Praxair – Near-Zero Emissions Flue Gas Purification

Project Title:

Near-Zero Emissions Oxy-Combustion Flue Gas Purification

Technology Area:	**Technology Maturity:**
Oxy-Combustion	Bench-scale, 0.5 kg of CO_2/hr

Primary Project Goal:

The goal of the project is to develop a near-zero emission flue gas purification technology for a retrofitted existing coal-fired power plant with oxy-combustion technology.

Technical Goals:

- Design a contaminant removal system that will produce saleable sulfuric acid and nitric acid without the need for flue gas desulfurization (FGD) or selective catalytic reduction (SCR) units.
- Design a second contaminant removal system that will produce gypsum.
- Achieve greater than 95% carbon dioxide (CO_2) capture by incorporating a vacuum pressure swing adsorption (VPSA) unit in an existing plant with a high air ingress, and reduce sulfur oxide (SO_X) and mercury (Hg) emissions by more than 99% and nitrogen oxide (NO_X) emissions by more than 90% (high and low sulfur coal).
- Perform a techno-economic study and an operability and integration evaluation to assess the commercial viability of retrofitting an existing power plant with the proposed technology.

Technical Content:

Two approaches for SO_X/NO_X/Hg removal are proposed depending on the SO_X levels in the flue gas. By carrying out these unit operations at high pressure, it is envisioned that capital costs would be reduced while achieving very low levels of SO_X and NO_X in the CO_2 stream. For plants with existing FGD and SCR, operating cost savings could be realized by shutting down those units while operating the proposed SO_X/NO_X removal process. For plants burning low sulfur coal, there is no need for investment in separate FGD and SCR equipment for producing high purity CO_2.

High air ingress in existing plants limits the amount of CO_2 that can be recovered from oxy-combustion flue gas using a cold box alone to <65%. The CO_2 recovery limitation is overcome by using a hybrid process that combines a cold box and VPSA (Figure 1). In the proposed hybrid process, up to 90% of CO_2 in the cold box vent stream is recovered by CO_2 VPSA and then recycled and mixed with the flue gas stream upstream of the compressor. The recovery from the process will be >95%.

Pollutant Removal

The high sulfur coal tests will be bench-scale and will utilize a single gas/liquid contact column that operates at up to 17 atm (250 pounds per square inch absolute [psia]) and 150°C (300°F) for testing multiple reactions. Nitric oxide (NO) in the flue gas is converted to nitrogen dioxide (NO_2), which catalyzes sulfur dioxide (SO_2) oxidation to SO_3. The hydrolysis of SO_3 and NO_2 forms sulfuric and nitric acids.

The low sulfur coal experiments will use a single column unit (2.5 cm [1 inch] diameter, 3.8 cm [1.5 inch] long), and operate up to 17 atm (250 psia) and 93°C (200°F). Activated carbon is used as an adsorbent/catalyst for the capture of SO_X and NO_X from the flue gas. The activated carbon oxidizes the SO_2 to SO_3, and a periodic water wash will be used to remove the acid.

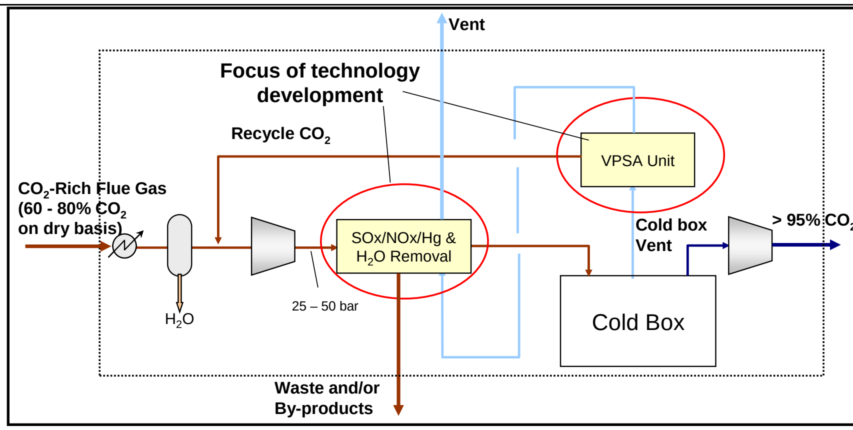

Figure 1: Technology Concept

The chemical reactions for the high and low sulfur coal pollutant removal system are summarized below.

High Sulfur Coal Reactions

$NO_2 + SO_2 \rightarrow NO + SO_3$

$NO + 1/2O_2 \rightarrow NO_2$

$SO_3 + H_2O \rightarrow H_2SO_4$

$NOx + H_2SO_4 \leftrightarrow H_2SO_4 \bullet NOx$

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

Figure 2: High Sulfur Coal Pollutant Removal System

Low Sulfur Coal Reactions

$SO_2 + 1/2O_2 \rightarrow SO_3$

$NO + 1/2O_2 \rightarrow NO_2$

$SO_3 + H_2O \rightarrow H_2SO_4$

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

Figure 3: Low Sulfur Coal Pollutant Removal System

High CO_2 Recovery Using VPSA

The VPSA unit is a multi-bed unit that performs multiple depressurization/re-pressurizations steps. Oxy-combustion flue gas will enter the CO_2 VPSA from the "cold box" (25 to 35 atm and ambient temperature) that will recover additional CO_2 (produce 80% to 95% CO_2 concentration) and recycle the CO_2 back into the CO_2-rich flue gas stream at ambient pressure. The flue gas stream not recycled from the VPSA contains mainly oxygen (O_2), nitrogen (N_2), and argon (Ar) that will be vented to the atmosphere.

Technology Advantages:

Cold box-VPSA hybrid technology achieves >95% CO_2 recovery even for plants with high air ingress. The flue gas purification process for high sulfur coal has lower capital and operating costs than FGD and SCR and it allows for revenue from sale of acids.

R&D Challenges:

- SO_X/NO_X/Hg removal from high sulfur coal:
  - Reactor materials must be able to withstand the operating conditions in the process.
  - Determine an effective NO_X catalyst for producing saleable sulfuric acid.
- SO_X/NO_X/Hg removal from low sulfur coal:
  - Find activated carbon materials that are effective for regeneration based on sorption capacity

and ability to maintain performance.

- Identify adsorbents with a tolerance to residual SO_X/NO_X to be used in the VPSA process.
- Determine VPSA cost benefit for recovering additional CO_2.
- Establish proper modifications required for retrofitting existing plants.

Results To Date/Accomplishments:

Bench-scale experimental test systems have been built and commissioned for all three experimental programs.

- SO_X/NO_X/Hg removal from high sulfur coal:
  - Completed preliminary screening tests for NO_X catalyst.
- SO_X/NO_X/Hg removal from low sulfur coal:
  - Identified, through screening tests, three activated carbon materials with potential for SO_X removal and one activated carbon material with potential for both SO_X and NO_X removal.
- High CO_2 Recovery Using VPSA:
  - Identified, through screening tests, six VPSA adsorbents for bench-scale tests.
  - Tested three adsorbents on the bench-scale unit; two of them hold promise.
  - Completed the pilot-scale VPSA unit construction.

Next Steps:

- Perform contaminant (SO_X, NO_X, and Hg) removal tests for high and low sulfur coals.
- Complete bench-scale tests and select two adsorbents for the continuous operation tests.
- Commission pilot VPSA system.
- Conduct commercial viability assessment of the pollutant removal technologies.

Final test results will not be available until the December 2011 project completion date.

Available Reports/Technical Papers/Presentations:

Near-Zero Emissions Oxy-Combustion Flue Gas Purification - March 2009.

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