

Testing of Ammonia Based CO₂ Capture with Multi-Pollutant Control Technology

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ABSTRACT

Powerspan has been developing a CO₂ capture process, called ECO₂[®], 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 CO₂ 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 CO₂ per day. The pilot will demonstrate CO₂ capture through integration with the ECO[®] multi-pollutant control process. The pilot program will also prepare the technology for commercial scale carbon capture and sequestration (CCS) demonstration projects

INTRODUCTION

While CO₂ emissions from power plants are currently unregulated at the Federal level, there is a growing consensus that standards limiting CO₂ emissions are likely to be promulgated within the next five years. CO₂ emissions from the electric power sector account for 40 percent of total U.S. energy-related CO₂ 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 CO₂ 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 CO₂ 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 CO₂ capture solutions have capital and operating costs that are considered uneconomical for conventional coal-fired power plants.

Powerspan Corp. is developing a CO₂ capture process, called ECO₂[®], 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.

ECO₂ is a scrubbing process that uses an ammonia-based solution to capture CO₂ from flue gas. The

CO₂ capture takes place after NO_x, SO₂, Hg and fine particulate matter capture is accomplished in Powerspan's ECO multi-pollutant control technology, or other air pollution control systems. Once CO₂ is absorbed, the resulting solution is regenerated to release it. In addition to CO₂, NH₃ is released during regeneration. It is recovered and returned to the scrubbing process, and the product CO₂ 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 CO₂ capture with the ECO₂ process. The testing has demonstrated steady-state capture/regeneration operation with 90 percent CO₂ 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 ECO₂ process with power plant flue gas. The ECO₂ pilot is scheduled to begin operation in the Fall of 2008.

The ECO₂ pilot unit will process a 1-MW slipstream (equivalent to 20 tons of CO₂ per day) from the 50-MW Burger Plant ECO unit. The pilot program will demonstrate the ability of the CO₂ 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

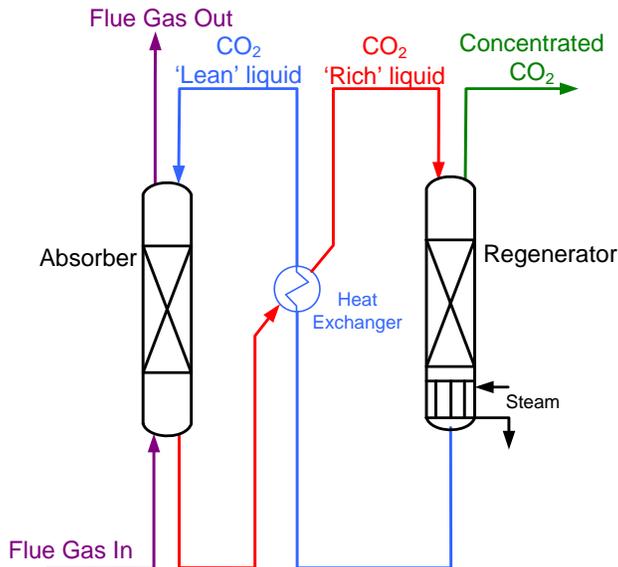
Post combustion carbon dioxide (CO₂) capture from coal-fired power plants takes place downstream of any employed sulfur dioxide (SO₂), nitrogen oxides (NO_x), and mercury (Hg) removal process steps. When integrated with the ECO multi-pollutant control process, CO₂ capture takes place after the SO₂, NO_x, mercury, and fine particulate matter are removed. Because the SO₂ capture efficiency of ECO is so effective (typically greater than 98%), no supplemental SO₂ capture is required.

The ECO₂ technology uses an ammonia-based solution to absorb CO₂ from flue gas. Once the CO₂ is absorbed, the solution containing CO₂ 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 CO₂ is then in a form that is ready for compression, pipeline transport and sequestration. The ECO₂ process does not consume ammonia and no separate by-product is created by an ECO₂ system.

The ECO₂ process is a thermal swing absorption (TSA) process for CO₂ capture. CO₂ 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 CO₂. The process is similar to other CO₂ capture technologies such as amine-based processes. Common to thermal swing absorption processes are the following key steps, which are depicted in Figure 1:

- CO₂ is absorbed in a solution through flue gas–solution contact,
- The solution is heated for regeneration,
- CO₂ is released from the heated solution, and
- The solution is cooled for reuse.

Fig. 1. Basic thermal swing absorption process.



In the ECO₂ process CO₂ 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 CO₂ while forming ammonium carbonate (reaction 2).



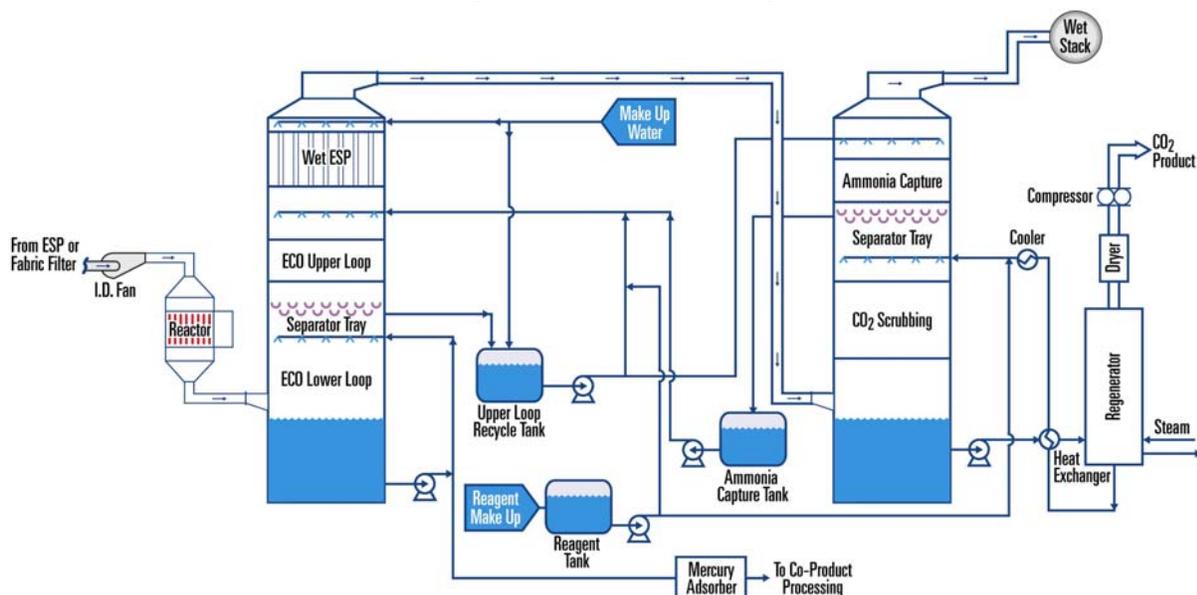
CO₂ released in reaction 2 is compressed for sequestration while the ammonium carbonate solution is returned to the scrubber for reuse.

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 CO₂ 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 CO₂ scrubbing, and to the product gas during solution regeneration. The ECO₂ process captures ammonia released to the flue gas during CO₂ scrubbing, reducing the concentration to less than 5 ppmv, and also recovers ammonia from the CO₂ product gas, after regeneration, for reuse.

An illustration how the ECO₂ 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_x, SO₂, mercury, and fine particulate matter. The wet scrubber uses aqueous ammonia for SO₂ scrubbing, producing ammonium sulfate fertilizer co-product.

Fig. 2. Incorporation of the ECO₂ 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 ECO₂ process is an important factor in the environmental impact and process economics of using ammonia for CO₂ capture. Figure 2 shows how ammonia vapor release from the ECO₂ scrubber is controlled using scrubbing liquor from the ECO Upper Loop. In an ECO system without the ECO₂ 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 CO₂ 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 CO₂ scrubbing section. The contact takes place in the Ammonia Capture section of the ECO₂ 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 SO₂ from the flue gas. In this configuration, ammonia that would have been added directly to the ECO process is instead added to the CO₂ Scrubbing section of the ECO₂ absorber, then captured in the Ammonia Capture section and carried to the ECO absorber.

Although the ECO₂ process is new and proprietary, the innovation is in process chemistry. The equipment required for operation of commercial ECO₂ systems (e.g., absorber, regenerator, heat exchangers, pumps, gas dryer, etc.) are commercially available at the required scale. Therefore, once the ECO₂ process is demonstrated at the pilot scale on an operating power plant, the scale up risk is manageable.

COMPARISON TO AMINE-BASED CO₂ CAPTURE SYSTEMS

Ammonia scrubbing of CO₂ potentially offers several advantages over the commercially available amine process for CO₂ 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 CO₂¹:

1. The traditional monoethanolamine (MEA) process for CO₂ removal has disadvantages of low CO₂ loading capacity (kg CO₂ absorbed per kg absorbent); high equipment corrosion rate;

- amine degradation by SO₂, NO₂, HCl, HF and O₂ 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 CO₂ absorption capacity;
 - Requires substantially less heat to release CO₂ and regenerate absorbent; and
 - Has lower reagent makeup costs.
 3. Another major benefit is that removal of other pollutants (principally SO₂ and NO_x) could be integrated with the aqua ammonia process for CO₂ removal (i.e. using the ECO multi-pollutant control technology). Due to the requirements of the MEA process, very low SO₂ flue gas is a necessary input (less than 10 ppm). Since most commercially available SO₂ scrubbing systems are not efficient enough to provide this low SO₂ flue gas to the CO₂ scrubbing system (especially on existing units with already-deployed SO₂ scrubbers), an auxiliary SO₂ scrubbing system would be needed, increasing the CO₂ capture system capital cost.

LABORATORY TESTING RESULTS

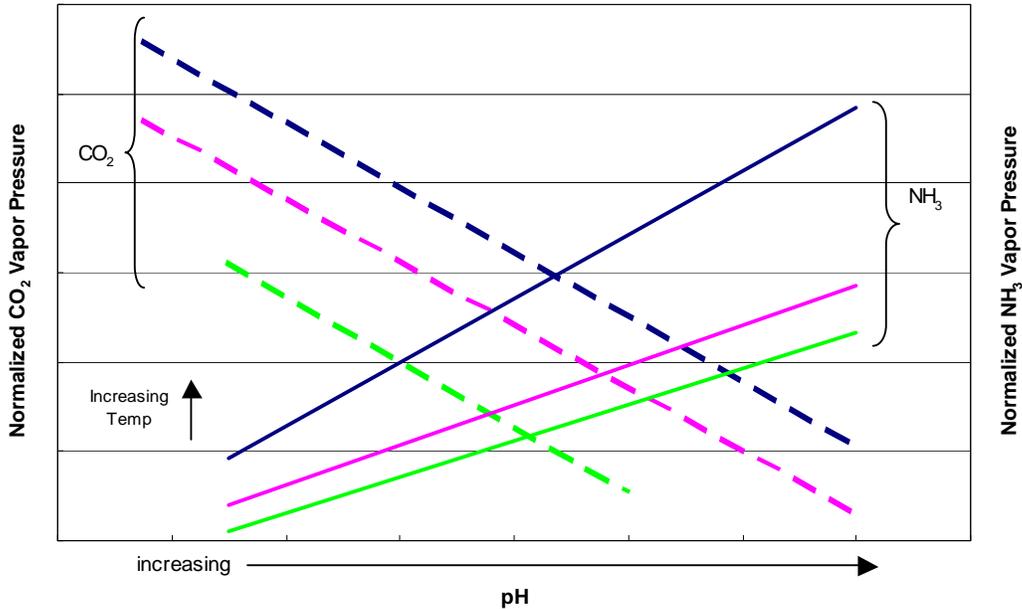
Powerspan has been developing the ECO₂ technology since 2004, in conjunction with U.S. DOE-NETL under a cooperative research and development agreement (CRADA). Initial laboratory testing conducted by Powerspan of the CO₂ absorption process demonstrated 90 percent CO₂ removal under conditions comparable to a commercial-scale absorber: temperature 130°F; residence time 4-5 seconds; L/G 65 gpm/kacfm; flue gas containing CO₂, O₂, and N₂.

Based on these promising initial results, Powerspan has conducted extensive laboratory testing over the last three years to establish the effectiveness of the ECO₂ process for CO₂ 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 CO₂ 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 CO₂ 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 CO₂ capture throughout the absorber. It also has established the limit on ammonia vapor release and CO₂ absorption capacity. Figure 3 shows the normalized ammonia and CO₂ vapor pressure as a function of solution pH for three temperatures.

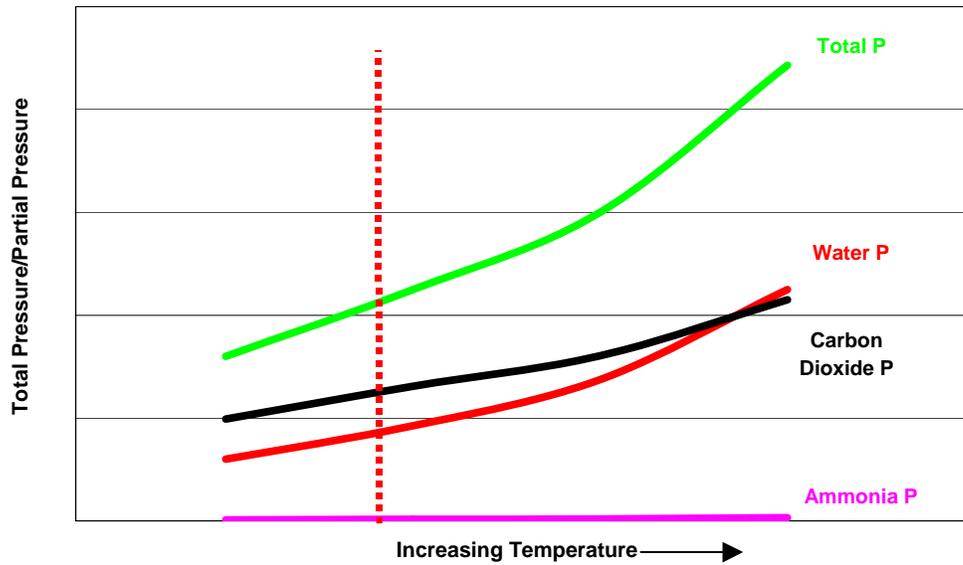
Fig. 3. Equilibrium ammonia and CO₂ vapor pressure under absorber conditions



As is expected, the ammonia vapor pressure increases with increasing pH and temperature, while the CO₂ 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 CO₂ release. This is shown in Figure 4, where it can be seen that increasing regeneration temperature increases the partial pressure of water vapor, CO₂ and NH₃, 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 CO₂, increasing the relative concentration of water vapor to CO₂. 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.

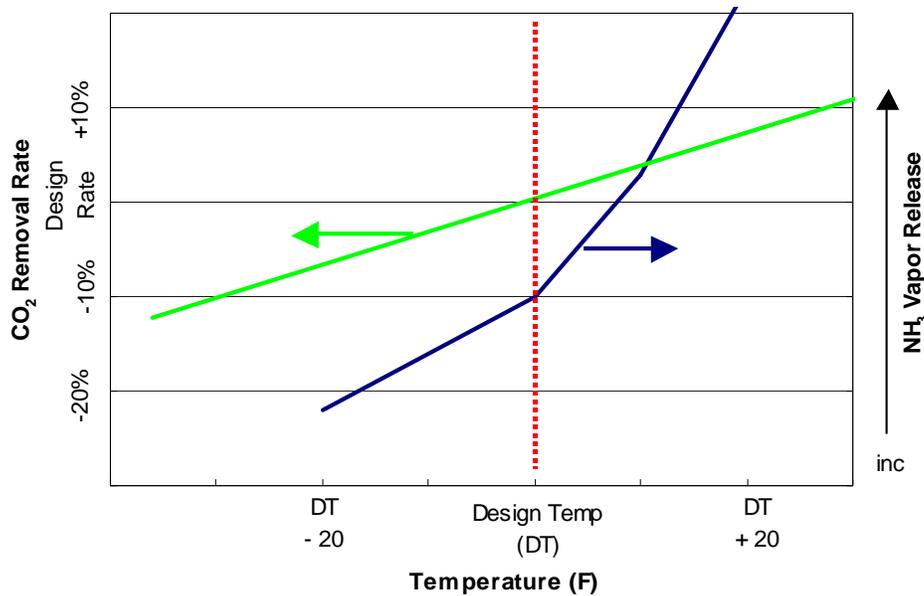
Absorption rate testing has been conducted in Powerspan's 4" diameter laboratory packed tower absorber. Performance of the laboratory absorber for SO₂ and NO₂ scrubbing in the ECO process has been correlated to the performance of Powerspan's 17 ft and 2.5 ft diameter scrubbing towers in operation at FirstEnergy's Burger plant. The laboratory absorber system uses flue gas from propane combustion, into which SO₂, NO_x, CO, O₂, N₂, CO₂, 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 CO₂ removal and ammonia vapor release. An example from the testing (Figure 5) shows the normalized effect of temperature on CO₂ absorption and ammonia vapor release rates from the CO₂ 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 CO₂ absorption rate also decreases. The design temperature (DT) depicted in the figure is the scrubbing temperature that maximizes the CO₂ scrubbing rate with an ammonia vapor release rate from the ECO₂ process that can be controlled to less than 5 ppm.

Fig. 5. Effect of temperature on CO₂ absorption and ammonia release rates.



Testing in a lab scale regenerator establishes the impact of temperature, pressure and residence time on the release of CO₂ 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 CO₂ 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 ECO₂ 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

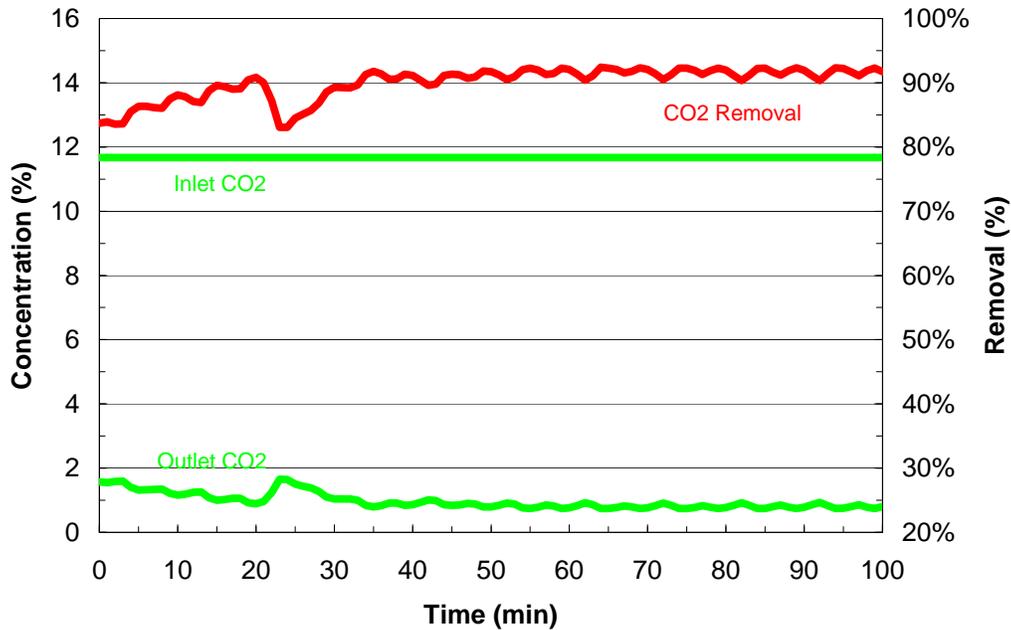


Shown in Figure 7 are the inlet and outlet CO₂ concentrations, and the CO₂ removal for one set of operating conditions. The figure shows performance for approximately 1 hour after steady state was achieved. The solution capacity for CO₂ during the test represented by the figure was 0.03 lbm-CO₂ per lbm of absorbing solution, at a liquid to gas ratio of 50 gpm/kacfm.

ECO₂ PILOT PROGRAM

Pilot scale testing of the ECO₂ technology is scheduled to begin in the Fall of 2008 at FirstEnergy's R.E. Burger Plant. The ECO₂ 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 CO₂ per day while achieving a 90 percent capture rate. Captured CO₂ will also be dried and compressed to demonstrate that the required quality CO₂ can be made available for pipeline transport and sequestration.

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



The ECO₂ pilot will demonstrate CO₂ 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.

ECO₂ PERFORMANCE COMPARISON

An analysis of the energy consumption of an ECO₂ 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 ECO₂ and an MEA system retrofit on an existing coal fired power plant, obtaining 90% CO₂ 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 ECO₂ process using the ammonia based ECO-SO₂ process for SO₂ removal. The analyses show that the power plant gross output is reduced from 463 MW to 449 MW with installation of the ECO₂ 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 ECO₂ for CO₂ capture, and by 30% when an MEA system is used.

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

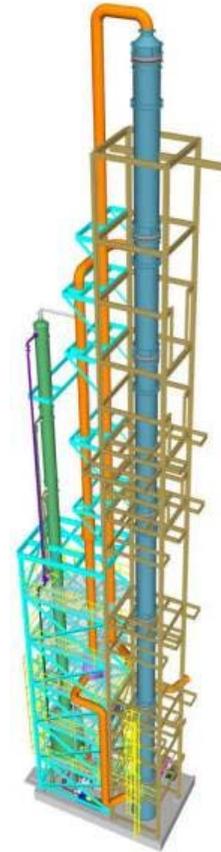


Table 1: CO₂ Capture Performance Comparison

	Base Plant w/o CO ₂ Capture	MEA w/ enhanced WFGD	ECO ₂ w/ ECO-SO ₂
Gross Output (MW)	463	388	449
Balance of Plant (MW)	30	30	30
CO ₂ 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 ECO₂ systems for CO₂ 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 CO₂, 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 ECO₂ 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 ECO₂ total energy requirement of 493 Btu/lb-CO₂ is 27% of the MEA energy requirement of 1,812 Btu/lb-CO₂.

	MEA ¹	ECO ₂
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 ECO₂ 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 CO₂ 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 CO₂ 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 CO₂ 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. CO₂ captured from the flue gas is expected to be used for enhanced oil recovery operations in the Houston area.

CONCLUSIONS

The ECO₂ process is a promising solution for post combustion capture of CO₂ 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 ECO₂ process for CO₂ 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 ECO₂ 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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