

Summary of Post-Combustion CO₂ Capture Technologies for Existing Coal-Fired Power Plants

Paper # 808

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ABSTRACT

Due to mounting concern over climate change due to anthropogenic greenhouse gases, carbon dioxide emission legislation is being discussed and is expected to be passed in the near future. Utilities are relying on science to develop and improve CO₂ capture technologies that will allow them to reduce their emissions as well as continue to provide customers with affordable electricity. Cleaner coal fired power plants are being planned and built, but the nation's current operating power plants must be retrofit to have the greatest impact on emissions in the near future. Although few are proven on a commercial scale, there are several post-combustion capture technologies that have shown great promise.

The most well-known capture technology is absorption by aqueous amines or ammonia. The solvents react with the CO₂, separating it from other flue gas constituents. The solution can be regenerated through heating. The carbon dioxide is released during this regeneration step and can be processed for sequestration. The major challenges to absorption technologies are the corrosive nature of the solutions, degradation from other pollutants and the energy required for regeneration. One ammonia-based technology is projected to be commercial by 2011. Solid sorbents are also a promising CO₂ capture technology, which may offer greater ease of handling. However, solid sorbents for CO₂ are still being developed that will meet the required CO₂ capacity, regeneration ability, selectivity and immunity to flue gas constituents. Another capture technology is membrane separation, which offers design simplicity. Membranes are currently being developed to improve their CO₂ selectivity. Solid sorbents and membranes are currently in laboratory and bench-scale development. In the end, it will require a range of solutions to achieve meaningful greenhouse gas reductions. This paper/presentation will provide the up to date status and results of several CO₂ capture technologies.

INTRODUCTION

Before the industrial revolution, anthropogenic greenhouse gas emissions were negligible. However, it was projected that over 30 billion tons of carbon dioxide would be released in 2007¹; in addition, emissions are expected to grow with increased power consumption of highly populated developing countries. Stationary point sources, such as coal-fired power plants, offer the most promising source for a reduction in carbon dioxide emissions in the near future.

Fossil fuels are currently used to meet 80% of the energy demand in the United States.² All fossil fuels are carbon-based. When these fuels are burned one of the products will inevitably be carbon dioxide. Approximately half the electricity in the United States is generated by burning coal.² When mixed with air and exposed to elevated temperature, the carbon in coal reacts with oxygen in air according to the following chemical reaction:



This reaction is highly exothermic, and thus the burning of coal results in a large amount of heat. The energy is used to heat water until it has been converted to high pressure steam, which impacts the blades of a turbine and causes both the turbine and the generator to turn. A magnetic field is created, resulting in electricity, which is then distributed across the grid to homes, business and industry alike. Emissions of gases such as oxides of nitrogen, oxides of sulfur, mercury as well as particulates (dust) can be controlled by current technologies.

One major difference between CO₂ and other emissions is the volume at which they are produced. SO_x, NO_x and Hg concentrations are measured in parts per million (ppm) while CO₂ is measured as a percentage of the flue gas. Without any modifications, 10-12% of the gas released by current coal-fired power plants is CO₂. Each ton of carbon in the coal produces nearly 4 tons of gaseous CO₂. This large volume of carbon dioxide must be stored. Carbon Capture and Sequestration (CCS) is the most promising solution. Obtaining a pure CO₂ stream is the first step of CCS. After the separation, CCS includes compression of the pure CO₂ and sequestration so that it does not enter the atmosphere.

The vast majority of coal-fired power plants burn pulverized coal in a boiler, and are thus referred to as PC plants. Post-combustion capture is one of the few viable options to retrofit such plants. The most developed separation technologies utilize liquid solvents. The two most well-known and proven solvents are amines and ammonia. CO₂ reacts with both of these solvents, and then is released as a pure gas when the solution is heated. For some solvents, it is possible to design a system to also capture other emissions, such as SO₂, NO_x and Hg. Solid sorbents are another promising capture technology. These sorbents can either react with the CO₂ or adsorb it onto the surface. A third post-combustion capture option may be membranes, which are being developed to selectively separate CO₂ from the other flue gas constituents.

The federal government, state governments, utilities and the environmental industry are working to accelerate technology development in order to make carbon capture and sequestration a safe, financially viable option for carbon management. To further the public knowledge about this subject, post-combustion strategies to retrofit PC power plants, will be discussed in detail in this paper.

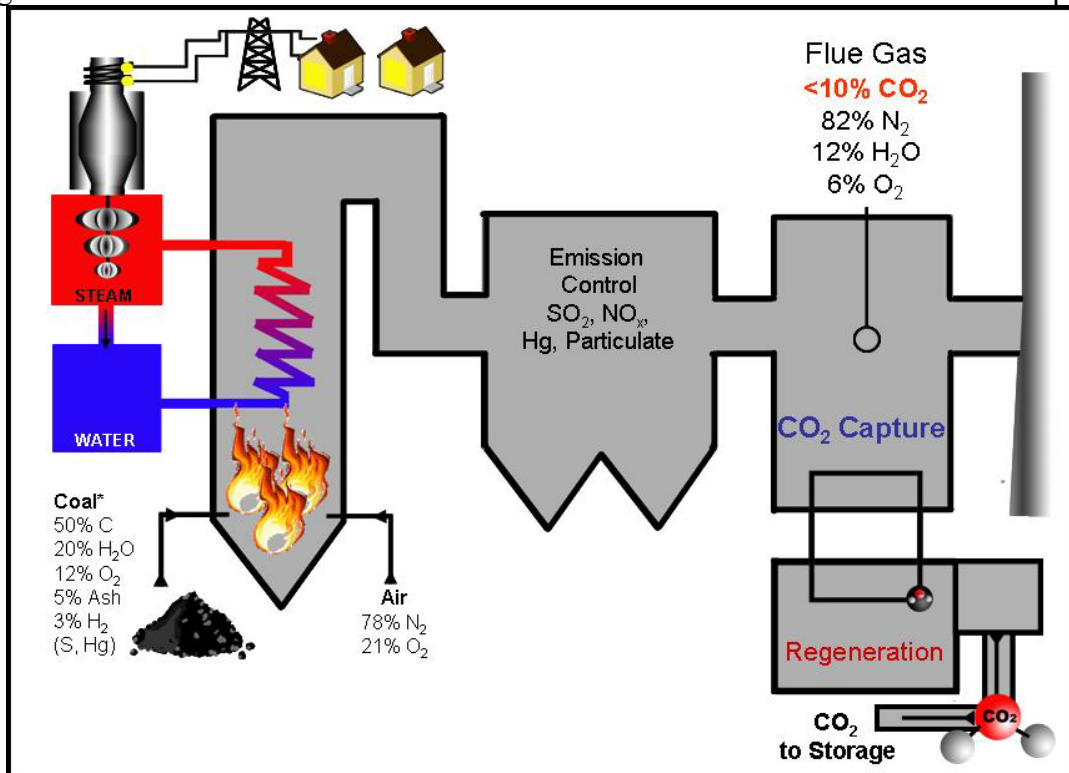
POST-COMBUSTION CO₂ MANAGEMENT OPTIONS

The current operating capacity of coal-fired power stations in the United States is 320 GW.² The 45 GW of proposed new generation can be designed for carbon capture and increased efficiency, but clearly the carbon emissions from the conventional plants must be addressed. Post-combustion technologies are being developed rapidly in order to meet the carbon management needs of the existing fleet of power plants. The capture technologies are widely varied in the mechanism of separation. Due to the scale, carbon dioxide capture and sequestration (CCS) promises to be difficult and will require diverse technologies to achieve success. The DOE has set the following requirements for CO₂ capture technologies:⁴

- 90% CO₂ capture
- 99% storage permanence
- <20% increase in the cost of electricity

For the third point to be achievable, a portfolio of carbon dioxide capture technologies will be necessary. With a wide array of coal types, air pollution control systems and operating conditions at different coal-fired power plants, technologies must be developed to meet capture standards under different scenarios. In addition, the scale of carbon capture will require using many different materials to minimize the demand and thus the related rise in cost of any one material. Figure 1 shows the main components of a conventional coal-fired power plant with the addition of a solvent or sorbent-based carbon capture system.

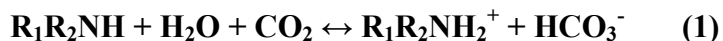
Figure 1. Conventional Coal-fired Electric Station with Post-Combustion Carbon Capture



In this figure, the solution or sorbent is used in a cyclic process. First, the material is sent through a contactor where it separates the CO₂ from the other flue gas constituents. Then, the CO₂-laden material is regenerated, usually through a change in temperature or pressure. The CO₂ gas is released in a nearly-pure stream and the CO₂-lean material is then used again to capture a new batch of CO₂. Due to the large volume of CO₂ to be captured, it is important that the material can be regenerated and used repeatedly. Although more research is needed, preliminary tests have shown that carbon capture technologies have the potential to remove nearly all the carbon dioxide from the flue gas. With adequate support, RD&D of this work can be accomplished quickly and efficiently.

Liquid Solvents

Chemical absorption technology consists of separating the CO₂ from the flue gas using a chemical absorbent. After the solution has reacted with the CO₂, it is heated to release the CO₂ and the solution is reused. There are several different solvents that have been demonstrated for carbon capture from flue gas. Amines scrubbers were one of the first solutions considered for flue gas CO₂ capture because amines are used to remove acid gases during natural gas sweetening. The amines are often viscous and corrosive and must be used in an aqueous solution. The chemical reaction between the CO₂ and an amine in an aqueous solution to produce bicarbonate is as follows:

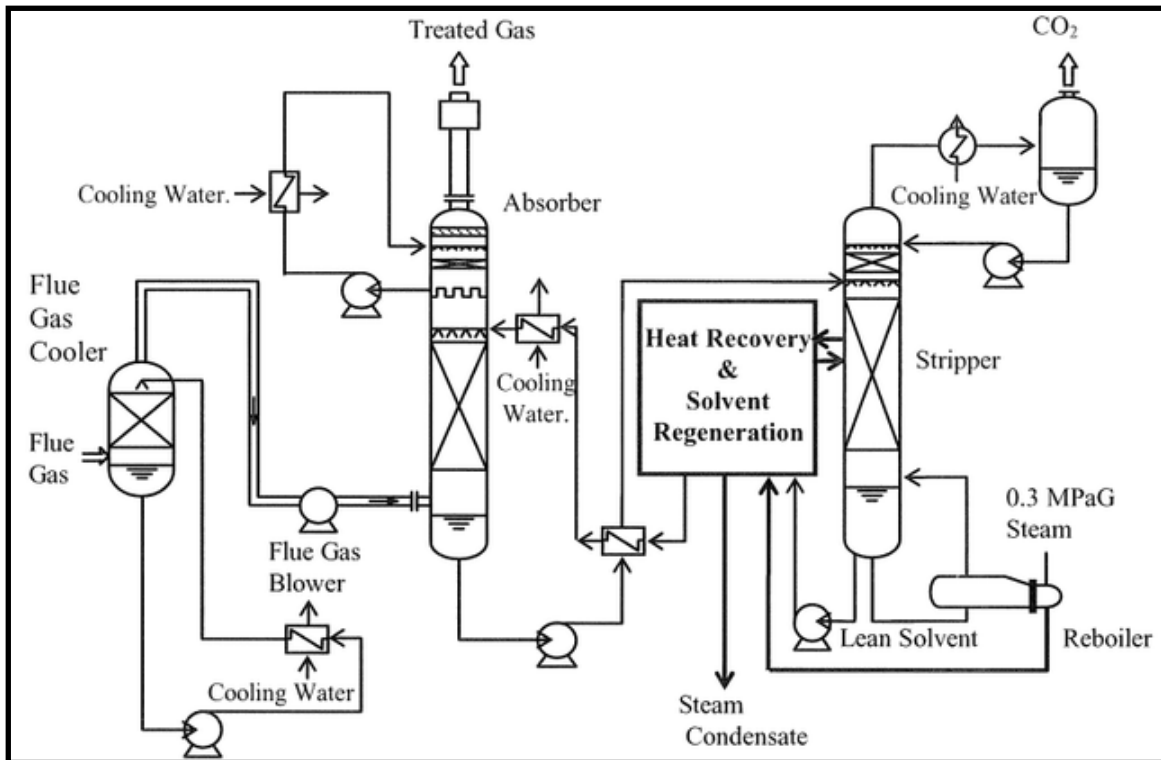


Monoethanolamine (MEA = C₂H₇NO) is one of the amines under consideration for possible CO₂ capture. In the process, MEA and flue gas flow are contacted counter-currently in a scrubber. Amines were an obvious choice because they are used to remove acid gases during natural gas sweetening. In addition, amines are used at coal-fired power plants to obtain food grade carbon dioxide.⁵ However, using current technology, carbon capture utilizing MEA is expected to be prohibitively expensive. For example, a conventional power plant with 34.3% efficiency would be reduced to 25.1% efficiency due to the parasitic energy requirements of an MEA-based capture process.² The majority of the expense is incurred during the regeneration, when the large volume of aqueous solution must be heated to approximately 110°C. A recent study released by NETL showed that capture cost (\$/ton CO₂) was linearly related to the amount captured.⁶ In this study based on the conditions at AEP's Conesville plant, unit 5, the cost of capturing 90% of the CO₂ was \$54/ton, while the cost of capturing 30% of the CO₂ was \$77/ton. The regeneration energy, the main source of cost, has been reduced by 34% below that in a 2001 study.⁷ In addition, it is expected that further improvements in the near future will reduce the cost of this process to \$52/ton CO₂. Although amine technology is developed and well-understood, more cost-reducing advancements will be necessary to make amines a viable carbon capture option.

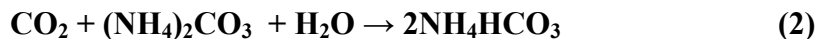
Using a mixture of amines, or a different solution can reduce the energy requirements. In fact, Mitsubishi Heavy Industries (MHI) is using a proprietary alkanolamine-based absorbent to capture CO₂ on a commercial scale and use it for chemical manufacturing. They have already begun using captured CO₂ as a feedstock for chemical manufacturing.

They are working toward economical CO₂ separation for enhanced oil recover and sequestration. The following figure shows the MHI processes for CO₂ capture:

Figure 2. MHI Process for CO₂ Separation Using a Proprietary Alkanolamine Solvent⁸



When the challenges related to MEA-based capture became apparent, alternative solutions were considered. Ammonia-based liquid solvents are a promising technology for CO₂ separation. One challenge of using ammonia is the volatility; at high temperature the ammonia tends to be carried away with the CO₂-lean flue gas. This is addressed in two different manners. Either the flue gas is cooled so that ammonia loss is negligible, or the evaporated ammonia can be recaptured in a process designed for multi-pollutant control. Capture using an ammonium slurry is more cost effective because, in part, the reaction to release the CO₂ is less energy consuming. In addition, tests show that the CO₂ capacity (g CO₂/g solvent) is higher for ammonia than MEA.⁹ The following reactions show the absorption and regeneration reactions, respectively, of CO₂ with an ammonia slurry:



Alstom has developed their proprietary Chilled Ammonia process, where the volatility of the ammonia is reduced by chilling the flue gas to temperatures between 2-15°C (35-60°F).¹² The flue gas flows counter-currently to a slurry containing ammonium carbonates and ammonium bicarbonates. The slurry is regenerated by heating to a temperature of 125°C (260°F). One advantage of this process is the ability to desorb the

CO₂ at high pressure, reducing the energy requirements for compression. Alstom has set the goal of making their Chilled Ammonia CO₂ capture process commercial by 2011. In order to accomplish this, they have paired with American Electric Power (AEP) for large scale, two phase testing and demonstration project. The first phase of testing will be completed at AEP's Mountaineer Plant, located in New Haven, on a 30 MWth slipstream. This test will use Alstom's process to capture up to 100,000 tons of CO₂ per year. This site has access to deep saline aquifers that will be used for sequestration of the CO₂. Testing is scheduled to start in late 2008 and is projected to continue for a period of 12-18 months. For the second phase of this project, Alstom will move to a 200 MW demonstration on a 450 MW unit at the Northeastern Station, located in Oologah, OK. The projected startup dates for this phase of demonstration is late 2011.¹¹ If the second phase is successful, it will lead to an important commercial validation of a CO₂ capture technology that is projected to meet the DOE's <20% increase in the cost of electricity limit.¹¹

Powerspan is also demonstrating an ammonia-based process, developed with NETL, for post-combustion capture. Unlike the Alstom process, the Powerspan ECO₂TM process does not prevent all ammonia vaporization. Instead, the evaporated ammonia captured and recycled for use in the ECOTM process to control other emissions, such as SO₂ and NO_x.¹² The ECO process is being demonstrated on First Energy's 50 MW at Burger Plant in Ohio. The ECO₂ process is designed to be implemented after the ECO process. The pilot scale, 1 MW slipstream, of the ECO₂ process is scheduled to begin in early 2008. This test is expected to capture 90% of the CO₂ in the flue gas, which will amount to approximately 20 tons CO₂/day. BP is providing support for the slipstream tests.

Solid Sorbents

Solid sorbents are a promising CO₂ capture technology. Although carbon dioxide capture by solid sorbents has yet to be demonstrated on the scale necessary to reduce emissions from power plants, this is not a new technology. For years solid sorbents designed for CO₂ capture have been used to purify breathing air in confined spaces, such as space shuttles and submarines. There are different classifications of sorbents; chemical sorbents that react with the CO₂ and physical sorbents that adsorb the CO₂. Amines and other chemicals, such as sodium carbonate, can be immobilized on the surface of solid supports to create a sorbent that reacts with the CO₂. Solid sorbents that physisorb the CO₂ onto the surface include activated carbon, carbon nanotubes and zeolites (both natural and synthetic).

Potential advantages of solid sorbents are as follows:

- Ease of material handling (coal plants are experienced with solids handling)
- Safe for local environment
- High CO₂ capacity
- Lower regeneration energy
- Multi-pollutant control

Chemical sorbents that react with the CO₂ in the flue gas include a support, usually high surface area, with an immobilized amine or other reactant on the surface. The surface area allows for numerous sites for the desired reaction to occur. Examples of commonly used supports are alumina or silica, while common reactants include amines such as polyethylenimine^{13,14} or chemicals such as sodium carbonate¹⁵ (Na₂CO₃). Although coal-fired power plants are experienced with solids handling, the design of the contactor must still be developed and optimized for this application.

While moisture may present a problem for some CO₂ capture options, the moisture in the flue gas stream is necessary for some chemisorption reactions. As an example, the following reactions demonstrate the reaction of sodium carbonate to sodium bicarbonate during capture:



When heated, the reaction will reverse; the bicarbonate will release the CO₂ and water, which will then be separated from each other during cooling and compression. After this step, the pure CO₂ can be geologically sequestered. Researchers from the Research Triangle Institute (RTI) have completed tests that have shown up over 90% recovery of CO₂ for multiple cycles.¹⁷ This group is currently working with a team advance the development and demonstration of this sorbent-based technology.

Physical adsorbents can separate the CO₂ from the other flue gas constituents, but do not react with it. Instead, they use their cage-like structure to act as molecular sieves. These sorbents can be regenerated using a pressure swing or a temperature swing, although the costs associated with pressure swing may be prohibitively high. Physisorbents such as activated carbon and zeolites will be safe for the local environment, and should be relatively inexpensive to manufacture.

The DOE/NETL have spearheaded many solid-sorbent development projects geared towards CO₂ capture. This research encompasses a wide range of technical areas, including carbonate chemical sorbents, metal organic frameworks (MOFs), amine grafted zeolites and supported amine sorbents.^{4,13} However, these projects have are currently being conducted on either lab or bench-scale and will require further support and development before they are commercially viable.⁴

Membranes

Although still in the developmental stage, membranes have the potential to selectively separate CO₂ from flue gas. In the fuel and chemical industries, membranes are often used to separate CO₂ from light hydrocarbons. Ceramic and metallic membranes use their porous structure to sieve molecules by size.¹⁶ Although current membranes are either not selective enough towards CO₂ (i.e. the separated gas contains unacceptable concentrations of other flue gas constituents) or not permeable enough (not separating enough of the CO₂) researchers may be able to improve membrane performance until it can be an economically feasible carbon capture technology. Membranes that are able to

achieve acceptable selectivity, but also satisfactory permeability are currently being researched on a lab-scale.

Another type of membrane is being researched, called an absorption membrane; these membranes are impregnated with a liquid that selectively reacts with the CO₂. Separation using membranes is simple, with few moving parts. In order to achieve the concentration necessary for sequestration, multiple stages of membranes may be necessary.¹⁷ The membrane research projects in the DOE/NETL portfolio are described as being in the laboratory research stage.⁴

Summary

Separation of CO₂ from coal-fired flue gas presents a significant challenge to the utility and environmental industries. It is important to recognize that because of the many differences in plant design, operating parameters and location, effectively addressing CO₂ from power generating facilities will require a wide array of technologies as there will not be a “silver bullet” that can be implemented universally. Chemical solvents, such as chilled ammonia, are projected to be commercial by 2011, while many other technologies are still being researched at a laboratory scale. Many of the technology options discussed in this paper are in the early stages of development and will require a great deal of R&D to overcome current technical limitations, produce innovations and further advancements needed to demonstrate the viability of each approach. This will require a great deal of R&D funding and time to develop, scale-up, and proved long-term testing to demonstrate reliability. New plants can be designed for decreased carbon emissions, but the large fleet of existing plants must also be addressed in order to have a meaningful effect on emissions of carbon dioxide. This challenge will be met and can be accelerated through cooperation of the federal and state governments, utilities and the environmental industry.

REFERENCES

1. NETL: Carbon Sequestration.
http://www.netl.doe.gov/technologies/carbon_seq/index.html (Accessed October 2007).
2. MIT, The Future of Coal, 2007,
web.mit.edu/coal/The_Future_of_Coal_Summary_Report.pdf (Accessed September 2007).
3. EIA 2005 annual statistics, www.eia.doe.gov, (Accessed September 2007).
4. Figueroa, J.D.; Plasynski, S.; Fout, T.; Long, D. *U.S. DOE Carbon Capture and Sequestration Program: An Update on a Technology Development Program with a Commercialization Focus*; Air Quality VI; Arlington, VA, September 24-26, 2007.

5. IEA Project Details
http://www.co2captureandstorage.info/project_specific.php?project_id=22 (Accessed February 2008).
6. NETL, Carbon Dioxide Capture from Existing Coal-Fired Power Plants Final Report, DOE/NETL-401/110907, December, 2006 (Revised November, 2007).
7. Bozzuto, C.R.; Nsakala, N.; Liljedahl, G.; Palkes, M.; Marion, J.; Vogel, D.; Fugate, M.; Guha, M., "Engineering Feasibility and Economics of CO₂ Sequestration/Use on an Existing Coal-Fired Power Plant. Volume I: AEP's Conesville Power Plant Unit No. 5 Retrofit Study," Prepared for the Ohio Department of Development, Ohio Coal Development Office and US Department of Energy, National Energy Technology Laboratory (June 30, 2001).
8. Yagi, Y.; Mimura, T.; Yonekawa, T.; Yoshiyama, R. Development and Improvement of CO₂-Capture System,
http://www.mhi.co.jp/mcec/product/recov_co2/download/pdf/GHTH8_Development.pdf (Accessed February 2008).
9. Pennline, H.; Fauth, D.; Gray, M.; Hoffman, J.; Jones, K.; Luebke, D.; Morsi, B.; Resnik, K.; Siriwardane, R.; Yeh, J. *Recent Advances in Carbon Dioxide Capture and Separation Techniques for Power Generation Point Sources*; AIChE Annual Meeting, Cincinnati, OH, November, 2005, paper 143m.
10. Rhudy, D. *EPRI CO₂ Testing Program: An Industry/EPRI Initiative to Develop CO₂ Capture and Storage Testing Capabilities*; CO₂ Capture Network Meeting,
<http://www.co2captureandstorage.info/docs/capture/M-Rhudy.pdf> (Accessed February 2008).
11. Alstom and American Electric Power sign Agreement to Bring CO₂ Capture Technology to Commercial,
http://www.alstom.com/pr_corp/2007/corp/41445.EN.php?languageId=EN&dir=/pr_corp/2007/corp/&idRubriqueCourante=15445 (Accessed February 2008).
12. Powerspan Corp. http://www.powerspancorp.com/technology/eco2_test.shtml (Accessed February 2008).
13. Gray, M.L.; Champagne, K.; Hoffman, J.; Hedge, S.; Fauth, D.; Baltrus, J.; Pennline, H. Systematic Design of Immobilized Solid Amine Sorbents for the Capture of Carbon Dioxide, Sixth Annual Conference on Carbon Capture and Sequestration, Pittsburg, PA, May 2007.
14. Xu, X.C.; Song, C.S.; Andresen, J.M.; Miller, B.G.; Scaroni, A.W. Novel Polyethylenimine-Modified Mesoporous Molecular Sieve of MCM-41 Type as High-Capacity Adsorbent for CO₂ Capture, *Energy & Fuels*, **16**(6), **2002**, 1463-1469.

15. Green, D.A., Turk, B.S., Portzer, J. W., Nelson, T. and Gupta, R. P. Carbon Dioxide Capture From Flue Gas Using Dry Regenerable Sorbents, Quarterly Technical Progress Report, Research Triangle Institute, March 2005.
16. Aaron, D., Tsouris, C. Separation of CO₂ from Flue Gas: A Review, *Separation Science and Technology*, 40 (2005), 321-348.
17. Merkel, T.; Lin, H.; Baker, R.; Membrane Process to Sequester CO₂ from Power Plant Flue Gas, DOE/NETL Technical Kickoff Meeting, Pittsburg, PA, June 2007.

KEYWORDS

Carbon dioxide, CO₂, Carbon capture and sequestration, Coal-fired power plants