# $CO_2$ Capture Utilizing Solid Sorbents

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## Introduction

Fossil fuels supply more than 98 percent of the world's energy needs, but combustion of fossil fuels is one of the major sources of the greenhouse gas carbon dioxide ($CO_2$). We need technologies that will allow us to utilize fossil fuels while reducing greenhouse gas emissions. Commercial $CO_2$ capture technology that exists today is very 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 potential techniques that could be applicable for removing $CO_2$ from both high- and low-pressure gas streams.

Researchers have reported that the PSA process can concentrate $CO_2$ to high purity from flue gas, but at a low recovery rate, and that higher energy penalties are associated with the utilization of molecular sieves than with the amine process.[1] During the last decade, researchers have described several new PSA concepts that improve process performance. Very promising results have also been reported with $CO_2$ removal from flue gas utilizing a combination of PSA and TSA (PTSA).[2] We are conducting a process optimization study in collaboration with Carnegie Mellon University (CMU) as part of this project to address these issues.

While it is important to consider the improved process design of PSA/TSA systems to enhance the $CO_2$ recovery rate, it is equally important to utilize sorbents with high $CO_2$ adsorption capacity, high selectivity for $CO_2$, high diffusivity, and high regenerability. Our research group tested various zeolites for this application, and promising results were observed with zeolite 13 X and UOP WEG-592. Water vapor present in the gas streams seemed to affect the performance of the zeolites, but the $CO_2$ adsorption capacity can be regained by increasing the regeneration temperature.

Our research group has also developed a novel sorbent utilizing a liquid impregnation technique. The sorbent was capable of capturing $CO_2$ in the presence of water at ambient temperature and it can be regenerated at temperatures below 80 °C. A recent systems analysis conducted at the National Energy Technology Laboratory (NETL) indicated that this technique is very economical compared to similar processes.

According to an International Energy Agency (IEA) report [3], PSA/TSA processes may be ideally suited to $CO_2$ capture from gasification processes. A system analysis conducted in the Netherlands [3] showed that PSA/TSA processes would be even more energy efficient for integrated gasification combined-cycle (IGCC) systems if the sorbents were operational at warm gas temperatures (250 to 350 °C). We evaluated the performance of various zeolites at 120 °C, and two zeolites showed good $CO_2$ adsorption capacity at 120 °C. However, the capacities at 120 °C were considerably lower than that at ambient temperature. Zeolites cannot be used above 200 °C for $CO_2$ capture since their capture capacities are extremely low at these temperatures.

Our research group at NETL developed novel sodium-based sorbents that can capture $CO_2$ at 200 to 400 °C to address this problem. The sorbents are regenerable at 700 °C. The capture process with these sorbents involves a chemical reaction. The sorbents have a very high $CO_2$ sorption capacity at 200 to 400 °C, which is considerably higher than that of the commercial Selexol process. However, according to

systems studies conducted at NETL, the regeneration process at 700 °C is energy intensive. Our research group is currently involved in modifying the sorbents to obtain regeneration at lower temperatures.

The objective of this work is to develop regenerable sorbents that have high selectivity, efficient regenerability, and high $CO_2$ adsorption capacity over wide temperature ranges. These properties are critical for the success of the PSA-PSS/TSA-TSS process.

## Experimental

Adsorption isotherms of pure $CO_2$, and nitrogen ($N_2$) were measured up to an equilibrium pressure of about 300 psi (~2 x $10^6$ Pa) utilizing a volumetric adsorption apparatus. Approximately 10 ml of the sorbent materials was placed in the sample chamber, which was evacuated to ~5 x $10^{-5}$ Torr (~6.75 x $10^{-3}$ Pa). The amount of $CO_2$ adsorbed was calculated utilizing pressure measurements before and after exposure of the sample chamber to $CO_2$.

Competitive gas adsorption studies were conducted in a laboratory-scale, fixed-bed reactor at both 14.7 psi (~1.01 x $10^5$ Pa) and 280 psi (~1.93 x $10^6$ Pa) using gas mixtures with two compositions: (a) 15-percent $CO_2$, 82-percent $N_2$, 3-percent oxygen ($O_2$) saturated with water vapor; and (b) 12-percent $CO_2$, 35.9-percent carbon monoxide (CO), 27.1-percent $H_2$, and 25-percent helium (He) saturated with water vapor. The samples were heated at 120 °C for 1 hour and cooled to ambient temperature before introducing the gas mixture.

## Results and Discussion

### *Zeolite Adsorbents*

Competitive gas adsorption tests were conducted with zeolites 13X, 4A, 5A, UOP-WE-G 592 and UOP APG-II with gas mixtures containing $CO_2$. Preferential gas adsorption was observed with all the zeolites at both ambient temperature and at 120 °C. Competitive gas adsorption data with the 13 X zeolite is shown in Figure 1.

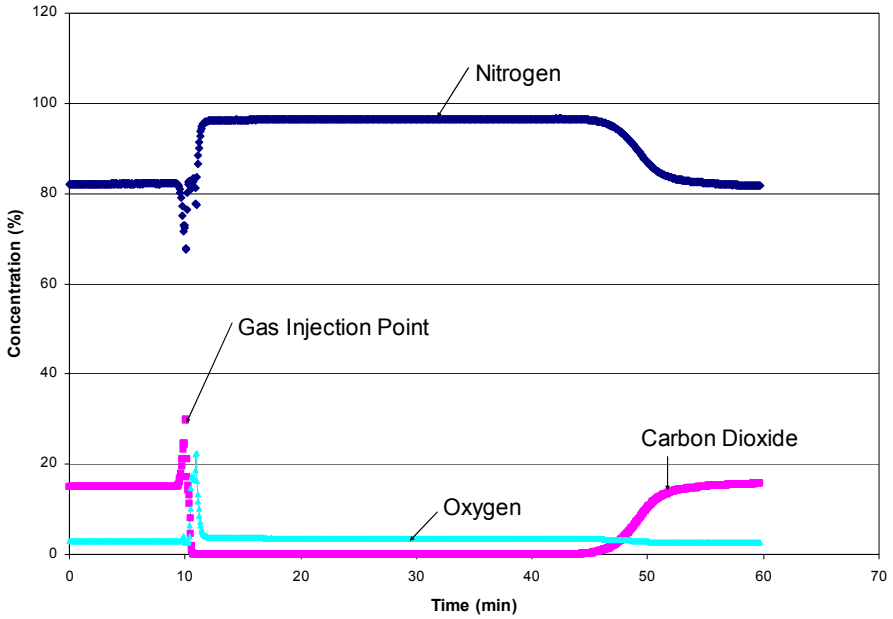


**Figure 1. Adsorption of $CO_2$, $N_2$, and $O_2$ on Molecular Sieve 13X Zeolite**
(15% $CO_2$, 3% $O_2$, 82% $N_2$, and saturated with water vapor at 25-50 °C;
15 cc/min; in an atmospheric reactor)

It was possible to remove $CO_2$ from 12 to 15 percent down to the ppm range with the zeolites. The $CO_2$ adsorption capacity at ambient temperature was in the range of 2.5 to 3.0 moles/kg. However, $CO_2$ adsorption capacities decreased to about 0.65 mole/kg at 120 °C. Zeolites 13 X and UOP- WE-G 592 showed the highest $CO_2$ adsorption capacity, especially at 120 °C. Temperature-programmed desorption tests indicated that there are two types of adsorption sites on zeolites: (1) weakly adsorbed $CO_2$ that can be removed at ambient temperature, and (2) strongly adsorbed $CO_2$ that can be removed at 120 °C.

The presence of water vapor in the gas stream did not affect the first adsorption cycle, but $CO_2$ adsorption capacity decreased during the second cycle when regeneration was conducted at 120 °C. When regeneration was conducted at 350 °C, full $CO_2$ adsorption capacity was regained. $CO_2$ adsorption capacities observed during volumetric gas adsorption tests in which regeneration was performed utilizing a vacuum were higher than those observed during the competitive gas adsorption tests. Thus, a combination of a vacuum and moderate temperature may be suitable in recovering adsorbed $CO_2$ from the zeolites. A process optimization study is currently being conducted at Carnegie Melon University to evaluate the feasibility of the $CO_2$ capture process with zeolites.

### *Novel Liquid-Impregnated Solid Sorbent for Ambient-Temperature $CO_2$ Capture*

Figure 2 shows results of a ten-cycle competitive gas sorption test on the novel liquid-impregnated solid sorbent at ambient temperature.

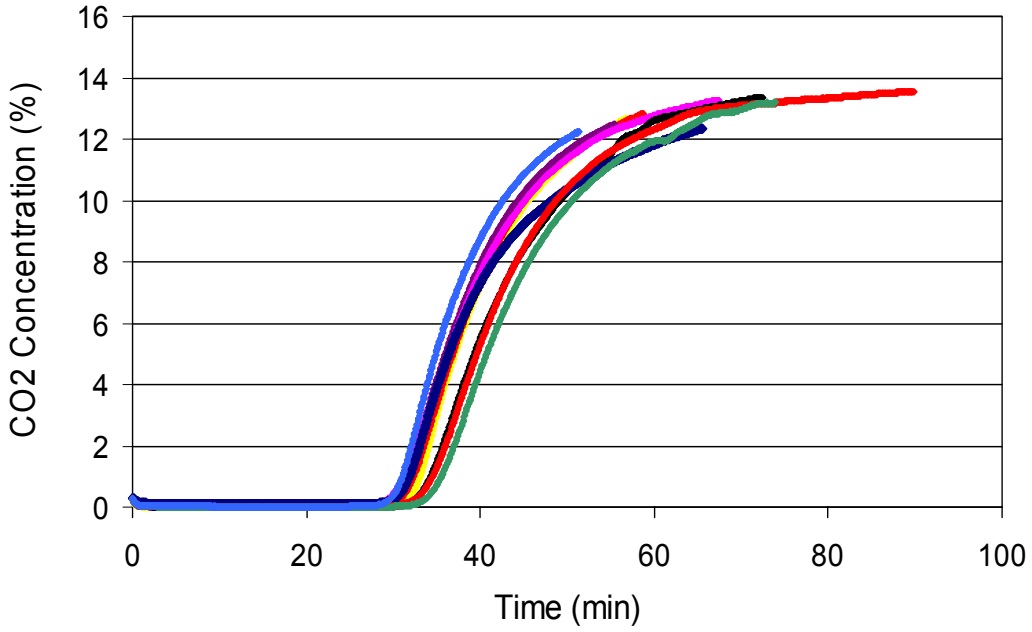


**Figure 2. Adsorption of $CO_2$ on the Novel Liquid-Impregnated Solid Sorbent in an Atmospheric Reactor**
(15% $CO_2$, 3% $O_2$, 82% $N_2$, and saturated with water vapor)

Sorbent regeneration tests were conducted at ambient temperature with $N_2$, and complete regeneration was obtained. Regeneration tests were also conducted at 50, 60, and 80 °C. Better $CO_2$ sorption capacities were observed when the sorbent was regenerated at these higher temperatures. The presence of water vapor did not affect sorbent performance. To obtain a concentrated gas stream of $CO_2$, regenerations will have to occur either with a gas stream containing steam or in the presence of a mild vacuum. These regenerations schemes will be investigated in the future.

Since steam does not affect sorbent performance, regeneration in the presence of steam would be a reasonable choice. The ability to regenerate the sorbent at lower temperatures and the resistance to steam are the advantages of this novel ambient-temperature $CO_2$-removal sorbent. An NETL engineering

analysis indicated that our novel process using solid sorbents that can adsorb $CO_2$ at ambient temperature and regenerate at 60 °C has better energy efficiency than the conventional amine technique.

### *Warm Gas Temperature Sorbents Suitable for IGCC Systems*

$CO_2$-capture sorbents that operate at 315 °C would be ideal for use in IGCC applications. The water-gas shift reactor converts the gas to $CO_2$ and $H_2$ at 200 to 350 °C. A pure hot $H_2$ stream can be obtained if $CO_2$ is removed at 315 °C. Several sodium-based sorbents were prepared at NETL and were tested in an atmospheric micro reactor at 315 °C with simulated Texaco gasification gas and with simulated shift reactor gas. Regeneration was conducted at 700 °C. A ten-cycle test conducted with the sodium-based sorbent indicated that the sorbent had a very high $CO_2$ capture capacity (4 to 6 moles/kg), as shown in Figure 3. Furthermore, the capacity increased during the ten-cycle test.

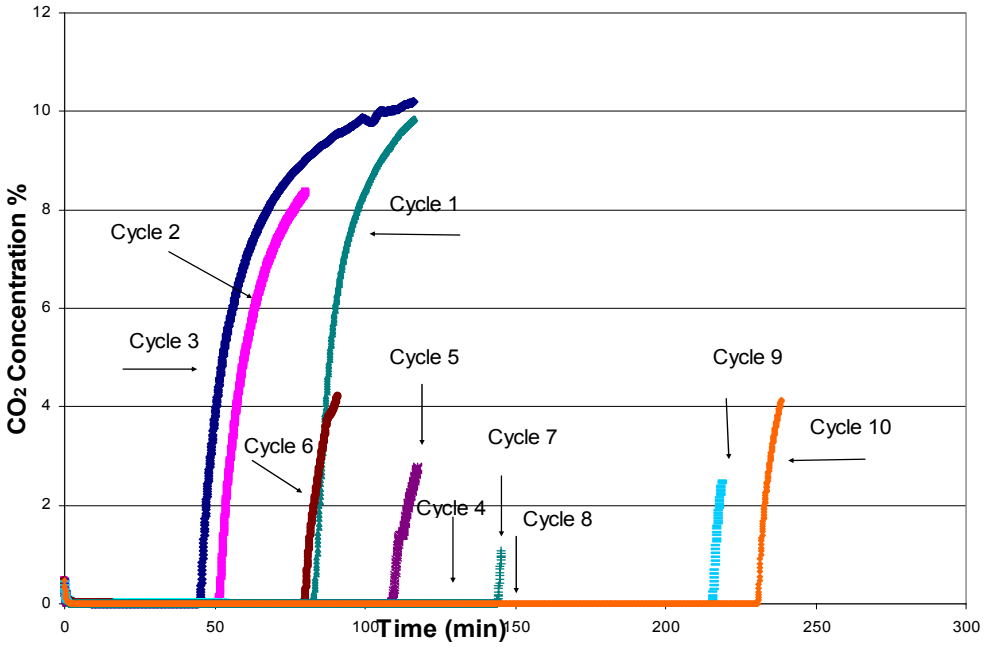


**Figure 3. Ten-Sorption Cycle Test of $CO_2$ From a Simulated IGCC Gas Stream on a Sodium-Based Sorbent at 315 °C and 1 atm**
(12% $CO_2$, 35.9% CO, 27.1% $H_2$, 25% He, saturated with $H_2O$, 5 cc/min)

The $CO_2$ capture capacity at the tenth cycle is 38 times better than that of the commercial Selexol solvent. Regenerable sorbents at 315 °C with high $CO_2$ capture capacities have not been reported in the literature. These novel sorbents offer great promise for IGCC applications. The high capacities will contribute to a low regeneration cost and a small vessel size. However, an engineering analysis conducted at NETL indicated that regeneration at 700 °C is energy intensive. Therefore, research is being conducted to modify the sorbent to obtain regeneration at lower temperatures.

## Summary

Zeolites were capable of separating $CO_2$ from gas streams at both ambient temperature and at 120 °C. However, the $CO_2$ adsorption capacity of the zeolites was substantially higher at ambient temperature than that at 120 °C. Water vapor did not affect the adsorption of $CO_2$ in the first cycle, but decreased the capacity in the second cycle. Novel liquid-impregenated solid sorbents showed stable $CO_2$ sorption performance at ambient temperature during a ten-cycle test and showed regenerability at below 80 °C. The novel sodium-based sorbent was able to capture $CO_2$ (4 to 6 moles/kg) at 315 °C, and it was possible to regenerate the sorbent at 700 °C.

## References


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2. Ishibashi, M., K. Otake, and S. Kanamori, Study of $CO_2$ Removal Technology from Flue Gas of Thermal Power Plant by Physical Adsorption Method, p. 95-100 in *Proceedings of 4th International Conference on Greenhouse Gas Control Technologies*, Switzerland, 1998, ed. B. Eliasson, P.Riemer, A. Wokaun.

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