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A Study on the Competitive Sorption Behavior of Aqueous Methane and Carbon Dioxide on Coal in Subsaturated Conditions

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Abstract

Background: Coal has tremendous capacity for sorbing gas due to its sponge-like nanoporous structure and consequent high surface area. Coalbeds naturally generate methane, which is both adsorbed to the surfaces, as well as absorbed in the bulk matrix of the coal, creating a valuable energy resource known as coalbed methane (CBM). Carbon dioxide is known to compete with methane for adsorption sites and will displace methane from coal. This has implications for enhancing CBM recovery and storing carbon dioxide.

Objectives: This study will measure the competitive sorption behavior of carbon dioxide and methane in a simulated coalbed subsurface environment.

Methods: Raman spectroscopy was used to measure the concentration of dissolved methane in a circulating high-pressure system. The methane concentration was kept below saturation and at pressures similar to what was observed in a field trial conducted by Carbon GeoCapture in 2023. The methane solution was passed through a sample of sieved and washed subbituminous Powder River Basin coal to sorb methane onto the coal. The amount of methane sorbed at a given dissolved concentration was quantified. Pure water free of dissolved gas was then passed through the sample to remove the methane solution and measure the desorption of methane from coal into the clean water. Finally, dissolved carbon dioxide was introduced to the system to measure the competitive behavior of carbon dioxide and methane.

Results: In the first stage of the experiment, methane sorbed to the coal. In the next stage, very little sorbed methane was displaced by clean water, and no increase in dissolved methane concentration was detectable. When carbon dioxide was introduced to the system, methane was rapidly displaced from the coal sample and the measured dissolved methane concentration rose rapidly, while the measured carbon dioxide concentration fell as it sorbed to the coal.

Applicability: The competitive behavior of carbon dioxide with methane offers some intriguing possibilities for enhanced CBM recovery as well as sequestering carbon dioxide in coal.

Introduction

Coal has tremendous potential for adsorbing gas due to its intricate nanoporous structure. A single gram of coal can have a surface area exceeding that of a couple of tennis courts, i.e. more than 200 m^2 (Medeiros 1979). Coalbeds naturally generate and sorb methane, creating a valuable energy resource (coalbed methane, CBM) (Mastalerz 2019). Carbon dioxide competes with methane for adsorption sites and will displace methane from coal (Arri 1992; Shi 2008). This has implications for enhancing CBM recovery and storing carbon dioxide (Liu 2025). This study will measure the competitive adsorption behavior of carbon dioxide and methane in a simulated subsurface environment.

Methods

Raman spectroscopy (Myers 2024) was used to measure changes in the concentration of dissolved methane and carbon dioxide in a circulating system of water, gas, and coal. A given experiment has three stages. In the first stage (I) of one experimental run, a 59-gram sample of subbituminous coal from Wyoming's Powder River Basin was isolated, evacuated, and pressurized with 85 mL of water to match simulated reservoir pressure, around 800 PSI. Next, a solution of dissolved methane in water was prepared using the mixing module with pump circulation through the flow loop at a pressure of 190 PSI for an equilibrium concentration of 19 mM dissolved methane. The mixing module was then bypassed, and the methane solution in the pump and flow loop was pressurized with water to match reservoir pressure with a final volume of 269 mL. The solution was then circulated through coal sample with the pump. Raman measurements of the aqueous concentration of dissolved methane in the spectrometer flow cell were used to quantify the amount of methane sorbed. In the second stage of the experiment (II), the coal sample was isolated with sorbed methane, and the fluid in the pump and flow loop was replaced with a solution of dissolved carbon dioxide using circulation through with the mixing module. The pressure was 300 PSI with a concentration of 700 mM. Finally, in stage three (III), the mixing module was bypassed and the carbon dioxide solution in the pump and flow loop was pressurized with water to match reservoir pressure and then circulated through the coal. To measure the competitive sorption behavior of carbon dioxide and methane, the concentrations of CO_2 and CH_4 were measured over time until they reached an equilibrium state.

Results

In the first stage of the experiment (I), methane adsorbed to the coal. This can be seen in Figure 1 below, where methane concentration is shown in orange using the left y-axis scale. From hour 0 to about 190, dissolved methane in the system is sorbing to the coal sample and reaching an equilibrium concentration around 10 mM. In the second stage (II), at 190 hours, the coal sample with sorbed methane is isolated and the methane solution is removed from the rest of the system. Carbon dioxide is then dissolved into the water, shown in blue using the y-axis scale on the right. The blue dots prior to 190 hours come from the levels being below our limit of detection (dashed blue line, 40 mM). The concentration is measured as carbon dioxide dissolves and then reaches an equilibrium around 700mM. The faint methane measurements between 190 hours and 235 hours are the result of methane being below the limit of detection (dashed orange line, 2.4 mM). In the third stage (III), at 238 hours, the dissolved carbon dioxide is injected into the coal sample. The carbon dioxide concentration falls rapidly, in part due to dilution and partly from sorption to the coal sample. The change in concentration due to dilution is 170 mM and the remainder is sorption. Methane concentration rises while CO_2 falls. The predicted methane concentration in the system would have been 2.4 mM due to the water with 10.3 mM methane in solution surrounding the coal mixing with the rest of the system. However, the observed methane concentration rose to 5.5 mM.

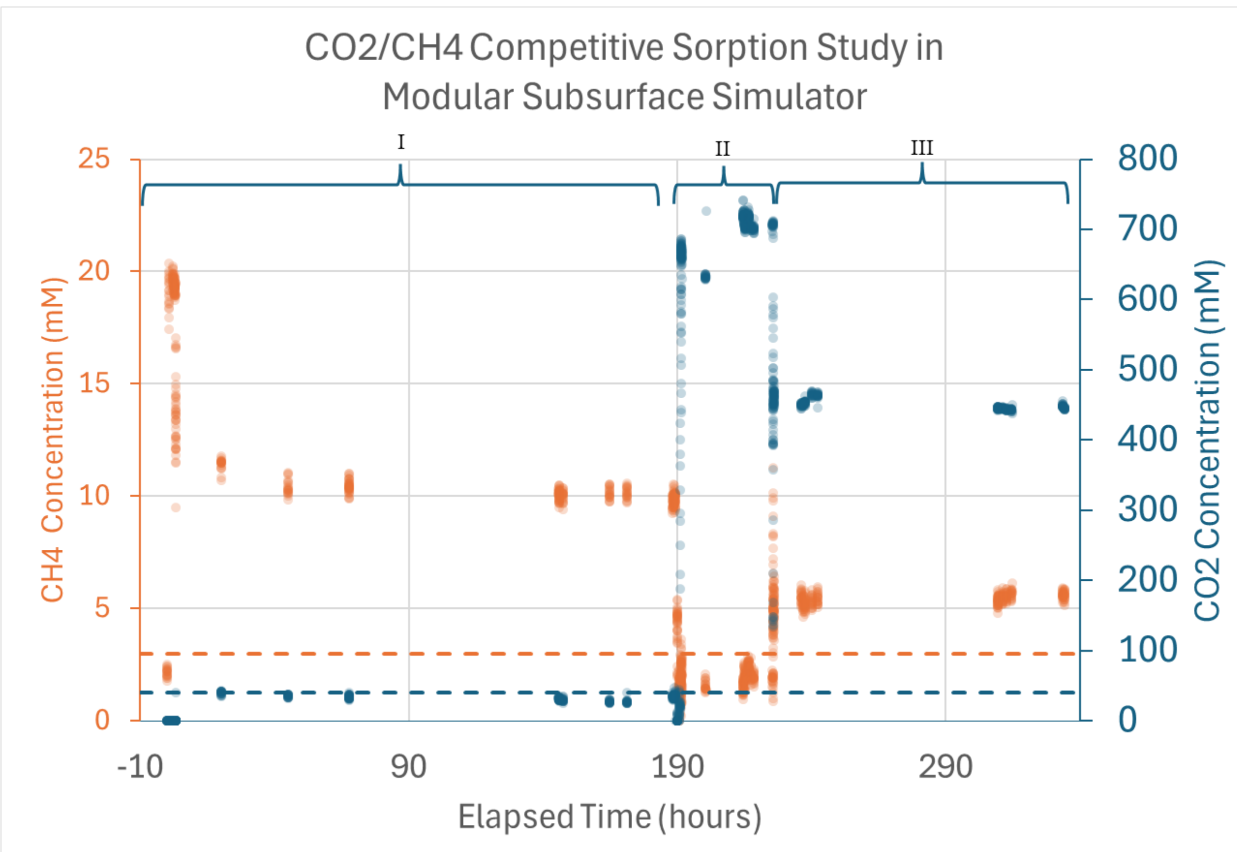

Figure 1. Plot of the measured dissolved concentrations of methane (orange-left axis) and carbon dioxide (blue-right axis) in the flow cell over time with Raman spectroscopy. The limits of detection are indicated with dashed lines: 2.4 mM for methane and 40 mM for carbon dioxide. In Phase I, methane is dissolved in the flow loop up to a concentration of 19 mM and then injected and circulated through the coal, resulting in a drop in concentration down to10 mM after 190 hours due to dilution and sorption. In Phase II, the coal sample is isolated and bypassed while fluid in the flow cell is replaced with dissolved carbon dioxide at a concentration of 700 mM and no methane. In phase III, the flow cell fluid is introduced to the coal and the measured concentration of CO2 falls to 440 mM due to dissolution and sorption while the measured concentration of methane rises to 5.5 mM due to displacement from the coal.

Discussion

During the initial injection of methane in solution, the concentration fell from 19mM to 10mM. Dilution accounts for a drop from 19 to 14.9mM, so the remaining 4.9mM is sorbed, or about 24 scf/ton^{US}. The difference between the carbon dioxide concentration predicted by dilution and the measured carbon dioxide concentration is attributable to sorption to the coal sample. In stage 3, the expected dilution from 700 mM due to a volume change from 269 mL to 354 mL was 24% to 530 mM. The measured concentration of carbon dioxide was 440mM, a difference of 90mM. 90mM concentration in a volume of 354 mL is 0.032 mols of carbon dioxide sorbed to 59 grams of coal, which would be 0.54 mols per kilogram of coal, equivalent to 410 scf/ton^{US}. The sorption of carbon dioxide resulted in methane being released from the coal. We measured a difference in methane concentration of 3.1 mM between the concentration predicted by dilution and the measured result, which is about 0.009 moles of methane released per kilogram of coal. The methane released when carbon dioxide was introduced was 63% of the sorbed methane.

Conclusions

During this experiment, we found that 410 scf/ton^{US} carbon dioxide can be sorbed to subbituminous coal in a submerged, subsaturated environment in a very short time. Methane displacement was rapid and efficient. About 0.0011 moles of methane were displaced out of 0.0017 moles sorbed, a 63% recovery rate from a single injection.

References

Arri, L. E., Yee, D., Morgan, W. D., & Jeansonne, M. W. (1992). Modeling Coalbed Methane Production With Binary Gas Sorption. *SPE Rocky Mountain Petroleum Technology Conference/Low-Permeability Reservoirs Symposium* (pp. SPE-24363). Casper, WY: SPE. Retrieved from https://doi.org/10.2118/24363-MS

Liu, A., Liu, S., Zhang, K., & Kaiwen, X. (2025). Competitive sorption of CH_4 and CO_2 on coals: Implications for carbon geo-storage. *Separation and Purification Technology*, 129399. doi:https://doi.org/10.1016/j.seppur.2024.129399

Mastalerz, M., & Pashin, J. (2019). *AAPG Energy Minerals Division Coalbed Methane Annual Report.* San Antonio, TX: AAPG. Retrieved 11 19, 2024, from https://www.aapg.org/Portals/0/docs/emd/reports/annual-meeting/2019-05-18/2019-05-18-EMD-AnnualMeetingCommitteeCoalbedMethane.pdf?ver=2019-05-15-132215-500&srsltid=AfmBOorO10gK75g_Rmc76_hX2HyveLjSecGaS4vJ0CAPu-et-nmkTt6N

Medeiros, D., & Petersen, E. E. (1979). Surface area variations of coal during solvent extraction. *Fuel*, 531-533. Retrieved from https://doi.org/10.1016/0016-2361(79)90172-8

Myers, G. A., Brown, T., Morgan, C., Bard, W. A., & Pope, J. M. (2024). Demonstration and Quantification with Raman spectroscopy of the displacement of adsorbed methane from coal by injected dissolved carbon dioxide for carbon sequestration. *Unconventional Resources Technology Conference* (pp. 394-408). Houston, TX: SEG. Retrieved from https://doi.org/10.15530/urtec-2024-4044480

Shi, J.-Q., & Durucan, S. (2008). Modeling of mixed-gas adsorption and diffusion in coalbed reservoirs. *SPE Unconventional Reservoirs Conference* (pp. SPE-114197-MS). Keystone, CO: SPE. Retrieved from https://doi.org/10.2118/114197-MS