Advanced Materials and Process for CO_2 Removal from Flue Gas

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ABSTRACT

ATMI and SRI working in collaboration have developed an innovative new CO_2 capture technology that offers promise as a new low-cost route to capture and reuse of CO_2 in a variety of industrial and power generation applications. The technology is based on ATMI's BrightBlack® family of precision carbon adsorbents and SRI's innovative adsorption fractionation process, which is based on continuous adsorbent recycle. The system is designed to take advantage of the recoveries and purities achievable with countercurrent separations processes while minimizing power requirements associated with pressure drop and adsorbent regeneration. The ATMI-SRI CO_2 capture system has been demonstrated in small lab and field pilots with flue gas feed streams ranging in CO_2 content from 4% to 15%, successfully achieving greater than 90% recovery and 99% CO_2 purity. A larger field pilot is under construction at the National Carbon Capture Center and will be ready for testing in 2013.

Keywords: CO_2 capture, carbon adsorbent, flue gas, adsorption fractionation

1 INTRODUCTION

Anthropogenic emissions of CO_2, have been established as a primary contributing factor in global warming and are the source of considerable global concern. In 2011, emissions reached a record level of 33.9 gigatonnes, having grown at a rate of roughly 2.6% over the previous decade [1]. These emissions are dominated by economic activity related to energy. The use of energy was responsible for 83% of anthropogenic emissions in 2010, and CO_2 emissions accounted for 92% of that share [2]. Coal combustion was the single largest contributor at 43% followed by oil and natural gas at 36% and 20%, respectively.

Concerns regarding the impact of these emissions on global climate change have driven significant public and private investment on research and development initiatives to create cleaner power generation technologies and to develop cost-effective technologies to capture CO_2 from combustion and other industrial process sources or to capture it directly from the atmosphere. Additional investment is focused on sequestration and storage of CO_2 once it has been captured.

Processes generating post-combustion flue gas streams like existing coal- and natural-gas-fired power generation applications pose significant challenges for prospective CO_2 capture technologies. These processes provide high flow rate streams at ambient pressure that are dilute in CO_2. Although the challenges are significant, these plants represent much of the existing inventory CO_2 emissions, and any meaningful greenhouse gas solution must address capture from these plants.

Current approaches to post-combustion CO_2 capture are dominated by liquid-phase absorption systems and more specifically by amine absorption systems. Amine absorption is mature technology and has been operated at significant commercial scale for decades. Examples of current generation amine offerings include Fluor's Econamine FG Plus™ technology and Mitsubishi's KM CDR Process®, which operate commercially today with individual plants recovering hundreds of tons of CO_2 per day, typically for use in chemical applications like urethane manufacture. Current efforts focus on improving cost effectiveness of these technologies by improving the chemical stability of the amine solvents and reducing the regeneration energy requirements to liberate CO_2 [3,4].

Alstom's chilled ammonia process is based on CO_2 absorption in an ammoniated carbonate solution. It has been demonstrated at commercial pilot scale, and Alstom is moving forward with plans for larger scale demonstration of the technology. Compared to amine-based systems, the chilled ammonia process offers higher absorptive loadings and uses a lower cost, more durable solvent system. However, energy consumption is still high.

2 TECHNOLOGY

The desire to reduce CO_2 capture costs continues to drive innovation in new process and materials research and development. As an alternative to absorption, researchers have focused on new adsorbent materials like MOFs and functionalized sorbents, but significant materials and process challenges remain. The challenges for adsorption processes are in many ways similar to those facing absorption processes: increase CO_2 loadings and minimize energy requirements associated with flue gas compression and adsorbent regeneration.

ATMI working collaboratively with SRI international has developed an adsorbent-based process solution to CO_2 capture in an effort to simultaneously address both the materials and process challenges and optimize the total system. Several objectives were laid out in designing an adsorbent material and adsorption process in order to provide attractive capital and operating costs, including:

1. Low pressure drop across the process to minimize compression energy requirements
2. Low heat of adsorption / desorption to minimize regeneration energy requirements
3. High CO_2 loadings to minimize adsorbent inventory and regeneration energy requirements
4. Fast adsorption-desorption dynamics to keep contact times short and vessel sizes manageable

The process concept identified by SRI was adsorption fractionation using the solid-gas analog to a continuous trickle bed process. The design concept provides for a single integrated column with adsorption, stripping and regeneration steps occurring countercurrent to a recirculating stream of falling adsorbent (see Figure 1). Unlike conventional PSA and TSA processes, which require multiple fixed beds and operate cyclically, the trickle bed process operates continuously and requires a recycle loop for the solid adsorbent.

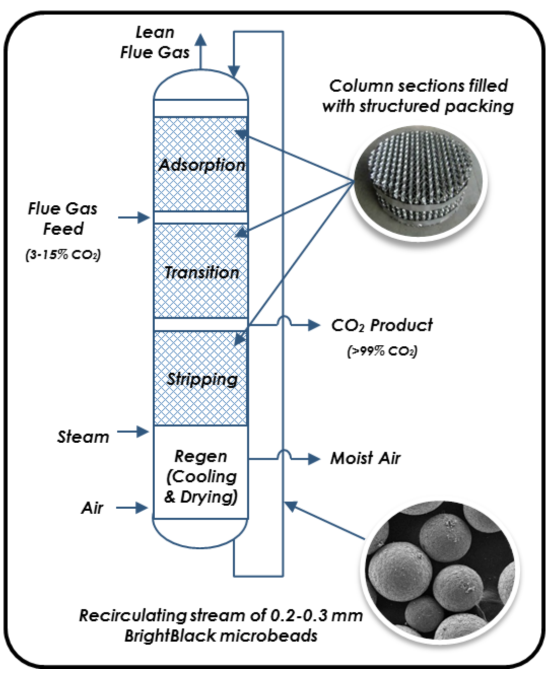

Figure 1: Adsorption fractionation process.

Adsorption fractionation with recirculated adsorbent is not a new process concept. It was originally developed more than seventy years ago in the petroleum refining industry and is currently operated commercially in solvent recovery systems [5]. Such systems have achieved only limited commercial success because of degradation and attrition of the adsorbent.

The SRI process differs in several respects from previous versions. It does not feature dense carbon beds and trays used previously. Instead, the SRI process utilizes a dilute "raining bed" of adsorbent and provides structured packing to distribute adsorbent particles radially in the column. It also uses direct contact with steam to strip CO_2 from the carbon, and the adsorbent is regenerated in a cooler / dehydrator to remove accumulated moisture from the steam stripping step and return the carbon to its feed condition for re-addition at the top of the column. Waste steam saturated at 100-110 °C is adequate for stripping, if available. Standard low pressure steam can be used if waste steam is not available.

A novel adsorbent is required to enable the SRI process. ATMI has developed a family of specialty materials, BrightBlack® precision adsorbents (see Figure 3), which are ideal for this application. These carbons are highly microporous with pore volume dominated by ultramicropores (widths < 0.7 nm). The combination of large pore volume and small pores makes BrightBlack carbons uniquely effective at physically adsorbing CO_2 at the low partial pressures typical of combustion flue gas. Typical adsorption isotherms for CO_2 on BrightBlack carbons are shown in Figure 2.

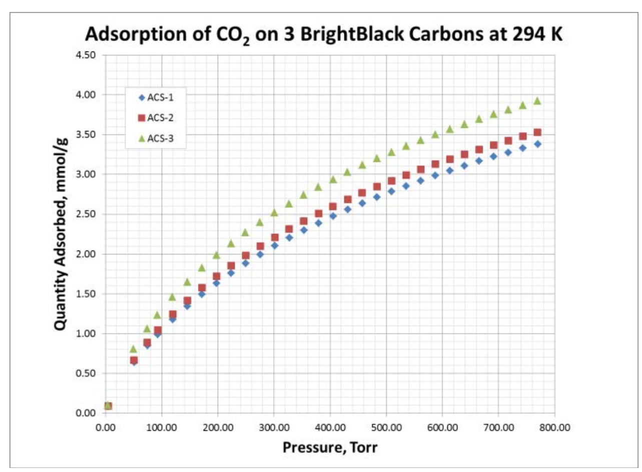

Figure 2: BrightBlack adsorption isotherms.

Typical adsorbent properties are provided in Table 1. In addition to capacity, the two key materials properties are attrition resistance and heat of adsorption. Attrition resistance is fundamentally enabling. If the individual carbon particles were not extremely hard and durable, a recycle process would not be feasible.

Heat of adsorption is important because it plays a central role in determining the overall steam requirement for the stripping step, and steam cost is the largest single component in total operating costs. Reduced heats of adsorption translate to reduced steam requirements and result in lower operating costs. Estimates of the steam requirement for the adsorption fractionation process are 50-70% below those for amine-based systems, providing attractive operating cost advantages relative to those for the established absorption technologies.

Property	Value
Particle Size, mm	0.15-0.3
Bulk Density, g/cm^3	0.65-0.7
N_2 BET Surface Area, m^2/g	1000-1250
Micropore Volume, cm^3/g	0.4-0.45
Heat of Adsorption, kJ/mol	25-28
CO_2 capacity at 114 Torr, mmol/g	1.1-1.5
Accelerated attrition testing (ASTM D5757), % loss/hr	< 0.01
Angle of Repose, °	25-30
Ash Content, %	< 0.1

Table 1: Typical properties of BrightBlack adsorbents [6].

Figure 3: SEM micrograph of BrightBlack microbeads.

3 SCALE UP

The adsorption fractionation process has been tested at small pilot scale in the lab on synthetic flue gas and in the field on a slip stream produced by the coal-fired stoker boiler at the University of Toledo. The test column used was 6 inches in diameter. Column height was limited to 20 feet due to constraints imposed by the high-bay ceiling height at the SRI facility. The field pilot column, shown in Figure 4, was extended to 45 feet in height to achieve higher recoveries and product purities.

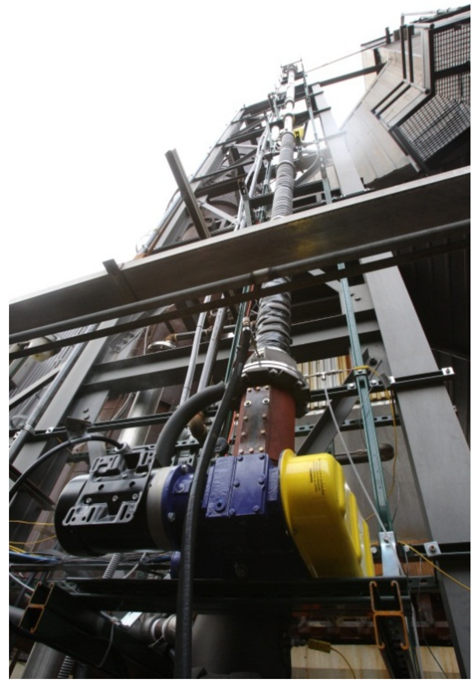

Figure 4: Field pilot column at the University of Toledo.

Test results are summarized in Table 2. Lab tests were conducted with synthetic flue gas comprising humidified air containing 14-15% CO_2 typical of coal-fired systems. The stoker boiler at Toledo was run fuel lean, providing a more dilute flue gas stream with only 4-4.5% CO_2, a value more typical of natural-gas-fired systems. The adsorption fractionation system performed well in both tests, meeting the success criteria established by DOE— greater than 90% recovery and greater than 90% CO_2 purity. Purities in the lab system were limited by column height, but 99% purities were demonstrated in the field test system on a more dilute feed. In both the lab and field pilot tests, very low flue gas pressure drops of less than 5 inches water column were achieved.

Test	Feed CO2 %	Column Size	Recovery / Purity %	Test length, cycles
Lab Pilot	14-15	6″×20′	90 / 95	~ 1000
Field Pilot	4-4.5	6″×45′	90 / 99	~ 7000

Table 2: Summary of pilot test performance.

Field testing was conducted over several weeks in January and February of 2012 at the University of Toledo. A total process run time of 130 hours was achieved operating one shift per day. Run time was constrained by a scheduled shut down of the boiler. The adsorbent was thermally cycled approximately 7000 times over the course of testing. No adsorbent losses due to attrition and no loss in CO_2 adsorptive capacity were observed during these tests. Adsorbent was free flowing throughout, and no solids handling issues were encountered. For the field test, adsorption recycle was accomplished by dilute pneumatic lift. Typical test data showing CO_2 recoveries and purities as a function of time are shown in Figure 5.

The next step in scale up is design and construction of a pilot unit capable of recovering 1-3 tpd CO_2, which will be tested at the National Carbon Capture Center (NCCC) in June 2013. The pilot will have rectangular cross section with dimension 18 inches × 18 inches. Testing at the NCCC will be focused on process optimization and the impact of continuous operation over an extended period. Tests will also track trace level impurities and investigate improved heat integration schemes to further reduce steam requirements. Testing at the NCCC will also yield improved capital and operating cost estimates for the process.

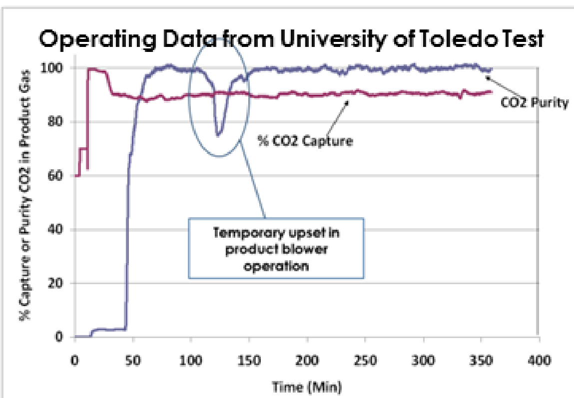

Figure 5 – Field test data from University of Toledo.

Plans are already in place for installation and testing of a commercial pilot unit capable of producing 20 tpd CO_2 in 2014-2015. Initial commercial targets for the technology are small to modest scale on site plants for capture and reuse of CO_2 in traditionally merchant applications. Larger scale power generation applications will be pursued after the technology has been demonstrated at significant commercial scale.

4 CONCLUSIONS

ATMI and SRI have developed a continuous adsorption fractionation process for capturing CO_2 from flue gas as a lower cost alternative to existing absorption technologies. The process is based on a high performance carbon adsorbent and has been demonstrated on small pilot scale in SRI's lab on synthetic flue gas and in a field test on a flue gas generated by a coal-fired boiler at the University of Toledo. The new process has successfully demonstrated capture of CO_2 from flue gas streams typical of coal-fired and natural-gas-fired systems, providing CO_2 recoveries of 90% and purities of 99%.

Longer term testing to demonstrate the technology at slightly larger scale using a system designed to recover 1-3 tpd CO_2 from a flue gas slip stream at the NCCC will begin in mid-2013. Deals for commercial pilots with industrial partners are currently in negotiations.

5 DISCLAIMER

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