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Demonstration of Sequestration of Carbon Dioxide in a Simulated Coalbed through Injection of Dissolved Gas

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Abstract

The objective is to demonstrate effective sequestration of CO_2 in coalbeds via injection of dissolved gas. We have developed a laboratory-scale apparatus to simulate processes involved in coalbed sequestration: 1) Preparation of injection fluid, 2) Flow of fluid through coal, 3) Recovery of displaced coal fluid for recycling at Step 1. The apparatus consists of three clear polycarbonate pressure compartments: a mixing tank, tubing packed with coal, and a recovery tank. These represent respectively the injection well, the coalbed, and peripheral production wells. Flow is driven by a single pump with valving to select for and simulate the three phases of sequestration. First, the pump moves headspace gas through a sparging stone in the mixing tank. Second, gas-saturated water is passed through coal packed in polycarbonate tubes and into the recovery tank. Third, the coal is isolated, and water is pumped from the recovery tank to the mixing tank. This effectively closes the loop so additional injection fluid can be prepared and cycled through the coal. Partitioning of CO_2 in the system is monitored with pressure, temperature, and pH sensors, as well as Raman spectroscopy.

In fluid saturated with CO_2, the Raman signature of dissolved CO_2 is observed. After passing through coal, lower CO_2 is observed in recovered fluid, even after replacing the entire volume of water in the pore-space of the coal several times over. Furthermore, when recovered fluid is returned to the mixing tank, the pressure drops immediately as residual CO_2 in the headspace dissolves into fresh fluid. Another indication of CO_2 retention in the coal is observed when the mixing and recovery tanks are vented to atmosphere post injection: much more gas exsolves from the mixing tank fluid as compared to recovered water. A final dramatic demonstration of sequestered CO_2 is observed when the coal is then vented. Microscopic gas bubbles in the coal expand rapidly, driving most of the water out of the coal and large amounts of gas also bubble out.

CO_2 injected as solution gas into the coal is rapidly adsorbed by the coal. This mechanism confirms that water can act as a carrier fluid to deliver CO_2 to coal in condensed phase, thereby avoiding the formation damage and two-phase flow challenges typically observed when injecting critical CO_2 into coalbeds.

Introduction

Carbon dioxide has been used continuously since the early 1970's as a fluid to displace oil in subterranean reservoirs for enhanced oil recovery. The industry already has a longstanding history of storing gas for future use (Kidnay 2019), and therefore has the requisite knowledge for gas storage that can be applied to carbon dioxide. Conventional carbon capture and storage projects generally leverage this knowledge, targeting deep, traditional, porous geologic formations for either temporary or permanent storage of greenhouse gases. There are several projects globally that are injecting CO_2 at depths where the carbon dioxide is in a condensed phase[1]. All these projects are using CO_2 in pure or near-pure form as this optimizes the use of the pore space in the target reservoir. Performing injection in this manner maximizes the amount of gas stored per unit volume in the reservoir.

While using its downhole Raman spectrometer system to observe methane and carbon dioxide in subterranean coalbeds in 2003, WellDog recognized that coalbeds represent a viable sink for greenhouse gases. Carbon GeoCapture (CGC) recognized in 2018 that the well-established ability of coal to preferentially sorb CO_2 in the presence of other gases and water meant that coalbeds could actively participate in scrubbing CO_2 from flue gases, reducing significantly the cost of carbon capture and storage using geologic formations.

Traditionally used for natural gas production, coalbeds are also a thoroughly studied carbon sink. When coalbed methane gas production achieved prevalence, methods to displace additional methane from the coal were investigated by many companies. Enhanced coalbed methane through the injection of various gases has been tried in the laboratory and in the field (Busch 2011). Carbon dioxide was found to be the most promising, though with widely variable results. The main issue with past attempts to inject a pure stream of CO_2 was subsequent observation of reduced injectivity and apparent near wellbore formation damage. Laboratory experiments confirm the propensity of the coal structure to adsorb large quantities of CO_2 and swell as a result when pure or nearly-pure CO_2 is injected into it, and to not swell or lose injectivity when low levels of CO_2 are injected into it.

As a result, we hypothesized that if we were to inject CO_2 into coalbeds at lower concentrations, i.e. similar to the natural concentrations that WellDog typically observed in coalbeds, any near-wellbore swelling effects would be reduced or eliminated. At the same time, the coals could adsorb CO_2 in a manner similar to the naturally occurring processes that have accumulated natural gas and CO_2 in coalbeds over geologic time. The fact that coals are ubiquitous globally and frequently located near greenhouse gas emitters gave additional support to the possibility that this CCS framework might represent a potential part of the solution to climate change.

In order to test this hypothesis, we have used water to dilute the CO_2. This reduces the effective concentration of CO_2 to e.g. about 3% at 520 psi and provides an incompressible fluid in which the CO_2 can be readily carried through the coal using standard injection processes. In the sequestration method, a peripheral production well is used to source formation water. CO_2 is dissolved into that water in the injector well and then the solution is gravity fed into the coal formation. The CO_2 sorbs from the water into the coal matrix. The injection process can be monitored in a nearby well *in situ* with a downhole reservoir Raman spectrometer system to measure changes in the concentrations of dissolved gases, as the CO_2 plume advances. This sequestration process can be operated in a closed loop, resulting in minimal formation perturbation, reduced environmental impact and transportation costs, and no injection of foreign fluids. Furthermore, carbon storage in remote, cold or arid climates is not precluded. When the

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[1] https://netl.doe.gov/carbon-management/carbon-storage/worldwide-ccs-database

injection of fluid into a central well is balanced with commensurate production from peripheral wells, it is possible to achieve sequestration without increasing the pressure on the formation - instead, the pressure of the CO_2 in the coal is intentionally selected to remain below the natural, long-term water pressure in the coalbed. This contrasts with conventional storage schemes where injection generally increases formation pressure, increasing injection cost and outburst risk over time. Another key departure from the conventional method is that here it is not necessary to rely on the integrity of a cap rock to ensure storage. As with long term natural storage of methane in coalbeds, the water pressure in the coalbed holds the CO_2 in place over geologic timeframes. In this scheme, long term monitoring is accomplished with downhole pressure gauges to verify that the hydrostatic pressure is unchanged. Should a drop in pressure be observed, the remediation is straightforward: halt the anthropogenic activities causing that pressure drop and/or add water to maintain the hydrostatic head. Periodic *in-situ* characterization of formation fluids across a storage field with a downhole reservoir Raman spectroscopy system can verify the location of the injected $CO_{2.}$

To explore this hypothesis, WellDog has conducted experiments at the micro and meso scales over the past twenty years. Recently, WellDog has constructed a closed-loop circulation system where we simulate an injector/producer pair and pass the mix through coals. The fluid is monitored along the loop from mixing, through injection, and recovery by a suite of sensors which include temperature, pressure, pH, and Raman spectroscopy. This paper describes that system and shares results collected using it.

Theory

Modern Raman spectroscopy is a laser-based analytical technique that can be applied to characterize the composition of borehole fluids in communication with the storage formation (Myers 2019). When monochromatic laser photons interact with polarizable electrons in covalent molecules, occasionally those interactions result in a partial transfer of energy that changes the vibrational state of the molecule and scatters a photon at a different wavelength. The shift in the scattered wavelength corresponds with the energy of the molecular vibration. By collecting and counting the spectrum of scattered light, the identity and quantity of those molecules can be measured (McCreery 2005).

The concentration of dissolved gases in reservoir fluids is directly related to the amount sorbed to the coal, $\gamma_{adsorbed}$, as characterized by the Langmuir adsorption parameters of the coal, including the surface capacity, γ_{max}, and the half-pressure, λ_{half}:

$$\gamma_{adsorbed} = \frac{\gamma_{max} * Pressure}{\lambda_{half} + Pressure}$$

When the gas pressure is equal to λ_{half}, it can be observed that the amount adsorbed is half of the capacity. For example, in **Figure 1**, Arri, et al, reports adsorption isotherms of carbon dioxide and methane to San Juan Basin Fruitland Coal at 115° F. Estimated Langmuir parameters were reported as a γ_{max} for CO_2 of 1130 standard cubic foot per ton (scf/ton) and λ_{half} of 200 PSI. For methane, the values were reported as 760 scf/ton and 360 PSI, respectively (Arri 1992). Other reports have indicated that coal can hold as much as ten times more CO_2 than methane (Shi 2008).

In a submerged coal system, the concentration of dissolved gases in reservoir fluids is related to the partial pressure of the gas in the system by Henry's proportionality constant. Henry's constant for methane at 115° F in water is 1.0×10^{-3} moles·kg^{-1}·PSI^{-1}, and for CO_2 at the same temperature, the Henry's constant is 20×10^{-3} moles·kg^{-1}·PSI^{-1} (Duan 1992). Thus, by measuring the *in-situ* concentration of dissolved gas with Raman spectroscopy, the effective partial pressure of gas in the reservoir can be estimated via Henry's constant, and then the Langmuir parameters can be used to calculate the gas in place on the coal.

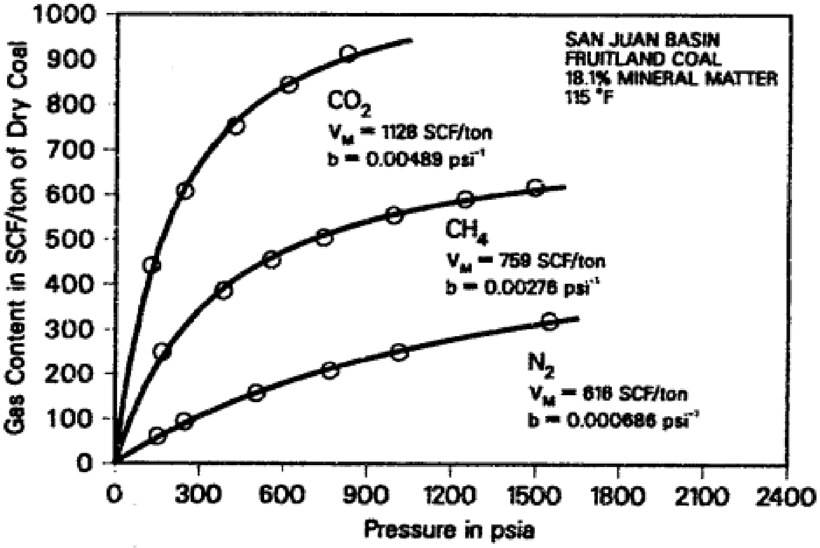

Figure 1. Pure gas sorption data adapted from Arri 1992

For example, if the measured equilibrium formation concentration of methane were 200×10^{-3} moles·kg^{-1}, then the effective partial pressure estimated would be 200 PSI CH_4. In turn, from the Langmuir equation and parameters for the San Juan coal above, the CH_4 gas in place estimated would be 270 scf/ton.

Methods

Apparatus

A practical model for visualization of the proposed sequestration process includes clear polycarbonate compartments that represent the injection well (I), the coalbed (II), and the production wells (III). It is convenient to describe the flow connections in terms of 'manifolds' associated with the circulation pump, the sensor loop, the coal compartment and the production well compartment. For our purposes, we use the term 'manifold' in the generic sense of a single flow line inwards or outwards that is divided into or amongst two or more flow lines. The ultimate flow path to or from the manifold is determined by the choice of which valves adjacent to the manifold are opened.

The injection compartment consists of a vertical 10-cm diameter cylinder fitted at the base with an outlet for water withdrawal and an inlet with a sparging stone for the introduction of gas. The top of the cylinder is fitted with one hybrid port to dispense water into the tank or to supply headspace gas to the pump, and a second dry port that connects to a pressure gauge, a gas tank, a vacuum pump and the headspace of the production well cylinder. The injection cylinder has a total volume of 3 liters and at the start of the demonstration is two-thirds full of water and pressurized with gas.

The coalbed compartment consists of a series of twelve horizontal, 45-cm long × 2.5-cm diameter polycarbonate tubes that are threaded and fitted on each end with push-connect adapters. The tubes are loosely packed with desiccated Powder River Basin subbituminous coal soaked in water and drained before loading. The total volume of the coalbed compartment is 1.5 L with 0.9 L of wet coal weighing a total of 1.2 kg. Sets of three adjacent tubes are connected in series, so that a 5-way connector distributes flow from the coal inlet manifold through four sets of three coal tubes, resulting in a total effective path length of 1.4 m. On the opposite end of the tubes is a second 5-way connector that collects the flow out of the four sets of coal tubes into the coal outlet manifold. A pressure gauge is fitted across the coal compartment to a manual three-way valve that communicates with either the inlet or outlet of the coal for measurement of the pressure-drop across the coal during injection. At the start of the demonstration, the void space of the coal compartment is completely filled with water.

The production well compartment consists of a vertical 10-cm diameter cylinder fitted at the base with a single inlet for flow of water to and from the production compartment manifold. The top of the cylinder is fitted with a single port that communicates with the dry port of the injection compartment. Inside the cylinder is a float that serves to allow pressure from the common headspace of the apparatus to communicate with the system. This float also limits the mixing of the gases in the apparatus headspace with the water recovered from the coal during injection and production operations. The volume of the cylinder is 2 L and at the start of the demonstration is nearly empty of water and pressurized with gas.

A schematic of the plumbing of the apparatus is shown in **Figure 2**. The circulation pump is a demand-type diaphragm pump capable of moving either water or gas through the system. The pump is equipped with a pressure cutoff switch set to 85 PSI. Polyethylene tubing either 0.6 cm or 0.8 cm in diameter was used for all connections. The volume of the tubing in the apparatus is lumped together with the volumes of the various compartments mentioned above. The sensor loop consists of a flow cell fitted to a laboratory Raman spectrometer and an inline pH sensor. The vacuum pump is used to evacuate gases from the apparatus after the demonstration so that the system can be rapidly reset. Solenoid valves and pump operations are controlled via a system of relays with an Arduino Nano microcontroller.

The water outlet at the base of the injection well cylinder (**Injection** Compartment I) is connected to the pump inlet manifold for the circulating pump. Solenoid valves adjacent to this manifold (S1, S2 and S3) allow for selection of gas from the top of the injection cylinder (S1), water from the base of the production well cylinder (S2), or water from the base of the injection cylinder (S3). On the outlet of the circulating pump, valves adjacent to the pump-outlet manifold allow for pumping of gas to the sparging stone at the base of the injection cylinder (S4), water to the top of the injection cylinder (S5), water to the sensor inlet manifold (S6), and water to the coalbed inlet manifold (S7). The sensor inlet manifold has adjacent valves for selection of the flow of water from either the pump outlet manifold (S6) or the coalbed output manifold (S10), and flow through the sensors to the sensor outlet manifold. The sensor outlet manifold has adjacent valves that allow for the direction of flow from the sensor loop either to the coalbed inlet manifold (S8) or to the production well manifold (S9). The coalbed inlet manifold has adjacent valves that allow for selection of the flow of water from either the pump outlet manifold (S7) or the sensor outlet manifold (S8) and flow through the coal to the coalbed outlet manifold. The coalbed outlet manifold has adjacent valves for direction of flow from the coal to the production well manifold (S11) or to the sensor loop inlet manifold (S10). The production well manifold has adjacent valves that allow for direction of flow to and from the base of production well cylinder, and as already noted, flow from the coal compartment outlet manifold (S11), or from the sensor outlet manifold (S9), or to the pump inlet manifold (S2). In Figure 2, dashed lines are used to indicate the connections for the coalbed pressure gauge, as well as the connections from the dry port of the injection compartment to the production compartment, pressure gauge, gas tank, and vacuum pump.

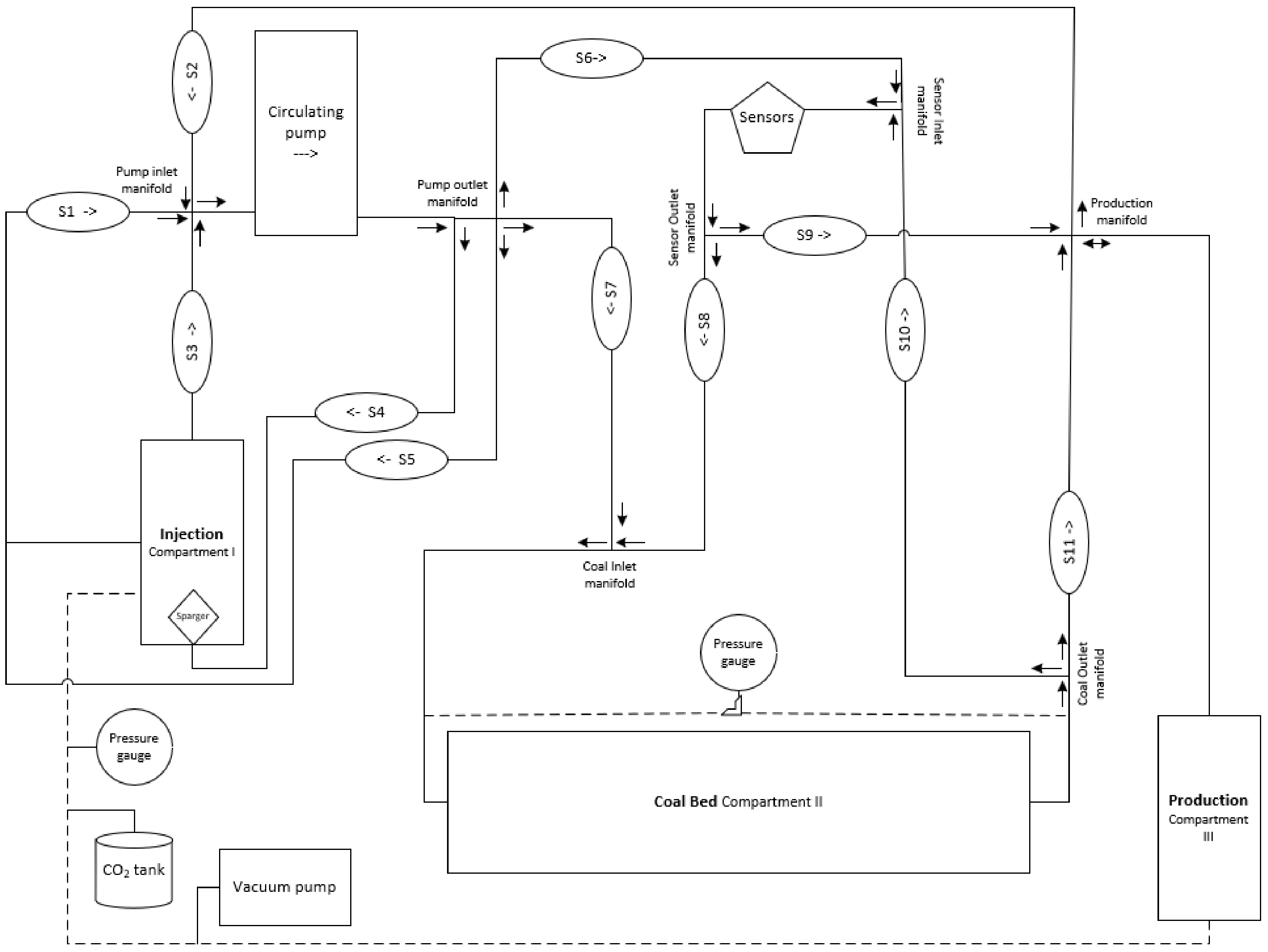

Figure 2. Schematic representation of the fluid routing in the demonstration apparatus

Operations

1. System Reset

The first operation performed is to use the vacuum pump to evacuate the common headspace of the entire apparatus, to remove atmospheric gases and dissolved and adsorbed CO_2 in the system from a previous demonstration. Next, we use the circulation pump to redistribute the water in the system, flushing voids from the coalbed compartment, and filling the injection well cylinder. Finally, the circulation pump is used to pressurize the coalbed with water pressure to simulate the hydrostatic head on the formation prior to injection.

The appropriate solenoid valves are opened, and the vacuum pump is powered while monitoring the pressure gauges on compartment I and the coalbed. After several minutes of operation, the near-vacuum system pressure remains stable after the vacuum line is closed. The outgassing of the coal and the boiling of water at low pressures during these operations will have displaced a large part of the fluid from coalbed into the production cylinder. The circulation pump does not function near vacuum, so it is necessary to crack a valve open slightly to allow a few PSI of atmosphere into the common apparatus headspace to enable redistribution of water in the system. Now the appropriate solenoid valves are opened, and the circulation pump is operated to return water from the production cylinder to compartment I. Next, the appropriate valves are actuated, and the circulating pump is operated to inject water from injection well into the coalbed, first with valves adjacent to the coal outlet manifold closed. In this way, the pump operates until the pressure in compartment II reaches the pump pressure switch limit of 85 PSI. Most, but not all the void space in the coal will be filled with water. Next, the full output of the circulation pump is directed from the base of the injection well cylinder through coalbed to flush the remaining void space with water and into production cylinder. Next, the valves adjacent to the coal outlet manifold are closed and the pump is again run up to its pressure switch cutoff to fully pressurize the coal. The appropriate valves are closed and opened to isolate the coalbed compartment and to pump water from production compartment back to injection compartment, and to flush water through the sample loop and eliminate voids in the system plumbing. Finally, the appropriate valves are closed and opened, and the vacuum pump is run to fully evacuate the common headspace of the apparatus. Now the system is ready for demonstration: the coalbed is full of water and pressurized, the injection cylinder and sample loop are full of 2L of water, and the production cylinder is empty.

2. System Pressurization and Demonstration of the Preparation of Sequestration Fluid

The appropriate valves are opened, and the gas tank regulator is set to 50 PSI to pressurize the common apparatus headspace with carbon dioxide. While the gas tank regulator is open, the circulation pump is operated to circulate fluid from the base of the injection cylinder through the sample loop and back to the top of the injection cylinder to distribute gas pressure through the system. The coalbed compartment remains isolated and at pressure from the previous operation. Next, the appropriate valves are closed and opened to circulate gas from the common apparatus headspace through the circulation pump and to the sparging stone at the base of the injection well cylinder. This step could represent one method of preparing sequestration fluid within the column of an injection wellbore similar to that employed in the Icelandic CarbFix injection project (Snæbjörnsdóttir 2020), where in the field tubing is deployed to the desired depth and gas is bubbled out the base of the tubing and up the water column in the annulus. In the demonstration apparatus, buoyant gas bubbles reach the surface of the truncated water column, but in the wellbore, when the column of water is tall enough, carbon dioxide bubbles will dissolve fully before reaching the surface of the column. Additionally, the rate of water pumped into the top of the injection wellbore can be adjusted to counteract the buoyancy of the bubbles to ensure full dilution and no loss of gas to the surface (Sigfússon 2015).

After several minutes of circulation in the apparatus, the pressure in the common apparatus headspace remains stable when the valve to the gas tank is closed, indicating that the injection fluid is at equilibrium and fully saturated with gas. When this solution is flowed through the sample loop, the pH probe registers a reduced pH, indicative of the dissolution and reaction of CO_2 with the water to form carbonic acid. Furthermore, Raman spectroscopy of the solution measures the distinct signature of dissolved carbon dioxide.

3. Demonstration of the Injection of Sequestration Fluid and the Displacement and Production of Formation Water

Next, the appropriate valves are opened, and the circulation pump is operated to push fluid from the injection well into the coalbed. This first displaces the 0.6 L of extant coalbed fluid into compartment III. Next, the front of injection fluid reaches the end of the coal and begins to fill the production well cylinder. During injection, a portion of the flow from the coal outlet manifold is passed through the sample loop so that the pH and Raman spectrum of the solution can be monitored in real time just as they are in the monitoring well in our sequestration scheme. The pressure-drop across the coalbed is measured during injection by manually switching the three-way valve on the coalbed pressure gauge from the front to the back of the coal tubes. After the full injection cylinder volume has been emptied, the valves adjacent to the coal outlet manifold are closed, and the pump is operated until the pressure in coalbed compartment reaches the pump pressure switch cutoff (85 PSI). At this point, the coal is isolated from the rest of the system.

4. Demonstration of the Recovery of Formation Fluid and the Closed Loop

The appropriate valves are closed and opened, and the pump is operated to empty the fluid from production compartment back into injection cylinder, thus closing the loop and demonstrating the reuse of water from the formation for the sequestration fluid. It will be recognized that the pressure in the common apparatus headspace will begin to drop as residual carbon dioxide dissolves into the CO_2-depleted water that was isolated from the headspace by the float in the production well cylinder. At this point, the system is re-pressurized up to 50 PSI with CO_2 and a second injection with the recycled water is performed by repeating Operations 2 and 3. Again, after emptying the production cylinder back into the injection cylinder, a drop in the pressure of the common apparatus headspace will be observed. This occurs despite the coalbed at this point having had its 0.6 L void volume effectively replaced several times over by water saturated with CO_2 at a pressure of 50 PSI. Additional cycles of pressurization, injection, production and recovery can be carried out. When a satisfactory number of cycles have been performed, on the final injection, the pump is stopped when the volume of water in the injection cylinder is roughly equal to the volume of water in the production cylinder before moving on to the final operation of the demonstration.

5. Demonstration of Gas Sequestration by Depressurization of System Compartments

While production of water from actual coalbeds is a challenging and long-term process, in the laboratory we can produce water from the production cylinder to release the sorbed CO_2 from the simulated coalbed. In order to accomplish this, the common apparatus headspace is depressurized by opening the appropriate valves to partially vent the system to atmosphere while keeping coalbed compartment isolated. It is apparent that the fluid in the injection well cylinder exsolves qualitatively more gas than the equal amount of fluid in the production well cylinder due to depletion of CO_2 after passing through the coalbed. Following that, the appropriate valves are closed and opened, and the circulation pump is operated to empty the production cylinder back into injection cylinder. Finally, the appropriate valves are opened to depressurize and vent the coalbed to the atmosphere. Gas adsorbed to the coal rapidly expands and displaces nearly all the water out of the coal tubes into the production well cylinder and even lifts the float to the top of the cylinder. The desorption continues from the coal for much longer than the exsolution from the residual fluid in the injection cylinder. Presumably, this is due to mass transport restrictions in the solid matrix. It should be emphasized that there is no real-world mechanism analogous to the rapid depressurization of the formation.

Results & Discussion

In a typical demonstration, after pressurization and circulation to equilibrium in compartment I, when the pressure is 50 PSI at room temperature, there are a total of 9 g of CO_2 dissolved in the 2 L of water in the injection well cylinder, 17 g of CO_2 in the 3 L of common apparatus headspace, and zero grams in the isolated coalbed compartment. This totals 26 g of gas in the entire apparatus. The concentration of CO_2 measured in the sample loop with Raman spectroscopy is 110×10^{-3} moles$\cdot$L^{-1}. Following the injection of those 2 L of sequestration fluid and subsequent recovery of fluid from the production well cylinder, when the circulation pump is run to equilibrate the fluid with residual headspace gas, the pressure in the system drops to 40 PSI. The amount of gas dissolved in the 2 L of recovered water at that pressure is 7.3 g. The amount of gas in the common headspace at that pressure is 13.5 g for a total of 20.8 g. The remainder of the gas in the apparatus must be in the coalbed compartment, a total of 5.2 g. A fraction of that 5.2 g must be in the 0.6-L water fraction of the coalbed. The upper limit of the concentration of CO_2 in the coalbed water is 4.5 g per liter (i.e. corresponding to the concentration at 50-PSI in the original sequestration fluid), so that there is, *at most* 2.7 g dissolved CO_2 in the coalbed compartment and *at least* 2.5 g sorbed to the coal. Extrapolated to the 1-short ton (907.2 kg) scale, 2.5 g of CO_2 on 1.2 kg of wet coal corresponds to 40 scf/ton. Note that the total 5.2 g in the coalbed is less than the 9 g of CO_2 in the original sequestration fluid. This indicates that not all the dissolved gas injected is necessarily retained by the coal, which is unsurprising given the loose packing, high permeability, short pathlength and high flow rate through the simulated coalbed in this demonstration. Nevertheless, the sorption of 40 scf/ton of coal in a matter of minutes on the first pass of injection is encouraging.

After repressurizing the system to 50 PSI, and equilibrating, the dissolved and free gas outside coalbed compartment is returned to 26 g total, a net increase of 5.2 g (matching what has been isolated in the coalbed) and the grand total amount of CO_2 in the apparatus is 31.2 g. When a second round of 2 L of sequestration fluid is injected and the depleted fluid is recovered from the production well cylinder, the system pressure drops typically to 46 PSI after equilibrating with residual CO_2. At this pressure, the amount of gas dissolved in the recovered water is 8.4 g and the amount in the common headspace of the apparatus is 15.6 g, for a total of 24 g. Now the remainder of gas in the system within the coalbed compartment is 7.2 g. Again, at most 2.7 g are dissolved in the fluid of the coalbed compartment, therefore, leaving at least 4.5 g sorbed to the coal. Scaled to 1 ton, this amount corresponds to 71 scf/ton.

Subsequent cycles continue to exhibit diminishing returns. After 4 to 5 cycles, the pressure drop after recovery of fluid is negligible. It should be noted that these estimates of sorbed gas to the coal in these expedited demonstrations are likely only to the most accessible surfaces. Consider that in the San Juan coal isotherm (Fig.1), the estimate for sorbed CO_2 at 50 PSI is 230 scf/ton on dry coal. During the demonstration, it is observed that the pressure of the coal compartment drops gradually after isolation post-injection, presumably due to the sorption of gas from solution. Slower injection flow rates, and longer soak times between injections would be expected to increase the amounts of gas ultimately stored on the coal. Furthermore, the relatively modest pressure of gas in this apparatus, 50 PSI, (comparable to the pressure of CO_2 in a bottled soft drink), is a small fraction of the hundreds of PSI observed in a typical coalbed.

While these demonstrations have been quite instructive, we have also undertaken quantitative experiments in more robust fixtures with conditions better representative of coal formations. These experiments include the added presence of methane sorbed to the coal prior to injection. In other future work, we will investigate the potential use of buffered solutions to enhance the density of dissolved CO_2 in the injection fluid.

Conclusions

We report that significant amounts of CO_2 can be introduced to coalbeds via injection in dissolved solutions at pressures well below fracture pressure and at concentrations well below those that lead to coal swelling. Further, injection water can be sourced directly from the formation so that the sequestration process can be a closed loop, resulting in minimal formation perturbation. And in this system, sequestration can be carried out in an underpressurized manner, avoiding the need to rely on the integrity of a cap rock to ensure storage. Long term monitoring can be accomplished with downhole pressure gauges to verify that the hydrostatic pressure remains at geologically historical levels. Periodic *in-situ* characterization of formation fluids across a storage field with a downhole reservoir Raman spectroscopy system can verify that the injected CO_2 remains in place. Yet another advantage of coalbed storage is the selectivity of both the water and the coal to preferentially dissolve and adsorb carbon dioxide over other gas constituents such as nitrogen, oxygen, and methane so that unrefined greenhouse gas streams can be accommodated. In essence, the coalbed sink participates in scrubbing CO_2 from mixed flue gas and atmosphere-derived gas streams, providing significant cost reductions when conducting CCS. Finally, the energy intensive gas compression requirements for storage in shallow formations are reduced as compared to conventional sequestration.

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References

Arri, L. E., Yee, D., Morgan, W. D., and Jeansonne, M. W. 1992. Modeling coalbed methane production with binary gas sorption. In *SPE Rocky Mountain Petroleum Technology Conference/Low-Permeability Reservoirs*. SPE-24363. https://doi.org/10.2118/24363-MS

Busch, A., and Gensterblum, Y. 2011. CBM and CO2-ECBM related sorption processes in coal: a review. *International Journal of Coal Geology* 87(2): 49-71. https://doi.org/10.1016/j.coal.2011.04.011

Duan, Z., Møller, N., Greenberg, J., and Weare, J. H. 1992. The prediction of methane solubility in natural waters to high ionic strength from 0 to 250 C and from 0 to 1600 bar. *Geochimica et Cosmochimica Acta*, *56*(4), 1451-1460. https://doi.org/10.1016/0016-7037(92)90215-5

Kidnay, A. J., William R. P., and McCartney, D. G. 1999. Fundamentals of natural gas processing. CRC press, Flow Simulation of Geologic Models. *SPE Res Eval & Eng* **2** (4): 351–367. SPE-57469-PA. http://dx.doi.org/10.2118/57469-PA.

McCreery, R. L. 2005. *Raman spectroscopy for chemical analysis*. John Wiley & Sons.

Myers, G. A., Cookman, A., and Ripepi, N. 2019 "In Situ Logs of Gas Composition of CO2-ECBM Trial in Buchanan Co. VA with Downhole Reservoir Raman System." In *Unconventional Resources Technology Conference, Denver, Colorado, 22-24 July 2019*, pp. 2777-2783. Unconventional Resources Technology Conference (URTeC); Society of Exploration Geophysicists, 2019. SPE URTEC-2019-933-MS. https://doi.org/10.15530/urtec-2019-933

Shi, J. Q., & Durucan, S. 2008. Modeling of mixed-gas adsorption and diffusion in coalbed reservoirs. In *SPE Unconventional Resources Conference/Gas Technology Symposium, Keystone, CO, February 2008*. SPE-114197. https://doi.org/10.2118/114197-MS

Sigfússon, B., Gislason, S. R., Matter, J. M., et al. 2015. Solving the carbon-dioxide buoyancy challenge: The design and field testing of a dissolved CO2 injection system. *International Journal of Greenhouse Gas Control*, *37*, 213-219. https://doi.org/10.1016/j.ijggc.2015.02.022

Snæbjörnsdóttir, S. Ó., Sigfússon, B., Marieni, C., et al. 2020. Carbon dioxide storage through mineral carbonation. *Nature Reviews Earth & Environment*, *1*(2), 90-102. https://doi.org/10.1038/s43017-019-0011-8