

# Testing of Ammonia Based CO<sub>2</sub> Capture with Multi-Pollutant Control Technology

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## ABSTRACT

Powerspan has been developing a CO<sub>2</sub> capture process, called ECO<sub>2</sub><sup>®</sup>, since 2004 in conjunction with the U.S. DOE National Energy Technology Laboratory (NETL) under a cooperative research and development agreement. In December 2007 Powerspan announced it exclusively licensed a patent for the process from NETL.

Powerspan has conducted extensive laboratory testing to establish the effectiveness of the process for CO<sub>2</sub> capture and has initiated a pilot test program with FirstEnergy at the R.E. Burger Plant. A 1-MW pilot demonstration is scheduled to begin in 2008, which will produce 20 tons of sequestration-ready CO<sub>2</sub> per day. The pilot will demonstrate CO<sub>2</sub> capture through integration with the ECO<sup>®</sup> multi-pollutant control process. The pilot program will also prepare the technology for commercial scale carbon capture and sequestration (CCS) demonstration projects

## INTRODUCTION

While CO<sub>2</sub> emissions from power plants are currently unregulated at the Federal level, there is a growing consensus that standards limiting CO<sub>2</sub> emissions are likely to be promulgated within the next five years. CO<sub>2</sub> emissions from the electric power sector account for 40 percent of total U.S. energy-related CO<sub>2</sub> emissions. With 50 percent of U.S. electricity generated from coal and many new coal-fired electric generating plants in the planning, permitting, or construction stages, it is becoming increasingly important that CO<sub>2</sub> capture solutions are developed which are suitable for the existing fleet of coal-burning power plants, as well as for planned, new capacity. Today, limited CO<sub>2</sub> capture technologies are commercially available for use on coal-fired power plants, and none has been deployed at the scale of the typical base loaded plant. In addition, existing CO<sub>2</sub> capture solutions have capital and operating costs that are considered uneconomical for conventional coal-fired power plants.

Powerspan Corp. is developing a CO<sub>2</sub> capture process, called ECO<sub>2</sub><sup>®</sup>, that can be applied to both existing and new coal-fired power plants. The process is being designed as an add-on system that could be deployed when needed and is particularly advantageous for sites where ammonia-based scrubbing, such as Powerspan's ECO process, of power plant emissions is employed.

ECO<sub>2</sub> is a scrubbing process that uses an ammonia-based solution to capture CO<sub>2</sub> from flue gas. The

CO<sub>2</sub> capture takes place after NO<sub>x</sub>, SO<sub>2</sub>, Hg and fine particulate matter capture is accomplished in Powerspan's ECO multi-pollutant control technology, or other air pollution control systems. Once CO<sub>2</sub> is absorbed, the resulting solution is regenerated to release it. In addition to CO<sub>2</sub>, NH<sub>3</sub> is released during regeneration. It is recovered and returned to the scrubbing process, and the product CO<sub>2</sub> is dried and compressed into a form that is sequestration ready. Ammonia is not consumed in the scrubbing process, and no separate by-product is created.

Powerspan has conducted extensive laboratory testing on the CO<sub>2</sub> capture with the ECO<sub>2</sub> process. The testing has demonstrated steady-state capture/regeneration operation with 90 percent CO<sub>2</sub> removal under conditions comparable to a commercial-scale absorber. Based on the test results to date, Powerspan is constructing a pilot unit to test the ECO<sub>2</sub> process with power plant flue gas. The ECO<sub>2</sub> pilot is scheduled to begin operation in the Fall of 2008.

The ECO<sub>2</sub> pilot unit will process a 1-MW slipstream (equivalent to 20 tons of CO<sub>2</sub> per day) from the 50-MW Burger Plant ECO unit. The pilot program will demonstrate the ability of the CO<sub>2</sub> capture process to be integrated with the ECO multi-pollutant control process and will confirm process design and cost estimates. It will also prepare the technology for commercial scale capture and sequestration demonstration projects.

## **TECHNOLOGY OVERVIEW**

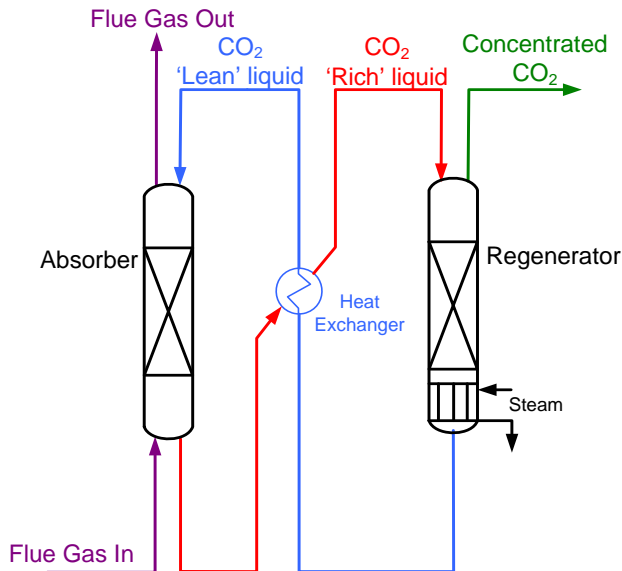
Post combustion carbon dioxide (CO<sub>2</sub>) capture from coal-fired power plants takes place downstream of any employed sulfur dioxide (SO<sub>2</sub>), nitrogen oxides (NO<sub>x</sub>), and mercury (Hg) removal process steps. When integrated with the ECO multi-pollutant control process, CO<sub>2</sub> capture takes place after the SO<sub>2</sub>, NO<sub>x</sub>, mercury, and fine particulate matter are removed. Because the SO<sub>2</sub> capture efficiency of ECO is so effective (typically greater than 98%), no supplemental SO<sub>2</sub> capture is required.

The ECO<sub>2</sub> technology uses an ammonia-based solution to absorb CO<sub>2</sub> from flue gas. Once the CO<sub>2</sub> is absorbed, the solution containing CO<sub>2</sub> is regenerated through heating to release the captured carbon dioxide. Ammonia and water vapor are also released during regeneration, though these are recovered and returned to the absorbing solution. The product CO<sub>2</sub> is then in a form that is ready for compression, pipeline transport and sequestration. The ECO<sub>2</sub> process does not consume ammonia and no separate by-product is created by an ECO<sub>2</sub> system.

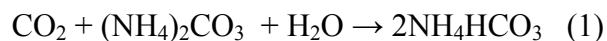
The ECO<sub>2</sub> process is a thermal swing absorption (TSA) process for CO<sub>2</sub> capture. CO<sub>2</sub> absorption into the ammonia based solvent takes place at low temperature, similar to temperatures achieved in wet flue gas scrubbing systems. The solvent is then heated to release the CO<sub>2</sub>. The process is similar to other CO<sub>2</sub> capture technologies such as amine-based processes. Common to thermal swing absorption processes are the following key steps, which are depicted in Figure 1:

- CO<sub>2</sub> is absorbed in a solution through flue gas–solution contact,
- The solution is heated for regeneration,
- CO<sub>2</sub> is released from the heated solution, and
- The solution is cooled for reuse.

Fig. 1. Basic thermal swing absorption process.



In the ECO<sub>2</sub> process CO<sub>2</sub> in the flue gas is scrubbed with an aqueous solution containing ammonium carbonate, forming ammonium bicarbonate as shown in reaction 1. The ammonium bicarbonate solution is then removed from the flue gas stream and heated, reversing the scrubbing reaction to release CO<sub>2</sub> while forming ammonium carbonate (reaction 2).



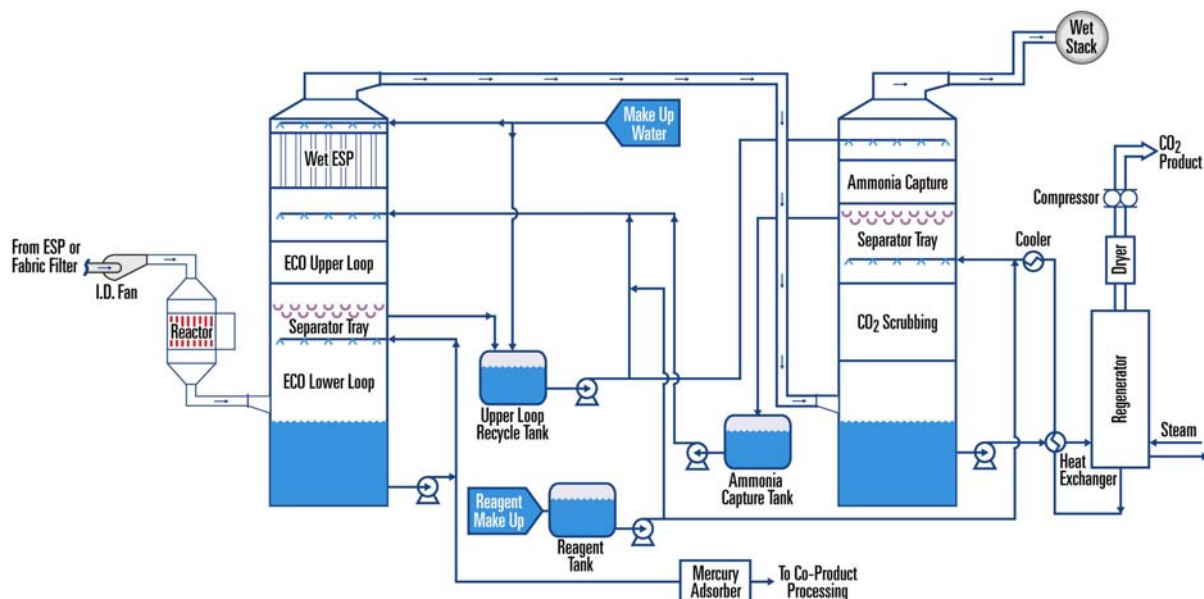
CO<sub>2</sub> released in reaction 2 is compressed for sequestration while the ammonium carbonate solution is returned to the scrubber for reuse.

The major advantage of an ammonia-based scrubbing solution is the reduced energy of reactions (1) and (2) when compared to amine-based and other CO<sub>2</sub> capture processes. This substantially reduces the energy consumption associated with solution regeneration. However, the ammonia's volatility requires control of ammonia vapor released to the flue gas during CO<sub>2</sub> scrubbing, and to the product gas during solution regeneration. The ECO<sub>2</sub> process captures ammonia released to the flue gas during CO<sub>2</sub> scrubbing, reducing the concentration to less than 5 ppmv, and also recovers ammonia from the CO<sub>2</sub> product gas, after regeneration, for reuse.

An illustration how the ECO<sub>2</sub> system is integrated with the ECO multi-pollutant control system is shown in Figure 2 below. The ECO system uses a barrier discharge reactor, wet scrubber and wet electrostatic precipitator to remove high levels of NO<sub>x</sub>, SO<sub>2</sub>, mercury, and fine particulate matter. The wet scrubber uses aqueous ammonia for SO<sub>2</sub> scrubbing, producing ammonium sulfate fertilizer co-product.

Fig. 2. Incorporation of the ECO<sub>2</sub> scrubbing process with Powerspan's commercially available

## multi-pollutant control ECO process



Managing ammonia vapor, which is released in the scrubbing and regeneration steps of the ECO<sub>2</sub> process is an important factor in the environmental impact and process economics of using ammonia for CO<sub>2</sub> capture. Figure 2 shows how ammonia vapor release from the ECO<sub>2</sub> scrubber is controlled using scrubbing liquor from the ECO Upper Loop. In an ECO system without the ECO<sub>2</sub> process, ammonia is added to the upper loop scrubbing liquor. This is done after the liquor is withdrawn from the absorber, and before returning the liquor to the upper loop packed section. When CO<sub>2</sub> scrubbing is employed, the bulk of the ammonia addition to the ECO upper loop is accomplished by contacting the upper loop solution with flue gas leaving the CO<sub>2</sub> scrubbing section. The contact takes place in the Ammonia Capture section of the ECO<sub>2</sub> absorber tower. The now ammonia rich liquid from the Ammonia Capture section is collected in the Ammonia Capture tank and pumped back to the ECO Upper Loop for scrubbing of SO<sub>2</sub> from the flue gas. In this configuration, ammonia that would have been added directly to the ECO process is instead added to the CO<sub>2</sub> Scrubbing section of the ECO<sub>2</sub> absorber, then captured in the Ammonia Capture section and carried to the ECO absorber.

Although the ECO<sub>2</sub> process is new and proprietary, the innovation is in process chemistry. The equipment required for operation of commercial ECO<sub>2</sub> systems (e.g., absorber, regenerator, heat exchangers, pumps, gas dryer, etc.) are commercially available at the required scale. Therefore, once the ECO<sub>2</sub> process is demonstrated at the pilot scale on an operating power plant, the scale up risk is manageable.

## COMPARISON TO AMINE-BASED CO<sub>2</sub> CAPTURE SYSTEMS

Ammonia scrubbing of CO<sub>2</sub> potentially offers several advantages over the commercially available amine process for CO<sub>2</sub> capture from coal-fired power plants. According to research conducted by the DOE-NETL and others on the use of aqua ammonia for absorption of CO<sub>2</sub><sup>1</sup>:

1. The traditional monoethanolamine (MEA) process for CO<sub>2</sub> removal has disadvantages of low CO<sub>2</sub> loading capacity (kg CO<sub>2</sub> absorbed per kg absorbent); high equipment corrosion rate;

- amine degradation by SO<sub>2</sub>, NO<sub>2</sub>, HCl, HF and O<sub>2</sub> in the flue gas, which requires a high absorbent makeup rate); and high energy consumption during absorbent regeneration.
2. By comparison, aqua ammonia has higher loading capacity; does not pose a corrosion problem; does not degrade in a flue gas environment, minimizing absorbent makeup; requires much less energy to regenerate; and costs much less than MEA. Specifically, the aqua ammonia process compared to MEA:
    - Has higher CO<sub>2</sub> absorption capacity;
    - Requires substantially less heat to release CO<sub>2</sub> and regenerate absorbent; and
    - Has lower reagent makeup costs.
  3. Another major benefit is that removal of other pollutants (principally SO<sub>2</sub> and NO<sub>x</sub>) could be integrated with the aqua ammonia process for CO<sub>2</sub> removal (i.e. using the ECO multi-pollutant control technology). Due to the requirements of the MEA process, very low SO<sub>2</sub> flue gas is a necessary input (less than 10 ppm). Since most commercially available SO<sub>2</sub> scrubbing systems are not efficient enough to provide this low SO<sub>2</sub> flue gas to the CO<sub>2</sub> scrubbing system (especially on existing units with already-deployed SO<sub>2</sub> scrubbers), an auxiliary SO<sub>2</sub> scrubbing system would be needed, increasing the CO<sub>2</sub> capture system capital cost.

## **LABORATORY TESTING RESULTS**

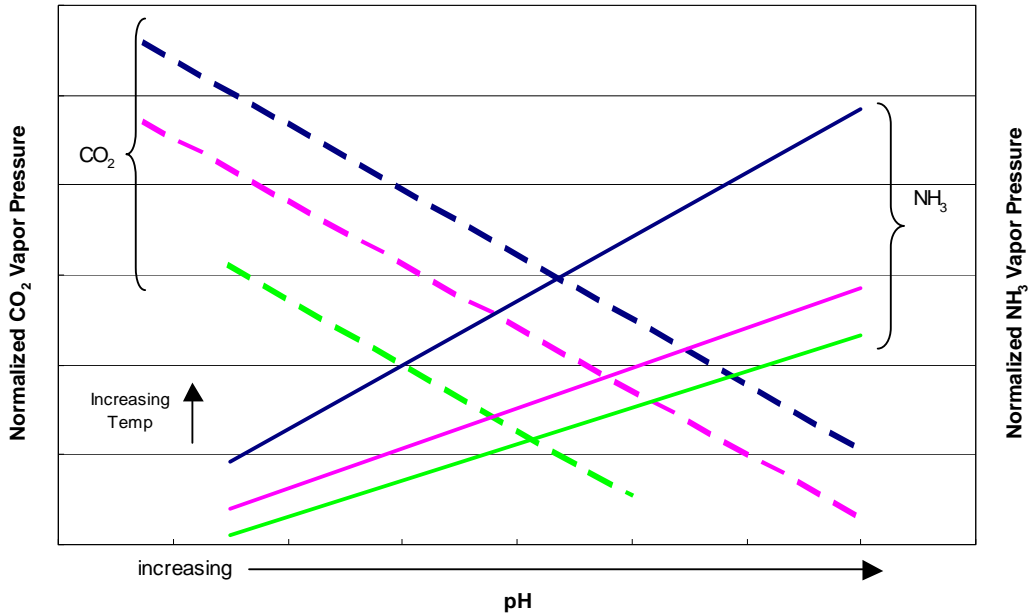
Powerspan has been developing the ECO<sub>2</sub> technology since 2004, in conjunction with U.S. DOE-NETL under a cooperative research and development agreement (CRADA). Initial laboratory testing conducted by Powerspan of the CO<sub>2</sub> absorption process demonstrated 90 percent CO<sub>2</sub> removal under conditions comparable to a commercial-scale absorber: temperature 130°F; residence time 4-5 seconds; L/G 65 gpm/kacfm; flue gas containing CO<sub>2</sub>, O<sub>2</sub>, and N<sub>2</sub>.

Based on these promising initial results, Powerspan has conducted extensive laboratory testing over the last three years to establish the effectiveness of the ECO<sub>2</sub> process for CO<sub>2</sub> capture. This testing has set the design parameters for the pilot unit currently under construction at FirstEnergy's R.E. Burger Plant near Shadyside, Ohio.

The laboratory testing has consisted of: 1) verification of analytical techniques for measurement of the composition of gas and liquid streams, 2) equilibrium testing and modeling to establish limits for absorption and regeneration, 3) absorption rate testing to predict the mass transfer requirements for CO<sub>2</sub> absorption under commercial conditions (gas velocity, liquid to gas ratio) and in commercial mass transfer media (packing), 4) regeneration testing to establish optimal conditions for CO<sub>2</sub> release, 5) ammonia recovery from the regenerator off-gas and 6) combined absorption and regeneration in a cycling system that operates under steady state conditions.

Equilibrium testing under absorption conditions has been used to define the solution composition, temperature and flow rate that maintains driving force for CO<sub>2</sub> capture throughout the absorber. It also has established the limit on ammonia vapor release and CO<sub>2</sub> absorption capacity. Figure 3 shows the normalized ammonia and CO<sub>2</sub> vapor pressure as a function of solution pH for three temperatures.

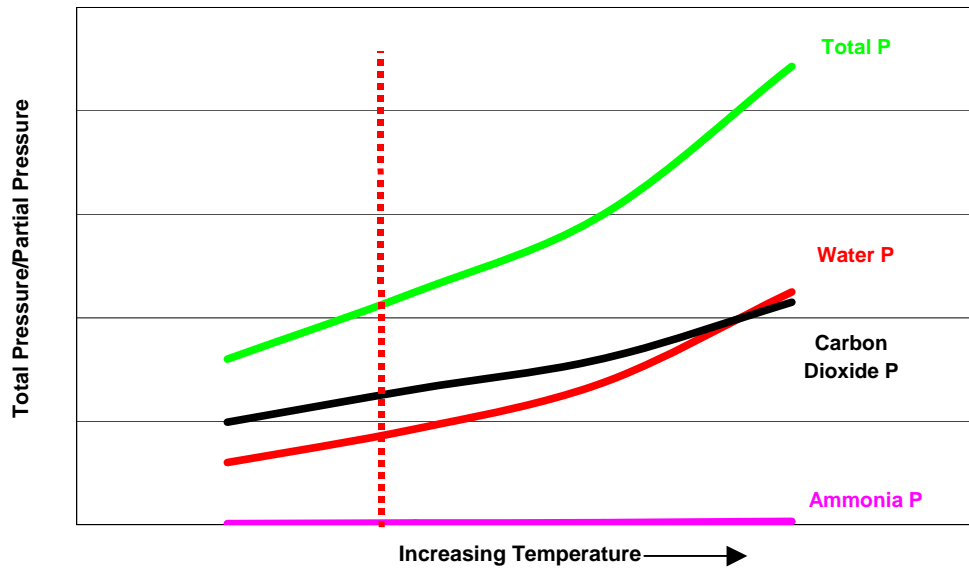
Fig. 3. Equilibrium ammonia and CO<sub>2</sub> vapor pressure under absorber conditions



As is expected, the ammonia vapor pressure increases with increasing pH and temperature, while the CO<sub>2</sub> vapor pressure decreases with increasing pH, and increases with increasing temperature. Similar equilibrium testing under regeneration conditions establishes the temperature and pressure for solution regeneration and the quantity of ammonia and water vapor released relative to the CO<sub>2</sub> release. This is shown in Figure 4, where it can be seen that increasing regeneration temperature increases the partial pressure of water vapor, CO<sub>2</sub> and NH<sub>3</sub>, and therefore the total pressure. However, the figure also shows that above the design temperature the increase in water vapor partial pressure with temperature is greater than that of CO<sub>2</sub>, increasing the relative concentration of water vapor to CO<sub>2</sub>. The design regeneration temperature is chosen based on minimizing the energy input to the regenerator in conjunction with minimizing the compression energy required to get to final system pressure.

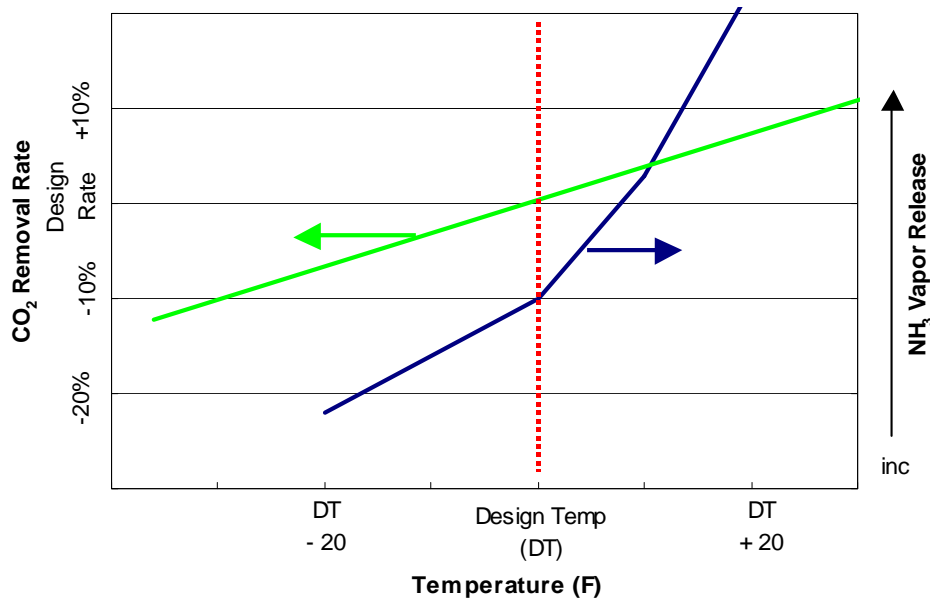
Absorption rate testing has been conducted in Powerspan's 4" diameter laboratory packed tower absorber. Performance of the laboratory absorber for SO<sub>2</sub> and NO<sub>2</sub> scrubbing in the ECO process has been correlated to the performance of Powerspan's 17 ft and 2.5 ft diameter scrubbing towers in operation at FirstEnergy's Burger plant. The laboratory absorber system uses flue gas from propane combustion, into which SO<sub>2</sub>, NO<sub>x</sub>, CO, O<sub>2</sub>, N<sub>2</sub>, CO<sub>2</sub>, HCl and Hg are added as needed to simulate the composition of coal combustion produced flue gas. The testing conducted included the effect of packing height, gas flow rate, solution composition and temperature on CO<sub>2</sub> removal and ammonia vapor release. An example from the testing (Figure 5) shows the normalized effect of temperature on CO<sub>2</sub> absorption and ammonia vapor release rates from the CO<sub>2</sub> scrubber for a given solution composition.

Fig. 4. Effect of temperature on solution regeneration



It can be seen that although the ammonia vapor release rate decreases with decreasing temperature, the CO<sub>2</sub> absorption rate also decreases. The design temperature (DT) depicted in the figure is the scrubbing temperature that maximizes the CO<sub>2</sub> scrubbing rate with an ammonia vapor release rate from the ECO<sub>2</sub> process that can be controlled to less than 5 ppm.

Fig. 5. Effect of temperature on CO<sub>2</sub> absorption and ammonia release rates.



Testing in a lab scale regenerator establishes the impact of temperature, pressure and residence time on the release of CO<sub>2</sub> from the absorbing solution. This testing also establishes the energy requirements for regeneration and the gas flow rates of ammonia and water. The energy input is compared to literature values to verify the regeneration reaction mechanism.

Shown in Figure 6 are photographs of two lab scale CO<sub>2</sub> absorption systems that also regenerate the scrubbing solution, and can each be run to a steady state condition. The larger of the two systems treats up to 20 scfm of simulated flue gas, and includes a full ECO system, containing the barrier discharge reactor, scrubber and wet electrostatic precipitator, upstream of the ECO<sub>2</sub> absorber and regenerator. These systems are used to obtain steady state performance under a variety of operating conditions, chosen for process optimization and to simulate flue gas conditions at specific operating plants. The systems also are in use to demonstrate control of the process chemistry.

Fig. 6. Lab scale absorption/regeneration systems

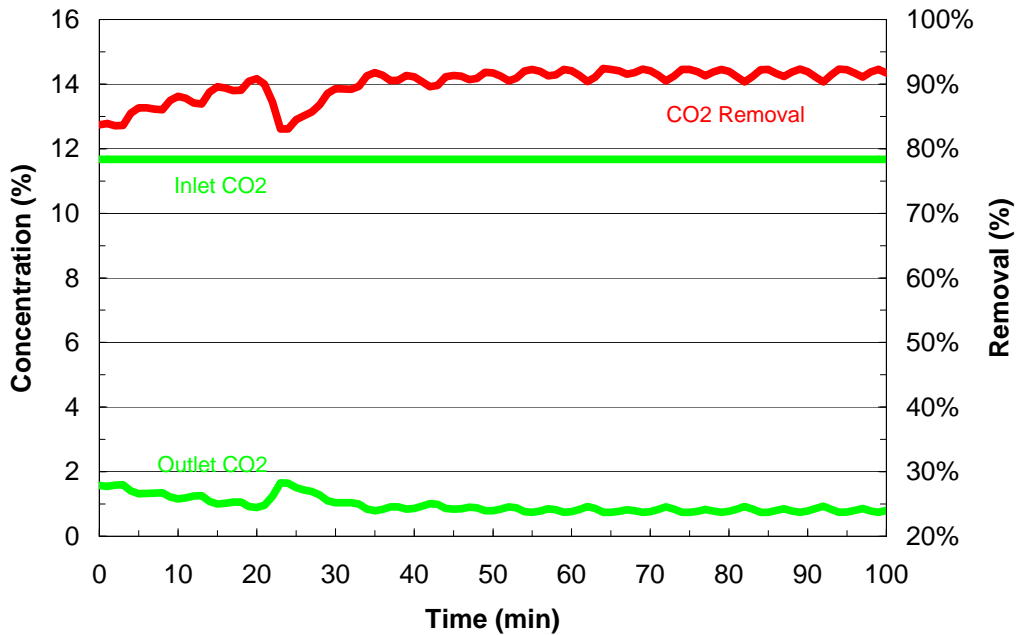


Shown in Figure 7 are the inlet and outlet CO<sub>2</sub> concentrations, and the CO<sub>2</sub> removal for one set of operating conditions. The figure shows performance for approximately 1 hour after steady state was achieved. The solution capacity for CO<sub>2</sub> during the test represented by the figure was 0.03 lbm-CO<sub>2</sub> per lbm of absorbing solution, at a liquid to gas ratio of 50 gpm/kacfm.

### **ECO<sub>2</sub> PILOT PROGRAM**

Pilot scale testing of the ECO<sub>2</sub> technology is scheduled to begin in the Fall of 2008 at FirstEnergy's R.E. Burger Plant. The ECO<sub>2</sub> pilot will process a 1-MW slipstream drawn from the outlet of the 50-MW Burger Plant ECO unit. It will capture 20 tons of CO<sub>2</sub> per day while achieving a 90 percent capture rate. Captured CO<sub>2</sub> will also be dried and compressed to demonstrate that the required quality CO<sub>2</sub> can be made available for pipeline transport and sequestration.

Fig. 7. Steady state absorption performance in lab scale absorption/regeneration system

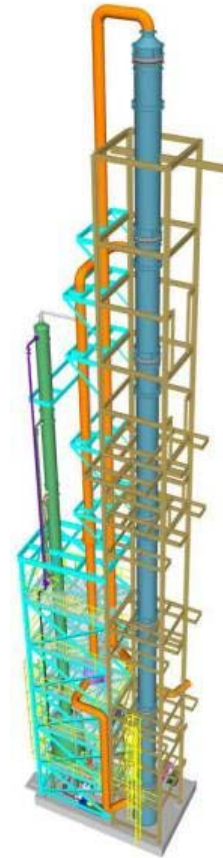


The ECO<sub>2</sub> pilot will demonstrate CO<sub>2</sub> capture, solution regeneration, and ammonia vapor control through integration with the ECO multi-pollutant control process. Operation of the pilot will confirm process performance and energy requirements, and the adequacy of the process equipment. The pilot program will provide the basis for cost estimates while preparing the technology for commercial scale capture and sequestration demonstration projects.

### ECO<sub>2</sub> PERFORMANCE COMPARISON

An analysis of the energy consumption of an ECO<sub>2</sub> process, and its impact on power plant output have been made based on the laboratory results obtained to date. Shown in Table 1 is an estimate of performance comparing an ECO<sub>2</sub> and an MEA system retrofit on an existing coal fired power plant, obtaining 90% CO<sub>2</sub> removal. Data for the base plant and MEA process were obtained from Reference 2. Shown in the table is the gross and net power output for the base plant with wet flue gas desulfurization (WFGD), an MEA process with enhanced WFGD, and the ECO<sub>2</sub> process using the ammonia based ECO-SO<sub>2</sub> process for SO<sub>2</sub> removal. The analyses show that the power plant gross output is reduced from 463 MW to 449 MW with installation of the ECO<sub>2</sub> process, and to 388 MW with an MEA system. The analysis also shows that the plant's net output is reduced by 16% when using ECO<sub>2</sub> for CO<sub>2</sub> capture, and by 30% when an MEA system is used.

Figure 7: ECO2 pilot (a) scrubber and (b) isometric drawing



**Table 1: CO<sub>2</sub> Capture Performance Comparison**

	Base Plant w/o CO <sub>2</sub> Capture	MEA w/ enhanced WFGD	ECO <sub>2</sub> w/ ECO-SO <sub>2</sub>
Gross Output (MW)	463	388	449
Balance of Plant (MW)	30	30	30
CO <sub>2</sub> Capture and Compression (MW)		55	57
Net Output (MW)	434	303	362
% Loss from Base Plant	-	30%	16%

A comparison of the energy usage in MEA and ECO<sub>2</sub> systems for CO<sub>2</sub> capture and regeneration is shown in Table 2. The process energy consumption can be segregated into three categories: 1) sensible heat, 2) reaction energy and 3) stripping steam. The sensible heat component is the energy needed to raise the temperature of the scrubbing solution to the regenerator temperature and which

can not be recovered. Reaction energy is simply the heat of reaction for absorption of CO<sub>2</sub>, and stripping steam is the energy associated with the steam needed or produced during the regeneration process. Table 1 shows that the energy requirement of the ECO<sub>2</sub> process is less than that of MEA in each category. Data for the MEA system is taken from Reference 3. The table shows that the ECO<sub>2</sub> total energy requirement of 493 Btu/lb-CO<sub>2</sub> is 27% of the MEA energy requirement of 1,812 Btu/lb-CO<sub>2</sub>.

**Table 2: Energy Usage in MEA and ECO<sub>2</sub> Systems for CO<sub>2</sub> Capture**

	MEA <sup>1</sup>	ECO <sub>2</sub>
Sensible Heat	372	128
Reaction Energy	825	277
Stripping Steam	615	88
Total Energy	1,812	493

## COMMERCIAL DEMONSTRATION PLANS

Powerspan recently completed a feasibility study for installation of a 120 MW ECO<sub>2</sub> system at Basin Electric Power Cooperative's Antelope Valley Station near Beulah, North Dakota. Powerspan was chosen from among six companies in the first competitive solicitation for a CO<sub>2</sub> capture demonstration in the U.S. The project is scheduled to move forward in 2009 and the facility is expected to be operational in 2012, capturing 1,000,000 tons per year of CO<sub>2</sub> for delivery into Dakota Gasification's existing pipeline delivery system. Dakota Gasification is a wholly owned subsidiary of Basin Electric. In addition, Powerspan was selected by NRG Energy to demonstrate CO<sub>2</sub> capture from flue gas equal in quantity to that from a 125 MW unit. The demonstration is to be conducted at NRG's W.A. Parish plant near Sugar Land, Texas and is expected to be in operation in 2012. CO<sub>2</sub> captured from the flue gas is expected to be used for enhanced oil recovery operations in the Houston area.

## CONCLUSIONS

The ECO<sub>2</sub> process is a promising solution for post combustion capture of CO<sub>2</sub> from both existing and new coal-fired power plants. Powerspan has conducted extensive laboratory testing over the last three years to establish the effectiveness of the ECO<sub>2</sub> process for CO<sub>2</sub> capture. This testing has established the design parameters for the pilot unit being constructed at FirstEnergy's R.E. Burger Plant in Shadyside, Ohio. Pilot testing of the process, scheduled to begin in the fall of 2008, will prepare the technology for commercial scale capture and sequestration demonstration projects. Testing completed to date indicates the ECO<sub>2</sub> technology could be economically applied to coal-fired power plants, thereby providing a potential option for their continued operation in a carbon-constrained environment.

## ACKNOWLEDGMENTS

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