

ADSORPTION AND DESORPTION OF CO₂ ON SOLID SORBENTS

Ranjani Siriwardane (rsiiw@netl.doe.gov; 304-285-4513)
Ming Shen (mshen@netl.doe.gov; 304-285-4112)
Edward Fisher (efishe@netl.doe.gov; 304-285-4011)
James Poston (jposto@netl.doe.gov; 304-285-4635)
Abolghasem Shamsi (ashams@netl.doe.gov; 304-285-4360)

U.S. Department of Energy, National Energy Technology Laboratory, 3610 Collins Ferry Road,
P.O.Box 880, Morgantown, WV 26507-0880

INTRODUCTION

Fossil fuels supply more than 98% of the world's energy needs. However, the combustion of fossil fuels is one of the major sources of the green house gas CO₂. It is necessary to develop technologies that will allow us to utilize the fossil fuels while reducing the emissions of green house gases. Commercial CO₂ capture technology that exists today is very expensive and energy intensive. Improved technologies for CO₂ capture are necessary to achieve low energy penalties. Pressure swing adsorption (PSA) is one of the potential techniques that could be applicable for removal of CO₂ from high pressure gas streams such as those encountered in Integrated Gasification Combined Cycle (IGCC) systems.

PSA processes¹⁻⁴ are based on preferential adsorption of the desired gas (eg. CO₂) on porous materials at a high pressure. When the pressure is decreased, the gas is desorbed from the porous sorbent and the sorbent can be reused for subsequent adsorption. PSA technology has gained interest due to low energy requirements and low capital investment costs. Development of regenerable sorbents that have high selectivity for CO₂ and high adsorption capacity for CO₂ is critical for the success of the PSA process.

OBJECTIVE

The objective of this work is to understand the adsorption properties of CO₂ on molecular sieves and activated carbon⁵ that can be utilized in PSA processes. In this work adsorption and desorption of CO₂ was studied on three sorbents namely molecular sieve 13X, natural zeolite ZS500A and activated carbon. Volumetric adsorption and desorption studies of CO₂, N₂, O₂ or H₂ with the three sorbents were conducted at 25 °C up to a pressure of 300 psi (~2x 10⁶ Pa). Competitive gas adsorption studies were also conducted with CO₂ containing gas mixtures in the presence of water vapor.

APPROACH

Zeochem-Z10-02/13X molecular sieve and activated carbon sorbents were obtained from Sud Chemie. Natural zeolite GSA ZS 500A was obtained from GSA Resources. Adsorption and

desorption isotherms at 25 °C of pure CO₂, N₂, O₂ and H₂ on molecular sieve 13X and activated carbon were measured up to an equilibrium pressure of about 300 psi (~2x 10⁶ Pa) utilizing a volumetric adsorption apparatus. Approximately 10 ml of the sorbent materials were placed in the sample chamber, which was evacuated to ~ 5x10⁻⁵ Torr. The amount of CO₂ adsorbed was calculated utilizing the pressure measurements before and after the exposure of the sample chamber to CO₂. Desorption studies were conducted by gradually decreasing the pressure from 300 psi after the adsorption cycle. After each cycle the sorbent was evacuated overnight. Competitive gas adsorption studies were conducted in lab scale fixed bed reactors at 14.7 psi and 250 psi using a gas mixture with a composition of 15%CO₂, 82%N₂, 3% O₂.in the presence of water vapor at ambient temperature. The samples were heated at 100 °C for one hour and cooled down to ambient temperature before the introduction of the gas mixture.

RESULTS AND DISCUSSION

Volumetric adsorption isotherms of CO₂, N₂, O₂ and H₂ on molecular sieve 13X at 25 °C are shown in Figure 1. The CO₂ adsorption increased rapidly when the pressure was increased up to 50 psi but the CO₂ adsorption after 50 psi appeared to be gradual. At all pressures, adsorption isotherms of nitrogen were lower than those of CO₂, and adsorption isotherms of hydrogen were significantly lower than those of CO₂. Preferential adsorption of CO₂ indicates that this material can be used for separation of CO₂ from some gas mixtures. The adsorption and desorption isotherms of CO₂ on molecular sieve 13X are also shown in Figure 1. The adsorption and desorption isotherms were very similar. This indicates that the adsorption of CO₂ on molecular sieve 13X is reversible. So the adsorbed CO₂ can be recovered by lowering the pressure.

The results of the competitive gas adsorption studies conducted utilizing a gas mixture of 15%CO₂, 82%N₂, 3% O₂ and water vapor on molecular sieve 13X in the atmospheric micro reactor are shown in Figure 2. The gas mixture was introduced to 1g of molecular sieve 13 X at a flow rate of 15 cc/min and at 25 °C. After the introduction of the gas mix to the molecular sieve 13X, the CO₂ concentration decreased to almost zero until the breakthrough. This indicates that an excellent separation of CO₂ can be obtained from a gas mixture of N₂, O₂, H₂O and CO₂ with molecular sieve 13X. The total amount of CO₂ adsorbed at the breakthrough or saturation as calculated from the data was about 3 moles/kg of the sorbent. This value is very similar to the amount of CO₂ adsorbed at 1 atm from volumetric equilibrium adsorption studies, as shown in Figure 1. This indicates that the full capacity of the molecular sieve 13X was utilized for CO₂ adsorption during competitive gas adsorption from a CO₂, N₂, O₂ and water vapor mixture. This indicated that the water vapor does not affect the adsorption of CO₂ on molecular sieve 13X.

The results of the competitive gas adsorption studies conducted utilizing 15%CO₂, 82%N₂, 3% O₂ and water vapor on molecular sieve 13X in the high pressure reactor are shown in Figure 3. The gas mixture was introduced to 1.3 g of molecular sieve 13 X at a flow rate of 19 cc/min, at 25 °C and at 250 psi. After the introduction of the gas mix to the molecular sieve 13X, the CO₂ concentration decreased to almost zero until the breakthrough. This indicates that an excellent separation of CO₂ from a gas mixture of N₂ and CO₂ can be obtained with molecular sieve 13X even at high pressure. The amount of CO₂ adsorbed per kg of the sorbent calculated from the data at breakthrough is about 6-7 moles/kg as shown in Figure 4. This is very similar to the amount of

CO₂ adsorbed at 250 psi from volumetric equilibrium adsorption studies, as shown in Figure 1. This indicates that the full capacity of the molecular sieve 13X was utilized for CO₂ adsorption during competitive gas adsorption at high pressure. There is some decrease in the CO₂ adsorption in the second cycle but the amount of adsorption was still very high. This sorbent may be suitable for separation of gases from high pressure gas mixtures.

The adsorption isotherms for activated carbon are shown in Figure 5. The CO₂ uptake for activated carbon was lower than that of the molecular sieve 13X at lower pressures, but at higher pressures (>100 psi) the CO₂ uptake for activated carbon was higher than that of the molecular sieves. The adsorption isotherm for activated carbon is also shown in Figure 5. The desorption isotherm was higher than that of the adsorption isotherm which indicated that the CO₂ is not fully desorbed during the desorption experiments. The hysteresis observed with activated carbon indicates that it is not possible to recover the adsorbed CO₂ by lowering the pressure. However, the activated carbon can be fully regenerated by evacuating the sample to 5×10^{-5} Torr.

When the competitive gas adsorption studies were conducted utilizing 15%CO₂, 82%N₂,3% O₂ and water vapor on activated carbon (0.5g) in the atmospheric reactor, it was necessary to use a lower flow rate (5 cc/min) for the adsorption of CO₂. After the introduction of the gas mix to the activated carbon, the CO₂ concentration decreased to almost zero and remained until the breakthrough. However, CO₂ uptake (1.1-1.2 moles/kg) at breakthrough was considerably lower in the presence of water vapor and oxygen in the gas mixture. The results of the gas adsorption studies with activated carbon (0.73g at flow rate 19 cc/min) conducted at 250 psi utilizing the same gas mixture are shown in Figure 6. The CO₂ concentration only decreased to 2% after the introduction of the gases and uptake (4 moles/kg) was lower than that for the molecular sieve 13X as shown in Figures 6 and 7. The activated carbon showed lower CO₂ uptake during competitive gas adsorption studies than that was observed during the equilibrium adsorption studies.

Adsorption isotherms of CO₂, H₂, O₂, and H₂ on natural zeolite GSA ZS 500 A are shown in Figure 8. It is clear that there is preferential adsorption of CO₂ on this natural zeolite indicating that it is suitable for separations of CO₂ from gas mixtures. The desorption isotherm also shown in Figure 8, was similar to that of the adsorption isotherm. This indicates that there is no substantial hysteresis during desorption and CO₂ can be fully recovered during desorption. The results of the competitive gas adsorption studies conducted utilizing 15%CO₂, 82%N₂, 3% O₂ and water vapor on natural zeolite GSA ZS 500A in the atmospheric reactor are shown in Figure 9. The gas mixture was introduced to 0.846g of the natural zeolite in the atmospheric reactor at a flow rate of 5 cc/min, at 25 °C. The separation of CO₂ from the gas mixture was very good as shown in Figure 9. There is a substantial amount of CO₂ adsorbed (1.2 moles/kg) at breakthrough even though the amount is slightly lower than that was adsorbed during equilibrium adsorption.

CONCLUSIONS

All three sorbents, molecular sieves 13X, activated carbon, and natural zeolite showed preferential adsorption of CO₂ over nitrogen, oxygen and water vapor at all pressures up to 250 psi. The molecular sieve 13X showed better CO₂ uptake than the natural zeolite. Water vapor and oxygen did not affect the adsorption of CO₂ on molecular sieve 13X during competitive gas adsorption studies at both low and high pressures but activated carbon showed lower CO₂ uptake in the presence of water vapor and oxygen. A very high CO₂ uptake was observed with molecular sieve 13X during high pressure competitive gas adsorption studies.

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Figure 1
Sorption-Desorption Isotherms of Molecular Sieve 13X

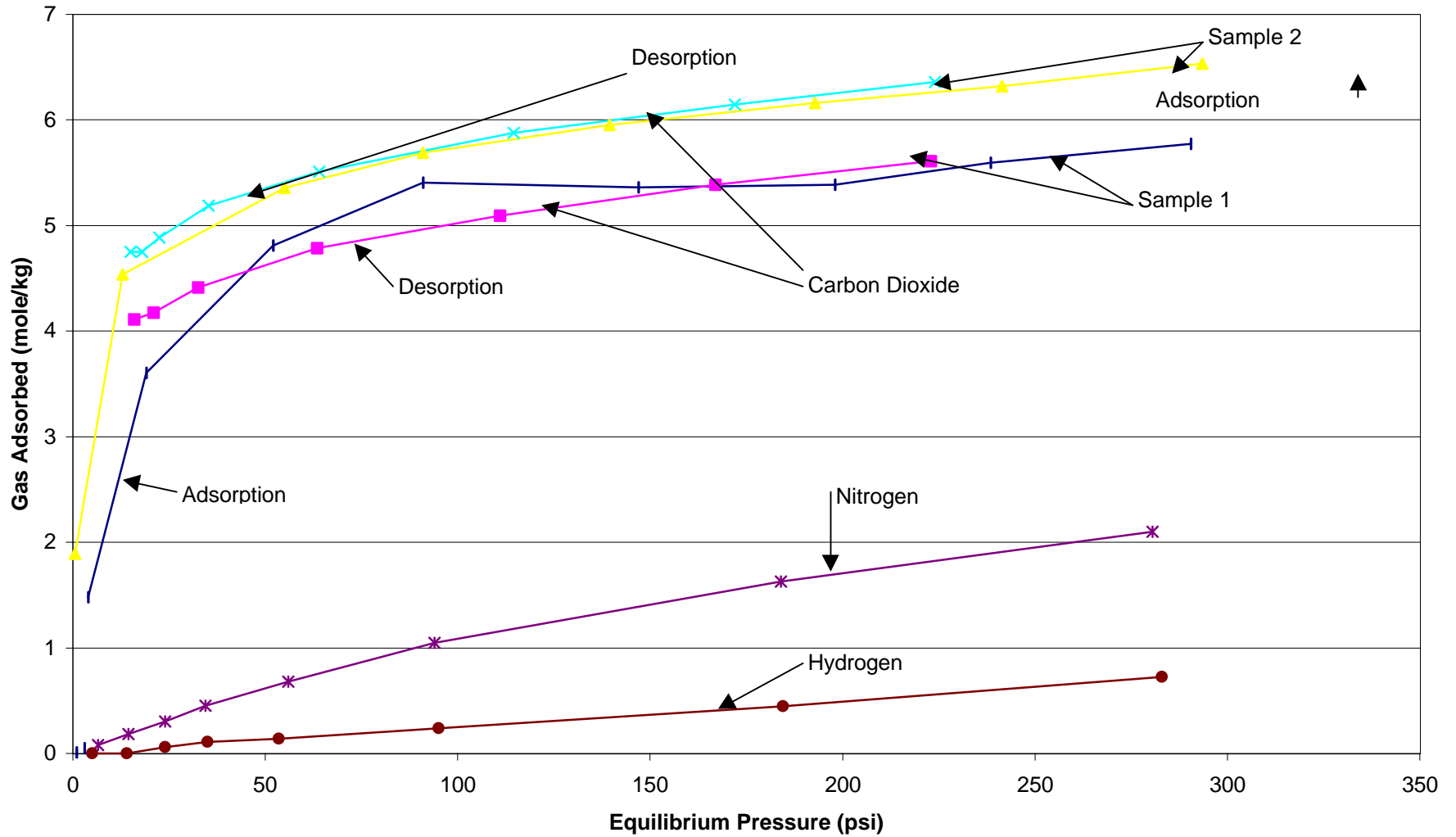


Figure 2
Adsorption of CO₂, N₂, and O₂ on Molecular Sieve 13X in Atmospheric Reactor
(15% CO₂, 3% O₂, 82% N₂, and saturated with water vapor at 25 C, 15 cc/min)

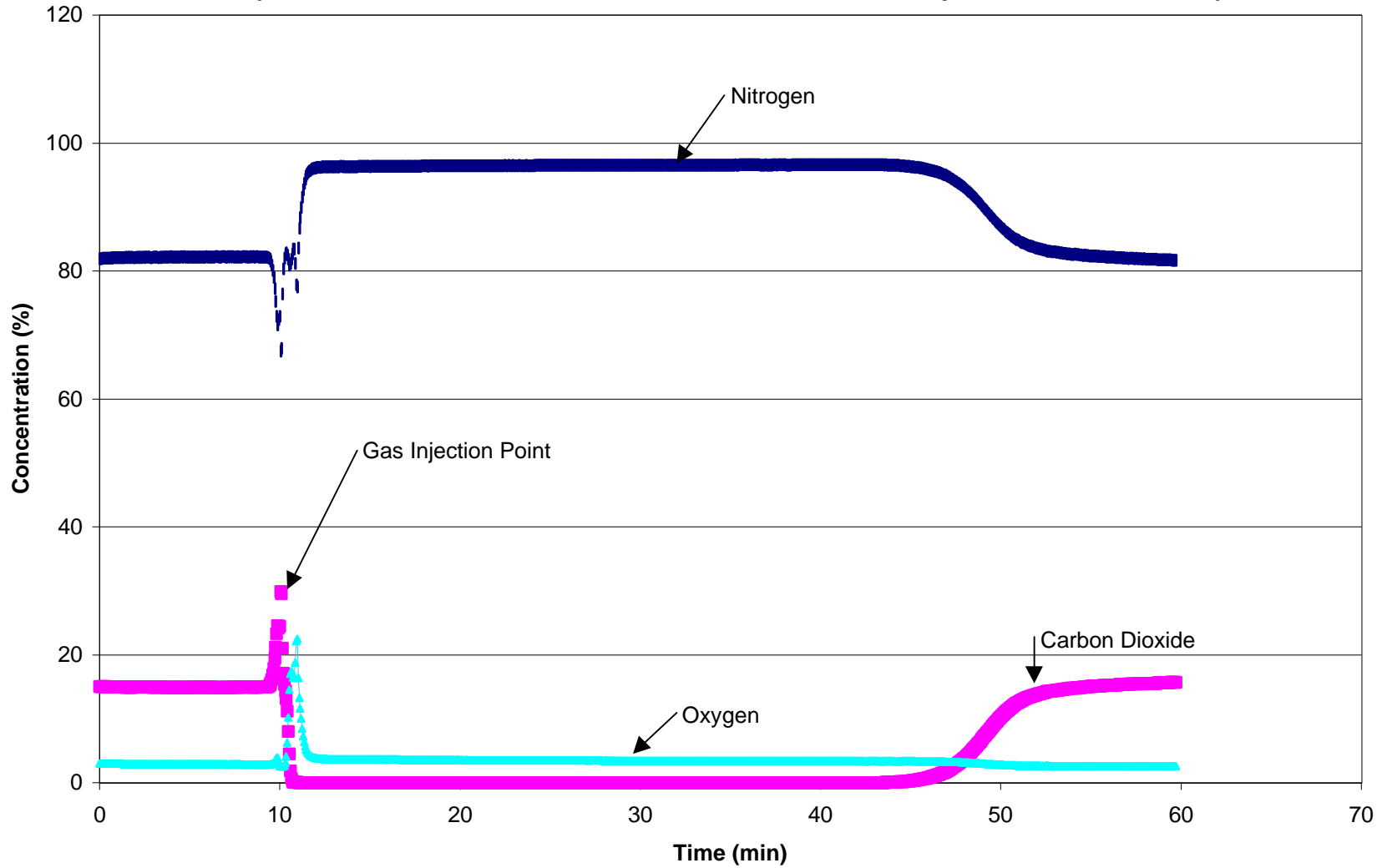


Figure 3
Adsorption of CO₂ on 13X at 22 °C, 250 psi
(15%CO₂, 82% N₂ and 3% O₂, and H₂O, 19.0 cc/min)

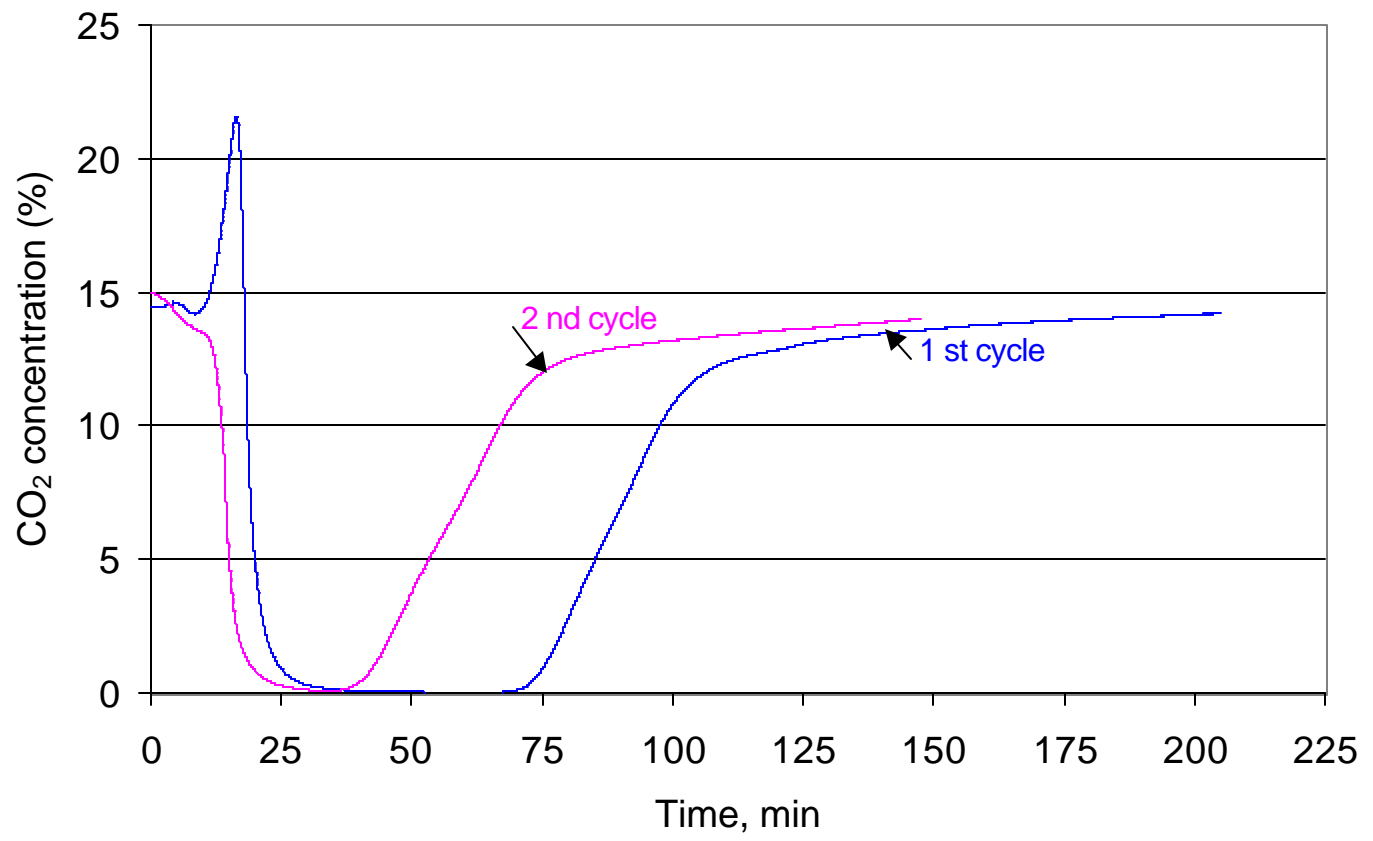


Figure 4

Adsorption of CO₂ on 13X at 22 °C, 250 psi
(15%CO₂, 82% N₂ and 3% O₂, and H₂O, 19.0 cc/min)

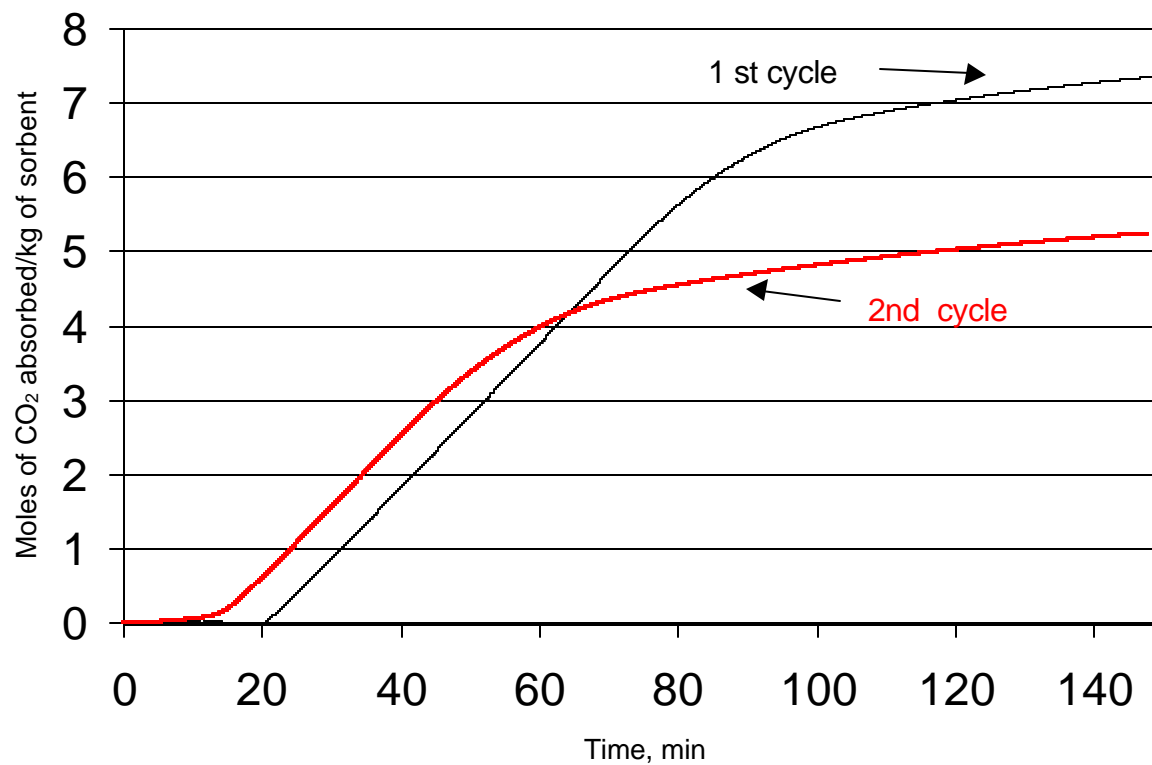


Figure 5
Adsorption - Desorption Isotherms of Activated Carbon

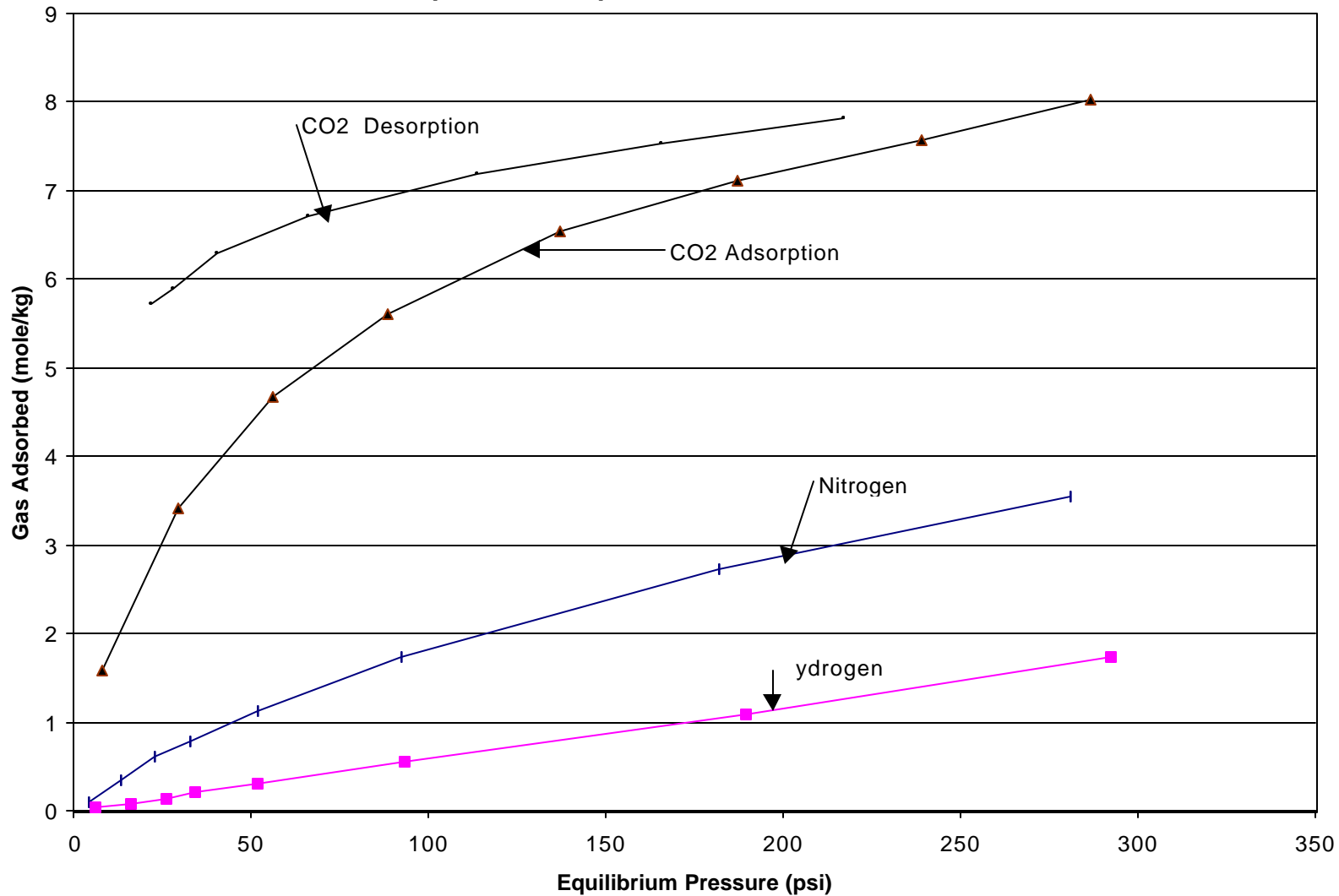


Figure 6.

Adsorption of CO₂ on activated carbon at 22 °C, 250 psi,
(15%CO₂, 82% N₂ and 3% O₂, and H₂O, 19 cc/min)

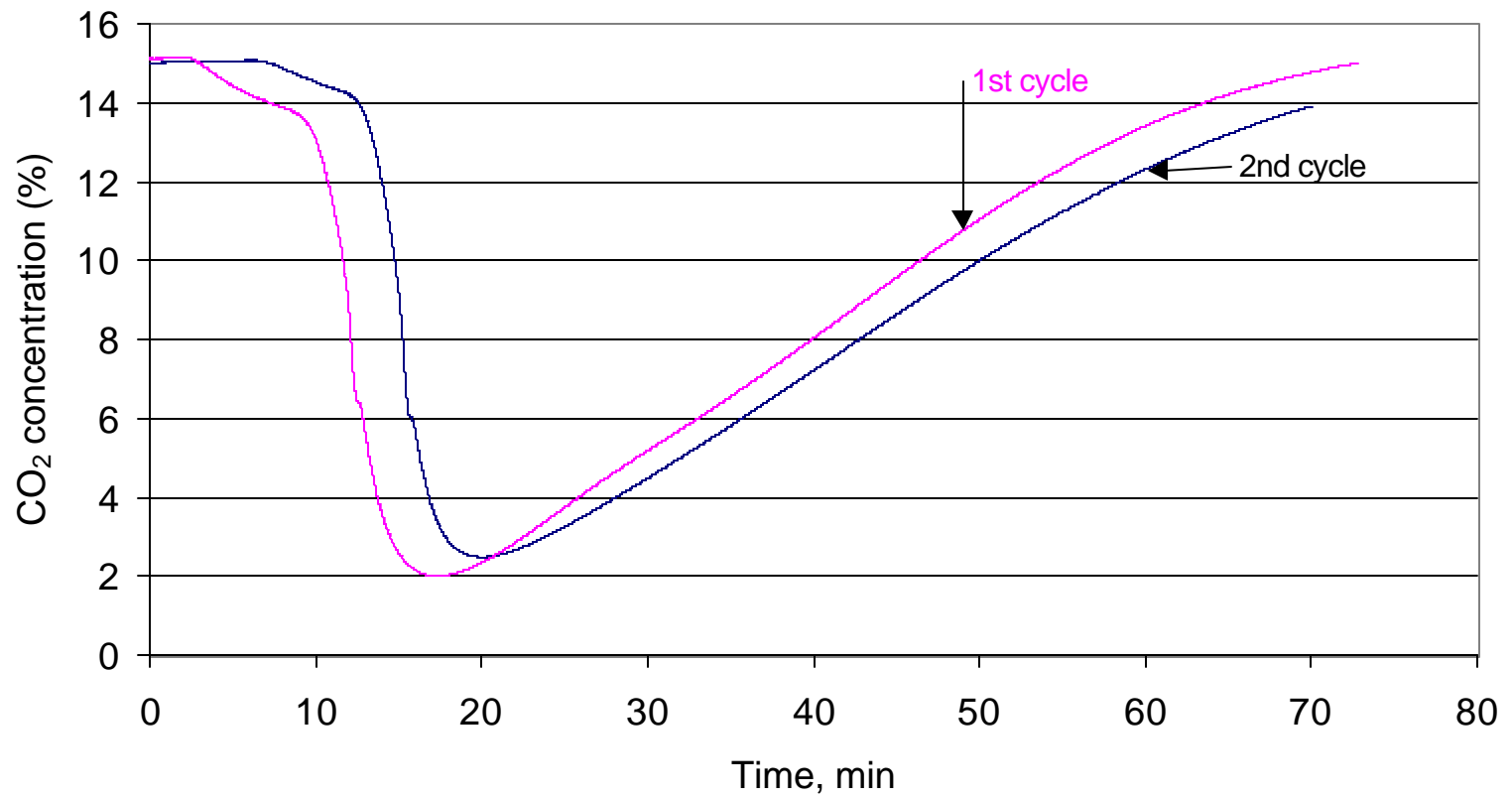


Figure 7.
Adsorption of CO₂ on activated carbon, 250 psi, 22 °C

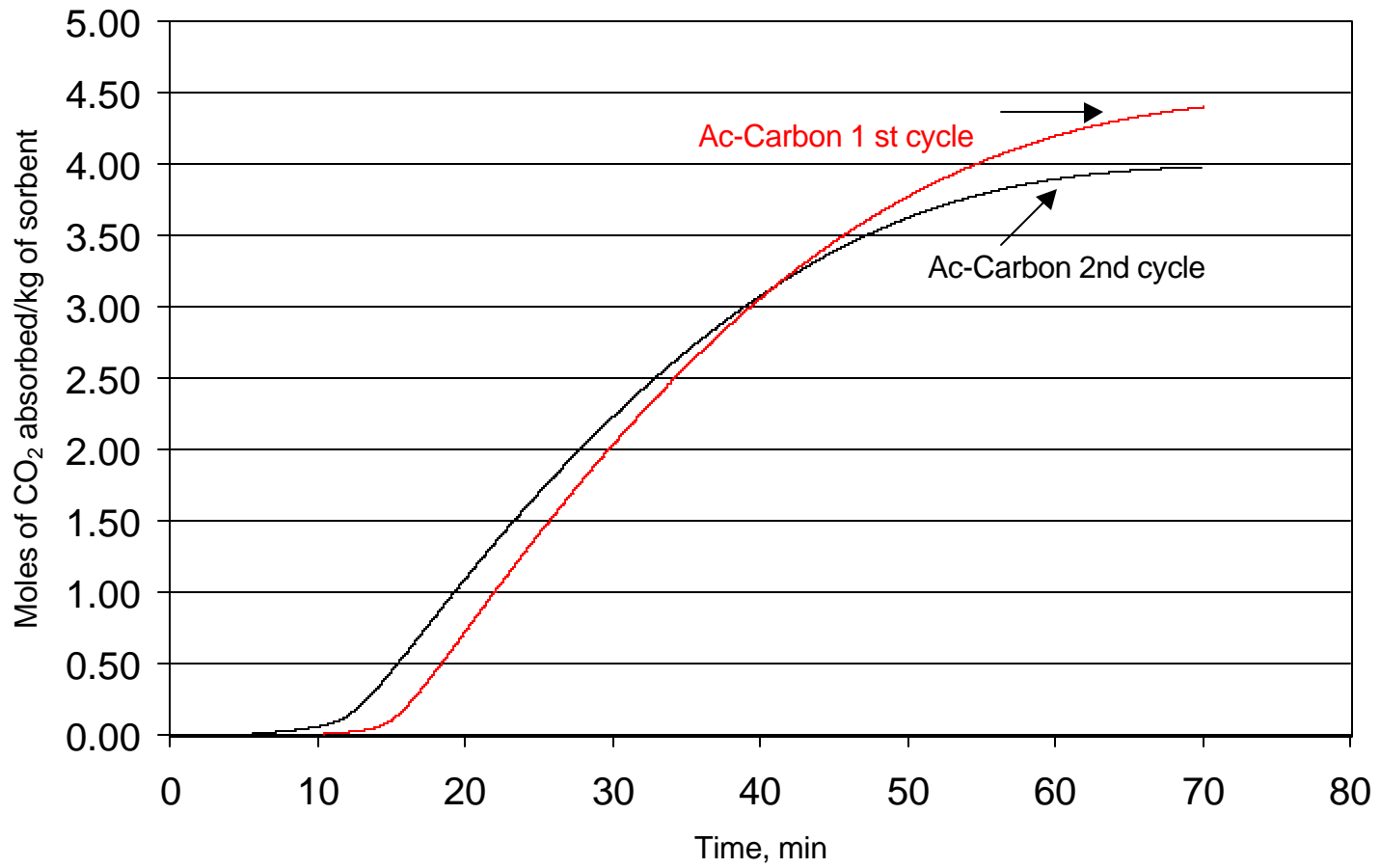


Figure 8
Adsorption-Desorption Isotherms of Natural Zeolite GSA ZS 500 A

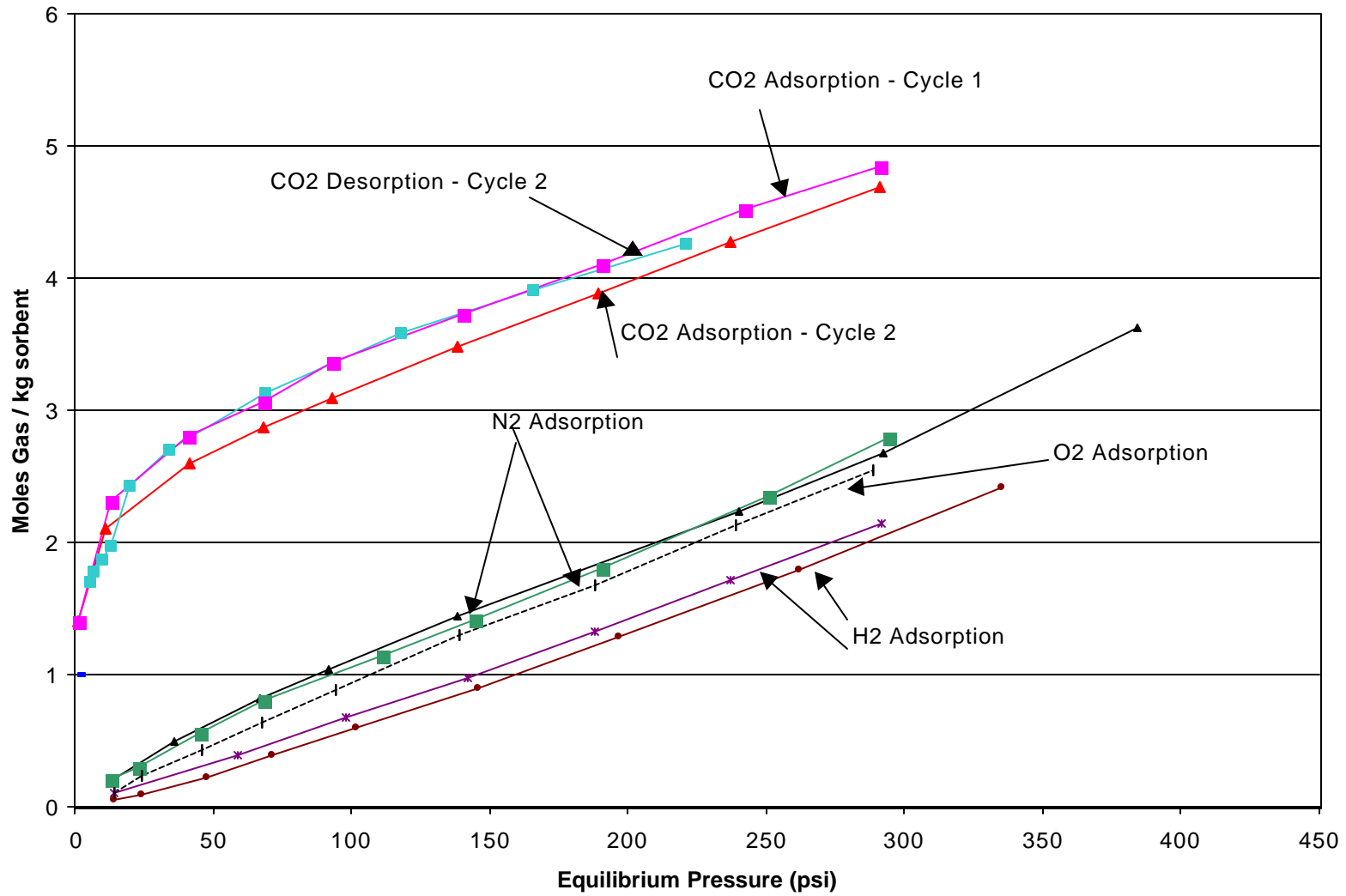


Figure 9
Adsorption of CO₂, N₂, and O₂ on Natural Zeolite
GSA ZS500A (15% CO₂, 3% O₂, 82% N₂ and H₂O at 25 C)

