Solid Sorbents for CO_2 Capture from Post-Combustion and Pre-Combustion Gas Streams

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Abstract

A novel liquid impregnated solid sorbent was developed for CO_2 removal in the temperature range of ambient to 60 °C for both fixed bed and fluidized bed reactor applications. The sorbent is regenerable at 60-80 °C. Multi-cycle tests conducted in an atmospheric bench scale reactor with simulated flue gas demonstrated that the sorbent retains its CO_2 sorption capacity with CO_2 removal efficiency of about 99%.

A second, novel solid sorbent containing mixture of alkali earth and alkali compounds was developed for CO_2 removal at 200-315 °C from high pressure gas streams (i.e., suitable for IGCC systems). The sorbent showed very high capacity for CO_2 removal from gas streams containing 28% CO_2 at 200 °C and 11.2 atm during lab-scale flow reactor tests as well as regenerability at 375 °C.

Keywords

CO_2 capture, adsorption, absorption

INTRODUCTION

Fossil fuels supply more than 98 percent of the world's energy needs. However, the combustion of fossil fuels is one of the major sources of carbon dioxide, a greenhouse gas. It is necessary to develop technologies that allow utilization of fossil fuels while reducing the greenhouse gas emissions. Commercial CO_2 capture technologies that exist today are expensive and energy intensive. Improved technologies for CO_2 capture are necessary to achieve low energy penalties. Pressure swing adsorption/sorption (PSA/PSS) and temperature swing adsorption/sorption (TSA/TSS) are some of the potential techniques that could be applicable for removal of CO_2 from both high- and low-pressure gas streams. Researchers at the National Energy Technology Lab (NETL) have been developing solid sorbents to capture CO_2 from both post-combustion and pre-combustion gas streams.

The NETL research group has developed a novel solid sorbent utilizing a liquid-impregnation technique. The sorbent consists of amines, glycols, and ethers incorporated in a clay matrix. The sorbent is capable of capturing CO_2 in the presence of steam at 30-60 °C and can be regenerated at temperatures below 80 °C. A recent systems analysis conducted at NETL indicates that this process is economically favorable. The liquid-impregnated solid sorbent showed high capacities during both low- and high-pressure tests. Results from the flow reactor tests with sorbent formulations prepared for various reactor (e.g., fixed bed, fluid bed) applications are discussed in this paper.

According to a 1999 IEA report, the PSA and TSA processes may be more suitable for CO_2 capture from coal gasification processes[1]. The system analysis conducted in the Netherlands shows claims that the PSA and TSA systems would be even more energy efficient for integrated gasification combined-cycle (IGCC) systems if the sorbents are operational at warm gas temperatures (250–350 °C).[1] Furthermore, this sorbent can be utilized to enhance the water-gas shift reaction by removing CO_2 from the gas stream. Researchers at NETL developed a novel magnesium-based sorbent that can capture CO_2 at 200-315 °C and is regenerable at 375 °C. The capture process with this novel warm gas CO_2 removal sorbent involves a chemical reaction. The sorbent demonstrated a high CO_2 sorption capacity of about 4 mol/kg at 200-400 °C, which is considerably higher than that of the Selexol process.

The objective of this work is to develop regenerable sorbents that have high selectivity, efficient regenerability, and high sorption capacity for CO_2 over a wide range of temperatures. These properties are critical for the success of the PSA/PSS and TSA/TSS processes.

Experimental

The liquid-impregnated solid sorbent pellets suitable for fixed-bed applications were prepared at Sud-Chemie utilizing the procedure provided by NETL researchers.[2] Competitive gas adsorption studies were conducted in a bench-scale, fixed-bed reactor at 1 atm (~1.01×10^5 Pa) and at 30-60 °C using a gas mixture representative of flue gas (15 percent CO_2, 82 percent nitrogen, and 3 percent oxygen, saturated with water vapor). The regeneration was conducted at 80 °C with steam and N_2 mixture. A liquid impregnated solid sorbent (<600 μm) suitable for other reactor bed applications such as fluidized reactor bed was also prepared. These sorbents were also tested in a lab-scale flow reactor (reactor volume = approx. 1.08 ml) with the simulated flue gas mix at 30-60 °C at flow rate of 15 cm^3/min and were regenerated at 80-100 °C. After the CO_2 sorption process, temperature-programmed desorption studies were conducted to understand the desorption of CO_2 and water after the adsorption. Thermogravimetric analysis was conducted to obtain the fractional CO_2 conversions and rate of CO_2 uptake information.

A 10-cycle test was conducted with the warm gas temperature pre-combustion solid sorbent at 200-250 °C in flow reactors at 11.2–30.0 atm and was regenerated at 375 °C at both 1 atm and 11.2 atm with steam and N_2. The space velocity used for the test was 250-500 h^{-1}.

RESULTS AND DISCUSSION

Atmospheric Pressure Tests with the Liquid-Impregnated Solid Sorbent Suitable for Fixed-Bed Reactors

At atmospheric pressure and 30 °C, the sorbent was able to remove CO_2 to parts per million (ppm) levels at a space velocity of 1,000 h^{-1} from a gas mixture containing 15-17 percent CO_2, 3 percent O_2, and 82 percent N_2, saturated with water. This performance equates to a removal efficiency greater than 99 percent. Multi-cycle tests conducted with the sorbent in a fixed-bed configuration

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[1] I. Smith, "CO_2 Reduction Prospects for Coal," IEA research report, ISBN 92-9029-336-5, 1999.

[2] R. V. Siriwardane, "Solid Sorbents for Removal of Carbon Dioxide from Gas Streams at Low Temperatures," U.S. Patent 6,908,497 B1, June 21, 2005.

showed stable, reproducible reactivity indicating that regeneration of the sorbent at 80 °C with steam did not negatively affect the sorbent's performance as shown in Figure 1. The sorbent's CO_2 sorption capacity was determined to be 1.5–2.0 mol/kg of sorbent (3-4 mol/liter of sorbent). Preliminary systems analysis conducted at NETL indicated that CO_2 removal utilizing the solid sorbent is more economical than the liquid amine process since the regeneration of the solid sorbent requires less energy.[3] Since steam does not affect the sorbent's performance, regeneration in the presence of steam is a viable option. The sorbent's low regeneration temperature as well as its resistance to steam are the primary advantages of this novel, ambient-temperature CO_2 removal sorbent.

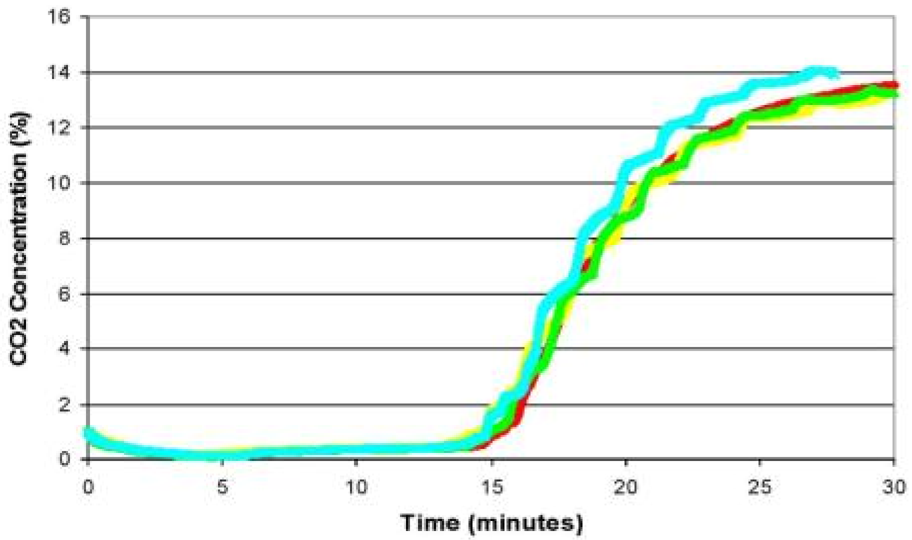

FIGURE 1: Bench-scale flow reactor multi-cycle test data with the fixed-bed version of NETL liquid-impregnated solid sorbent (Süd-Chemie prepared extrudates) at 1 atm; 30 °C; SV = 1,000 h^{-1}; Feed composition = 16% CO_2, 3% O_2, 82% N_2, saturated with water vapor).

Atmospheric Pressure Tests with the Liquid-Impregnated Solid Sorbent Suitable for Fluidized-Bed and Isothermal-Bed Reactors

The sorbent was prepared with a particle size less than 600 μm as required for fluidized-bed and isothermal-bed reactors. The reactor design studies conducted at NETL indicated that heat of regeneration of the sorbent is strongly depended on the specific heat capacity of the sorbent, the CO_2 capture delta capacity (difference between CO_2 sorption capacity at the absorption temperature and the CO_2 sorption capacity at regeneration temperature) and the heat of sorption of CO_2. For the liquid impregnated clay sorbent, the required minimum CO_2 delta capacity is estimated to be about 1.6-1.9 mol/kg for isothermal-bed reactors. However, this requirement may be lower for the fluidized-bed reactors. The sorbent (<600 μm) was tested with simulated flue gas; results of the testing yielded a 99 percent removal efficiency of CO_2 and a capture capacity of approximately 2.1 mol CO_2/kg of sorbent at 40 °C as shown in Figure 2. Since the particle density of the sorbent is ~2 g/cm^3, the corresponding CO_2 capture capacity (volume basis) is approximately 4.6 mol/liter of sorbent. The sorbent can be regenerated at 80-100 °C; since steam will likely be utilized during regeneration, the majority of the regenerations were conducted at 100 °C. The CO_2 capture delta capacity for sorption at 40 °C and regeneration at 100 °C was determined to be

[3] T. Tarka, "System Analysis of NETL Solid Sorbent," internal report, U.S. Department of Energy, NETL, 2005.

1.6 mol/kg (3.2 mol/liter) and 1.3 mol/kg (2.6 mol/liter) for sorption at 60 °C. The value obtained at 40 ^{0}C is very close to the acceptable CO_2 capture delta capacities identified by the reactor design studies. A 10-cycle test performed with capture at 60 °C and regeneration at 100 °C showed stable reactivity as shown in Figure 3. The sorbent preparations were also made in collaboration with Süd Chemie, Inc. to develop materials with more attrition resistance.

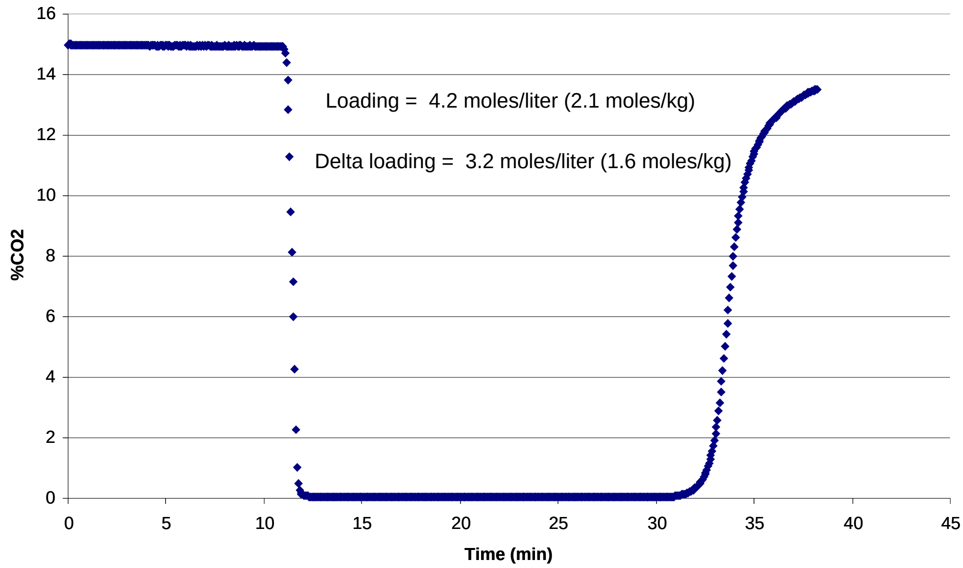

FIGURE 2: Lab-scale flow reactor test data with sorbent (particle diameter < 600 μm) suitable for fluidized-bed/isothermal-bed reactors at 1 atm; 40 °C; SV ~ 500 h^{-1}; Feed composition = 16% CO_2, 3% O_2, 82% N_2, saturated with water vapor.

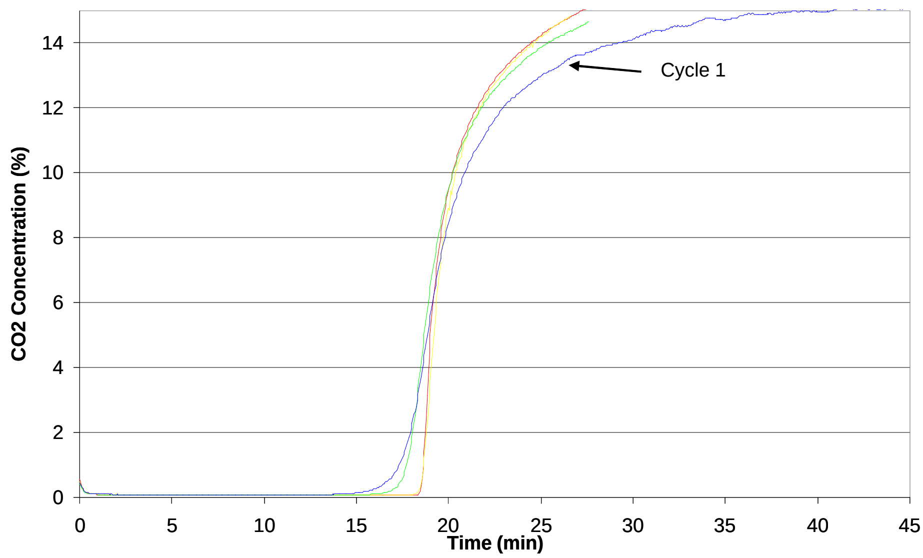

FIGURE 3: Lab-scale flow reactor multi-cycle test data with sorbent (particle diameter less than 600 μm) suitable for fluidized-bed/isothermal-bed reactors at 1 atm; 60 °C; SV ~ 500 h^{-1}; Feed composition = 16% CO_2, 3% O_2, 82% N_2, saturated with water vapor.

Warm Gas Temperature CO_2 Capture Sorbents Suitable for IGCC Systems

CO_2 capture sorbents that can operate at 200–315 °C would be very useful for IGCC applications. The water-gas shift reactor converts the coal gas to CO_2 and H_2 at 200–350 °C; a pure hot H_2 stream can be directly obtained if CO_2 is removed at 200–315 °C. Since the sorbent removes the CO_2 product gas from the gas stream, the water-gas shift reaction may also be enhanced. The warm temperature sorbents prepared at NETL were tested in a lab-scale flow reactor at 200–250 °C at 11.2 atm with 28 percent CO_2 in He saturated with steam. Regeneration was conducted at 375 °C and 11.2 atm. A 10-cycle flow reactor test conducted at 250 h^{-1} space velocity with ~3 g of magnesium-based sorbent indicated that the sorbent has a very high CO_2 capture capacity (4 mol/kg) as shown in Table 1. A decrease in capacity was not observed during the cyclic tests, suggesting that regeneration at 375 °C does not affect the performance of the sorbent. The sorbent (~9 g) was also tested in a bench-scale flow reactor. High CO_2 capture efficiencies and capture capacities were observed during the bench-scale tests as shown in Figure 4. Regenerable sorbents at 200–315 °C with high CO_2 capture capacities are not reported in the literature; these novel sorbents offer great promise for IGCC applications. The high capacities will contribute to low regeneration cost and small vessel size. The regeneration temperature of the sorbent is 375 °C, yielding a temperature swing from absorption to regeneration that is very low. NETL is conducting an engineering analysis to evaluate whether this process is economical.

TABLE 1: Test Conditions and Capture Capacities During the 10-Cycle Test of Warm Gas Temperature CO_2 Removal Sorbent (Inlet gas: 28% CO_2 in N_2, saturated with steam).

	CO_2 Sorption			**Regeneration**	
Cycle	T (°C)	P (atm)	Capacity (mol/kg)	T (°C)	P (atm)
1	200	7.8	1.47	375	1.0
2	250	7.8	2.11	375	1.0
3	250	11.2	2.13	375	1.0
4	200	11.2	2.84	375	1.0
5	200	7.8	2.40	375	1.0
6	200	11.2	3.46	375	11.2
7	200	11.2	4.09	375	11.2
8	200	11.2	4.14	375	11.2
9	200	11.2	4.27	375	11.2
10	200	11.2	3.22	--	--

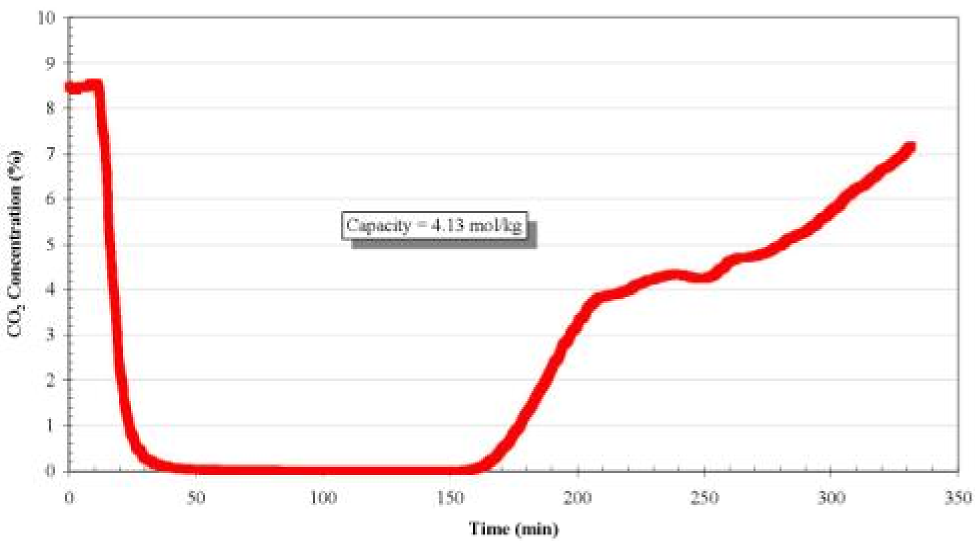

FIGURE 4: Bench-scale flow reactor test data with the NETL warm gas temperature sorbent at 14.6 atm; 200 °C; SV = 250 h^{-1}; Feed composition = 10% CO_2, 10% H_2O, N_2 balance.

SUMMARY

The novel liquid-impregnated solid sorbent showed stable CO_2 sorption performance at ambient temperature and atmospheric pressure during a multi-cycle test, and regenerability at 80-100 °C. The sorbent was prepared for both fixed-bed and fluidized-bed applications. The sorbent's performance was not affected by the presence of steam. The CO_2 removal efficiency of the sorbent is 99 percent, and an acceptable CO_2 capture capacity of 4.2 mol/liter (2.1 mol/kg) was obtained at 40 ^{0}C.

The novel warm gas temperature sorbent suitable for CO_2 capture from IGCC gas streams was able to capture CO_2 (4 mol/kg) at 200–250 °C and at 11.2-14.6 atm. It was possible to regenerate the sorbent at 375 °C and 11.2 atm. The performance was stable during a 10-cycle test.

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