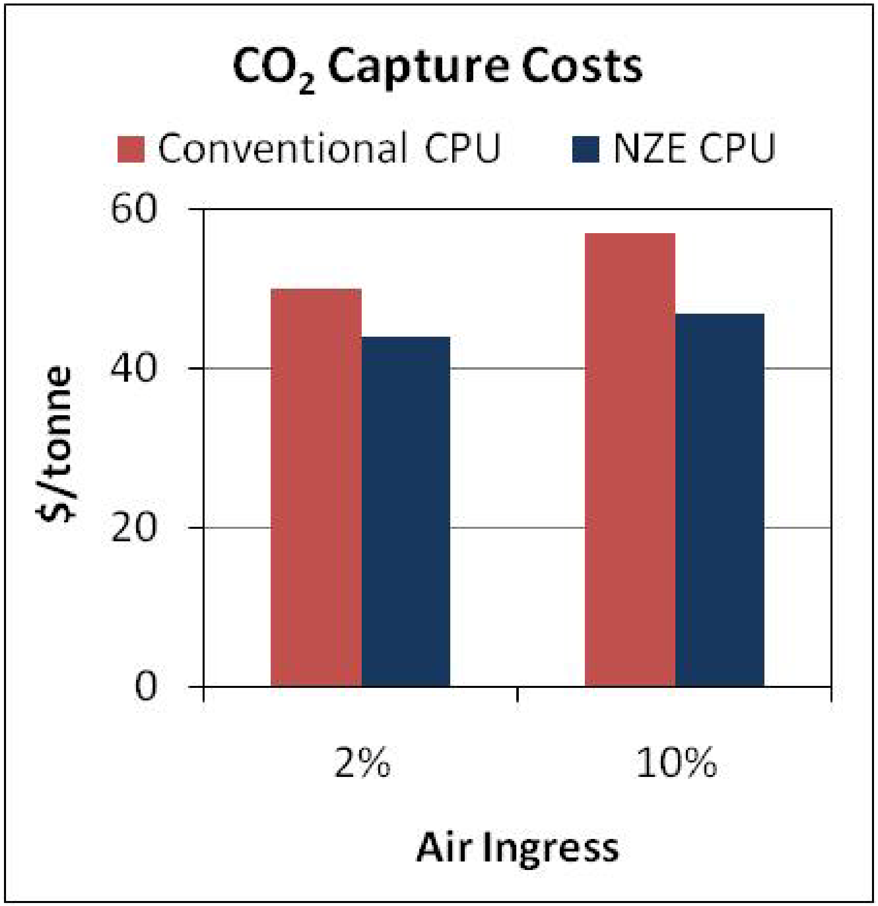
Near Zero Emissions CPU Performance

Compositions			
Vol. % or ppm	**CPU Feed**	**Purified CO_2**	**CPU Vent**
CO_2, %	~61%	>99.99%	~7%
SOx, ppm	1875 ppm	2 ppm	0
NOx, ppm	156 ppm	11 ppm	9 ppm
CO, ppm	280 ppm	0	< 10 ppm

CO_2 Capture Rate		
Air Ingress	**2%**	**10%**
CO_2 capture rate, %	99%	97%

Cost Comparison

- **Lower capture costs for NZE CPU are due to:**
  - Smaller FGD and elimination of SCR
  - Higher CO_2 capture rate compared to conventional CPU



Note:
1 tonne = 1000 kg
CO_2 purity >99.9%
CO_2 pressure 153 bar
CO_2 transportation and storage costs included

R&D Needs for CPU

- Impact of trace impurities on performance and reliability of various equipment in the process
- Fate of mercury in CPU
- Treatment and disposal of process condensate
- Disposal of dilute acid
- Demonstration and scale-up of an integrated system

Summary

- Near zero emissions CPU technology components successfully tested at bench/pilot scale
- Ability to manage air ingress
- High CO_2 recovery, high purity CO_2 and near zero stack emissions while lowering capture costs

Acknowledgement & Disclaimer

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