

# Adsorption Kinetics of Pure and Mixed CO<sub>2</sub>-CH<sub>4</sub> Gases on Crushed Coal from the Black Warrior Basin, Westcentral Alabama

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The effects of particle size on the gas adsorption kinetics of Black Warrior Basin, Alabama coal were investigated using ~60 gram, 1-2 and 5-10 mm size fraction samples from the Littleton Mine (Twin Pine Coal Company), Jefferson County, Alabama. The samples were contacted with pure and mixed gases—CO<sub>2</sub>, CH<sub>4</sub>, a CO<sub>2</sub>-CH<sub>4</sub> mixture (~50 mole % CO<sub>2</sub>), H<sub>2</sub>O-saturated pure and mixed CO<sub>2</sub>-CH<sub>4</sub> gas, and He—at 35 and 40°C, 324 < P(psi) < 497, to determine the rates and magnitudes of gas adsorption. Samples were contained in a stainless steel wire-mesh sample holder and loaded into a 1.2 liter autoclave suspended in a 0.5 m<sup>3</sup>, cylindrical infrared oven. Temperature and pressure were measured with high precision ( $T, \pm 0.01^\circ\text{C}$ ;  $P, \pm 0.05$  psi) and accuracy ( $T, \pm 0.05^\circ\text{C}$ ;  $P, \pm 0.1$  psi) using high-quality thermistors and pressure transducers. After initial vacuum drying of the samples at 80°C for 36 hours, the oven temperature was adjusted to 35°C. A typical “dry” experiment consisted of: (1) evacuating the calibrated reference volume and autoclave to < 1 psi; (2) loading the calibrated reference volume with gas; and (3) releasing the gas into the autoclave and simultaneously recording gas pressure inside the two connected reservoirs. “Wet” experiments were conducted in an analogous manner, but without evacuation of the autoclave (step 1) between experiments. Instead, the pressure vessel containing wet coal was only vented to atmospheric pressure so that liquid water remained in the pressure vessel. The reference volume was always evacuated after completion of an experiment before charging with another gas or gas mixture.

Results of fifteen “dry” and water vapor (“moisture”)–saturated experiments with the 1-2 mm sample indicate that: (1) CO<sub>2</sub> adsorption on dry and moisture-saturated coal is much more rapid than CH<sub>4</sub> adsorption; (2) moisture saturation decreases the rates of CO<sub>2</sub>/CH<sub>4</sub> adsorption on coal surfaces, but it appears to have minimal effects on the final magnitudes of CO<sub>2</sub>/CH<sub>4</sub> adsorption; (3) CO<sub>2</sub>/CH<sub>4</sub> adsorption on coal surfaces is not strongly dependent on temperature; and (4) there is negligible adsorption of He on coal surfaces.

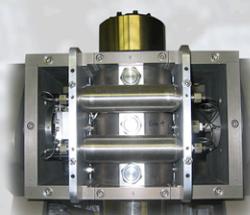
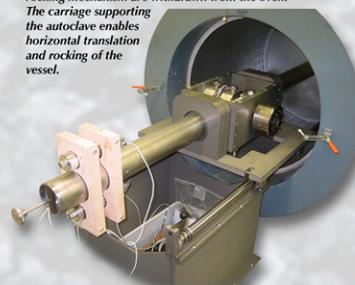
Results of eight “dry” experiments in the sequence (1) CO<sub>2</sub>, (2) CO<sub>2</sub>, (3) CH<sub>4</sub>, (4) CH<sub>4</sub>, (5) CO<sub>2</sub>-CH<sub>4</sub>, (6) CO<sub>2</sub>-CH<sub>4</sub>, (7) He, and (8) He – with the 5-10 mm sample performed at 35°C indicate that the magnitudes of gas adsorption are reproducible between successive experiments with the same gas, and are nearly identical to results obtained using the dry 1-2 mm sample. The time to reach steady state conditions changed significantly between the first (53 hrs) and second (20 hrs) exposure to CO<sub>2</sub>. Subsequent replicate experiments with CH<sub>4</sub>, CO<sub>2</sub>-CH<sub>4</sub>, and He showed similar trends. CH<sub>4</sub> experiments reached steady state conditions in 105 hrs and 80 hrs, respectively; CO<sub>2</sub>-CH<sub>4</sub> experiments in 50 hrs and 33 hrs; and He experiments in 5 hrs and 5 hrs.

These results are consistent with sorption-site “conditioning” during successive experiments. The first experiment with this sample after evacuation at 80°C was with pure-CO<sub>2</sub>. A working hypothesis is that CO<sub>2</sub> molecules displaced H<sub>2</sub>O molecules during the initial experiment, and that the surface sites and pores occupied by H<sub>2</sub>O molecules were much reduced before the replicate experiment. The subsequent sets of experiments with pure-CH<sub>4</sub> and the CO<sub>2</sub>-CH<sub>4</sub> mixture are apparently affected by an analogous process involving displacement of residual competing gas molecules adsorbed during the previous experiment. It is worth noting that recent BET measurements using a separate aliquot from the 5-10 mm size fraction required an extensive period (112 hrs) of degassing at 70°C to yield consistent measurements with N<sub>2</sub>.

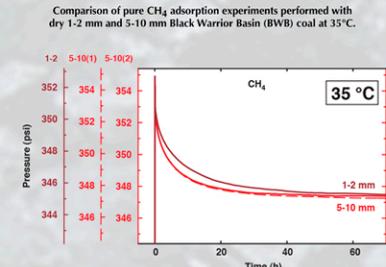
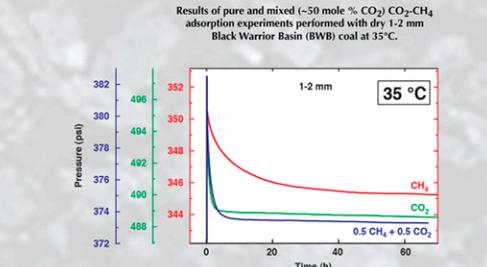
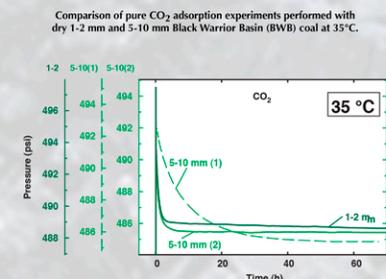
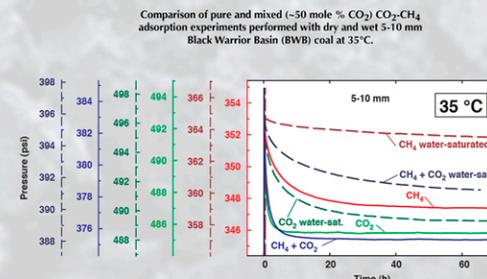
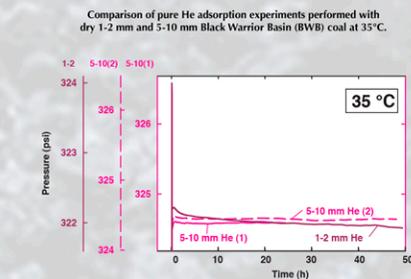
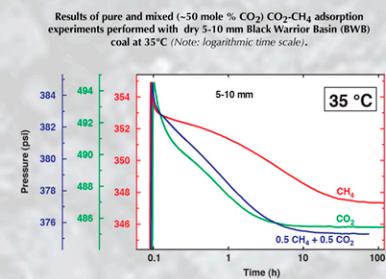
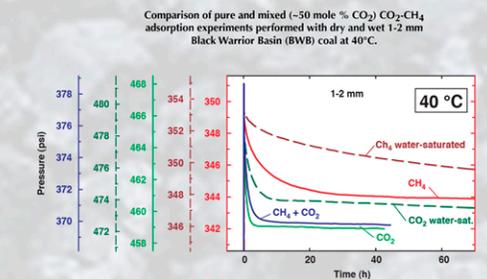
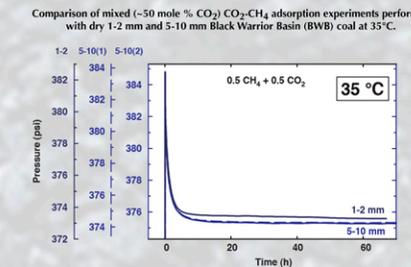
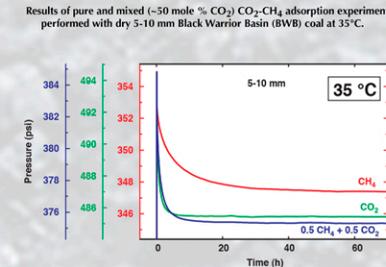
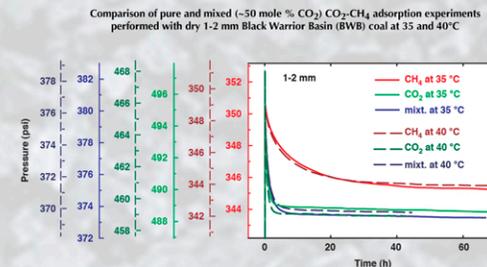
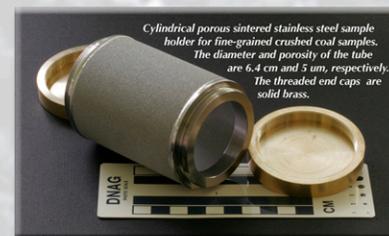
Comparison of results from “dry” gas experiments with the 5-10mm size fraction with those from the 1-2mm size fraction of the same Black Warrior Basin coal sample indicate that no significant differences exist in either the kinetics or magnitude of pure gas and mixed gas adsorption. This result is counter intuitive, but has positive implications for relatively rapid CO<sub>2</sub> adsorption by coal volumes accessible via cleat fracture systems (i.e., fracture spacing on the order of 10 mm).

Three experiments with H<sub>2</sub>O-saturated gas were conducted in the sequence CO<sub>2</sub>, CH<sub>4</sub>, and mixed CO<sub>2</sub>-CH<sub>4</sub> gas after completing the “dry” experiments. In this series of experiments the autoclave was not evacuated between tests. The pressure drop accompanying “wet” CO<sub>2</sub> adsorption was approximately equal to that observed for earlier “dry” CO<sub>2</sub> experiments. However, steady state conditions were not attained during the duration of the experiment (211 hrs). Slower adsorption under wet conditions is consistent with results of experiments with the 1-2 mm sample and the replicate pair of experiments with “dry” CO<sub>2</sub> onto the 5-10 mm sample that suggest H<sub>2</sub>O is displaced by CO<sub>2</sub> (the “dry” CO<sub>2</sub> experiments conducted in succession reached steady state conditions in 50 hrs and 10 hrs, respectively). Subsequent experiments with CH<sub>4</sub>, and mixed CO<sub>2</sub>-CH<sub>4</sub> did not reach steady state conditions before terminating the tests at 190 hrs. More significantly, the observed pressure drops were only a fraction of that observed during the “dry” gas experiments. This reflects the strong adsorption of CO<sub>2</sub> onto coal observed by many investigators. Importantly, the results reported here indicate that adsorbed “wet” CO<sub>2</sub> is only moderately desorbed by cycling to atmospheric pressure and subsequent exposure to “wet” CH<sub>4</sub> and mixed “wet” CO<sub>2</sub>-CH<sub>4</sub>. This result has positive implications for CO<sub>2</sub> sequestration in subsurface coalbeds.

End view of the cylindrical infrared oven with insulating end covers removed. The autoclave and rocking mechanism are withdrawn from the oven. The carriage supporting the autoclave enables horizontal translation and rocking of the vessel.



The “upstream” calibrated volume, consisting of four interconnected gas cylinders attached to the autoclave support structure.



## Key Conclusions

- Differential CO<sub>2</sub>/CH<sub>4</sub> adsorption kinetics will play a key role in CO<sub>2</sub> sequestration/ECBM production in subterranean coalbeds.
- CO<sub>2</sub> adsorption on dry and water-saturated coal is much more rapid than CH<sub>4</sub> adsorption.
- Water saturation decreases the rates of CO<sub>2</sub>/CH<sub>4</sub> adsorption on coal surfaces, but it appears to have minimal effects on the final magnitudes of CO<sub>2</sub>/CH<sub>4</sub> adsorption if the coal is not previously exposed to CO<sub>2</sub>.
- CO<sub>2</sub>/CH<sub>4</sub> adsorption on coal surfaces is not strongly dependent on formation temperature.
- Gas adsorption onto coal surfaces is affected by sorption-site “conditioning” and sorption-site occupancy history.
- Retention of adsorbed CO<sub>2</sub> on coal surfaces is significant even with extreme pressure cycling.
- He adsorption on coal surfaces is negligible.