

A Special Autoclave Apparatus for Measuring Coal/Gas Properties and Interactions at Elevated Temperatures and Pressures

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Abstract

A custom-designed, 1.2-liter internal volume, autoclave apparatus is being used to determine the densities and viscosities of mixed CO₂-CH₄-N₂ gases at 30-70°C, 1-200 bars and to measure coal expansion and contraction as gas species adsorb onto, and desorb from, coal surfaces. Gas densities and viscosities are quantified precisely and accurately by: (1) transferring known masses of pure gas into the volume-calibrated autoclave at a fixed temperature, (2) inverting the autoclave repeatedly to induce mechanical mixing of the gas via gravity settling of a glass-tube-housed steel ball and two perforated steel disks, (3) recording temperature and pressure after complete gas homogenization has been achieved, and (4) repeatedly measuring the rate at which the steel ball rolls down the glass tube after the autoclave is alternately rotated clockwise and counterclockwise from a horizontal position to shallow angles of equal magnitude but opposite sign. Rates and magnitudes of coal swelling and shrinkage are measured in separate experiments using miniature strain gauges attached to the surfaces of coherent fragments of coal.

Background

Evidence is mounting that rising levels of atmospheric CO₂, caused primarily by combustion of fossil fuels, will lead to rapid global warming. To address this problem, numerous nations are developing plans for lowering CO₂ emissions to the atmosphere. The principal approaches under consideration are: improving energy efficiency; making greater use of alternative sources of energy; and creating economically viable technologies for capture, separation, and long-term storage of CO₂. The latter strategy, which keeps large masses of CO₂ separate from the Earth's atmosphere for hundreds to thousands of years (a concept commonly known as "CO₂ sequestration"), is receiving increasing attention because it permits continued use of high-carbon fossil fuels to generate electrical power while ensuring that CO₂ releases to the atmosphere are reduced.

A potentially attractive means for terrestrial CO₂ sequestration is injection of gaseous CO₂ into underground reservoirs. The primary candidate sites are active or depleted oil and gas fields, deep brine formations, and unmineable, underground coalbeds. To date, studies to determine the feasibility of geologic CO₂ sequestration have focused on oil and gas fields, and deep brine formations. However, four characteristics of deep, unmineable coalbeds make them extremely attractive for wide-scale CO₂ sequestration. (1) Like deep brine formations, unmineable subsurface coalseams are widely distributed across the U.S. (2) When CO₂ is injected into a coalbed, it efficiently displaces adsorbed methane (Figure 1). Therefore, CO₂ sequestration and coalbed methane (CBM) production are synergistic technologies, the additional natural gas produced by CO₂ sequestration serving to offset the costs of CO₂ injection. (3) CO₂ is twice as adsorbing on coal as CH₄, and remains tightly bound to coal surfaces after CH₄ is displaced. Therefore, after being injected into an underground coalbed, there is little risk that sequestered CO₂ will leak to overlying strata, or to the surface. This is an enormous advantage over CO₂ storage in deep saline formations, where escape of gas through caprock is a serious problem. (4) Many unmineable coalseams are located near coal-fired power plants, which are large point sources of CO₂. Thus, minimal pipeline transport of CO₂ would be required to deliver it to a suitable site for subsurface injection. In contrast, oil and gas fields, and particularly deep saline formations, are often far removed from fossil fuel-fired power plants.

CBM recovery, accomplished principally by pumping formation water out of a subterranean coalbed, is a mature technology. In contrast, CO₂-enhanced CBM recovery is a recent concept, which has been demonstrated only in pilot tests. Consequently, opportunities abound in fundamental and applied research aimed toward advancing this rapidly emerging technology.

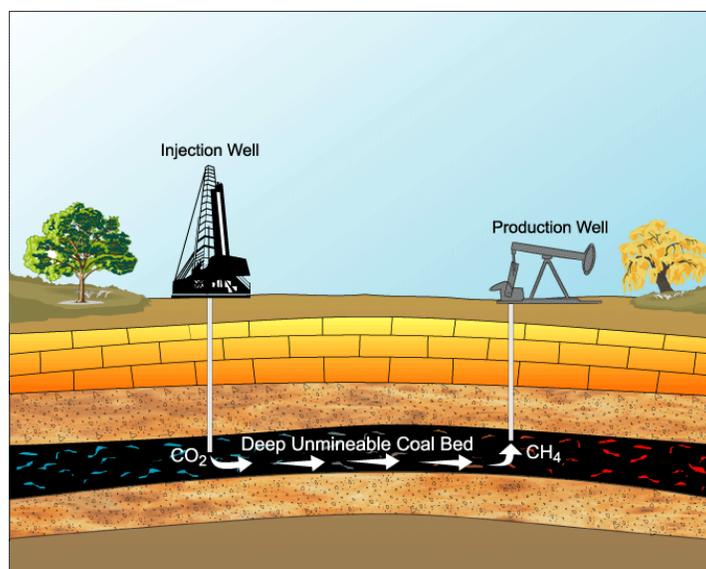


Figure 1. A schematic diagram of CO₂-enhanced coalbed methane (CBM) production.

Purpose

The central purpose of the research is to acquire critically important technical information for assessing the feasibility of sequestering CO₂ in deep unmineable coalbeds. This carbon management technology is currently in its embryonic stages; therefore, vigorous fundamental and applied research programs are needed to fill major knowledge gaps. A particularly important line of scientific inquiry arises from the observations that underground coalbeds are often rich in methane (CH₄), and that CO₂ injected into those formations will adsorb on coal surfaces, causing CH₄ to desorb. Thus, it has been proposed that CO₂ sequestration can be combined with coalbed methane recovery operations to enhance natural gas production. Brought to full fruition, this synergistic coupling could greatly reduce the costs of CO₂ sequestration. However, to enable reliable numerical modeling of CO₂-enhanced natural gas production, the effects of temperature and CO₂(±nitrogen, N₂)-CH₄ mixing on gas pressures, gas viscosities, gas sorption-desorption reactions, and gas sorption/desorption-induced coal swelling and shrinkage, must be known quantitatively. These effects cannot be predicted accurately by modern methods of process modeling and simulation; consequently, experiments must be performed to obtain the required information. Accordingly, this project is focused on data analysis and equation development designed to quantitatively characterize the effects of temperature and CO₂-CH₄ mixing on coal/gas interactions that influence the efficiency and cost-effectiveness of sequestering CO₂ in CH₄-rich underground coal seams.

Approach

The equilibrium densities and viscosities of CO₂-CH₄ mixtures will be determined experimentally at 30-70°C, 10-200 bars, using a custom-designed autoclave apparatus with a 1.2 liter internal volume (Figure 2). The following procedure will be applied to make the measurements: (1) The autoclave is heated to a predetermined temperature in an infrared, forced-air convection oven (Figure 3), then evacuated to a pressure <10 torr with a vacuum pump; (2) The autoclave is then filled with pure CH₄ to a predetermined pressure, and a precalculated mass of (denser) CO₂ injected into the upper section of the autoclave. The CO₂ will sink toward the bottom of the vessel, mixing with CH₄ as it descends. (3) After the partially mixed gas has settled to the bottom of the vessel, the autoclave is inverted to induce gravity settling of any remaining, unmixed CO₂. (4) Step 3 is repeated until complete gas mixing is achieved. Rates of CO₂-CH₄ mixing will be monitored by continuously recording changes in pressure. Because mixed CO₂-CH₄ gases have large positive excess molar volumes at *P-T* conditions near the critical point of CO₂, mingling of the two species is reflected by increases in gas pressure. When a plateau value is reached, complete homogenization of the mixed gas is indicated. (5) After the gas mixture has been

completely homogenized: (i) a final pressure reading is taken to determine the equilibrium density of the gas, and (ii) a viscosity measurement is made using a rolling-ball apparatus. Densities and viscosities measured in this way for wide ranges of temperature, gas pressure, and gas composition can be used to develop mathematical expressions for predicting the fluctuations in gas pressure and viscosity that will occur when CO_2 mixes with CH_4 —either during mixed-gas/coal adsorption-desorption experiments, or in field tests when CO_2 is injected into a methane-saturated subsurface coalbed.



Figure 2. Photograph of the rocking autoclave.

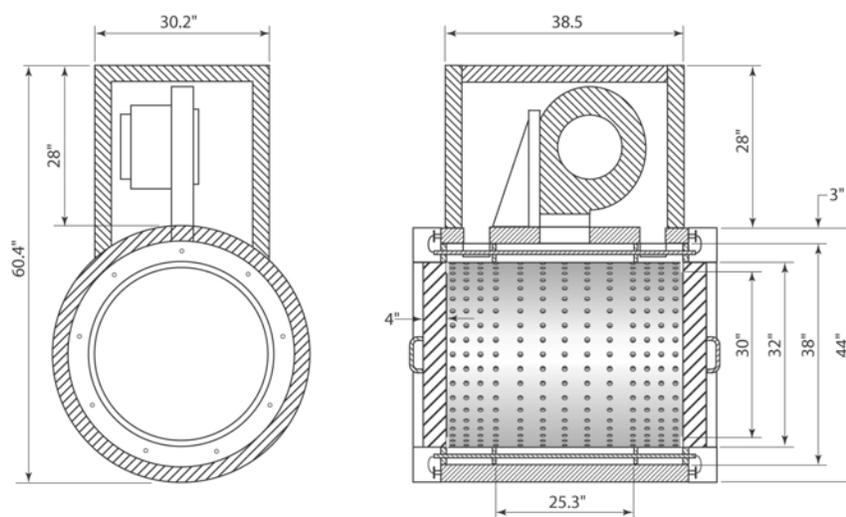


Figure 3. Front and side engineering drawings of the infrared, forced-air convection oven that was built to heat the rocking autoclave to temperatures as high as 100°C .

Status of the Project

Construction of the special autoclave facility is nearly complete, and data collection is scheduled to start in late June, 2003. Initial experiments will be performed at closely spaced temperature intervals between 30 and 40°C, and at a series of pressures between 10 and 200 bars for numerous intermediate gas compositions, to determine the effects of temperature and total gas pressure on the volumetric properties and viscosities of CO₂-CH₄ gases. The array of data produced by the experiments will indicate the changes in formation pressure and gas viscosity that will occur when CO₂ is injected into a CH₄-saturated, subterranean coalbed. The results are likely to show that the *P-V-T* properties and viscosities of CO₂-CH₄ mixtures are highly dependent on proximity to the critical point of CO₂ (located at approximately 31°C and 74 bars). Due partly to the highly nonideal mixing of CO₂-CH₄ gases at 30-40°C, 50-100 bars, large increases in pressure and gas viscosity will occur as CO₂ mixes with CH₄. The magnitudes of these pressure increases and viscosity variations, as a function of temperature, total gas pressure, and gas composition—presently unknown—must be determined precisely and accurately to enable reliable numerical modeling of CO₂ sequestration in CH₄-rich underground coalbeds.

Research conducted for this project in out years will build on the results obtained in FYs 2003 and 2004. Experiments will be performed to quantify the equilibrium densities and viscosities of CO₂-CH₄ gases at 40-50°C, 10-200 bars. In addition, the density data obtained in FYs 2003 and 2004 will be used to interpret the results of mixed-gas/coal adsorption-desorption experiments performed at other laboratories. The rates and extents of CO₂ adsorption on—and CH₄ desorption from—coal surfaces will depend on temperature, total gas pressure, coal rank and composition, and initial mixed-gas composition. The net effects of these variables cannot be predicted accurately before experiments are performed; however, it seems likely that results will indicate that gas adsorption/desorption varies systematically with the thermodynamic mixing properties of the gas from which CO₂ is being extracted, and into which CH₄ is being released. If so, it would then be possible to develop numerical expressions that relate the thermodynamic mixing properties of CO₂-CH₄ gases with the adsorption/desorption that occurs when mixed CO₂-CH₄ gas comes into contact with buried coal. This would be an exciting and highly significant outcome of our research, as numerical expressions of that kind are badly needed to further develop computer codes for predicting the nature and extent of CO₂ capture and retention during and after injection into an underground coal seam.

Future Work

The research performed for this project will lead naturally to subsequent laboratory work aimed at elucidating the effects of injecting CO₂-N₂ mixtures into subsurface coalbeds. This future research

direction stems partly from ongoing efforts to gauge the feasibility of injecting processed (deoxygenated) flue gas, rather than pure CO₂, into deep-seated coal layers. Evaluations of this potential CO₂-sequestration technology are prompted by economics. It is expensive to separate CO₂ from flue gas prior to subsurface sequestration. It is much less expensive to strip oxygen from flue gas and inject the remaining gases (mostly CO₂ and N₂) directly into a coal seam. Significantly, it has already been demonstrated in field tests performed in the San Juan Basin (New Mexico/Colorado) that injecting pure N₂ into a coal layer can greatly enhance flow of CH₄ toward a production well. Therefore, the idea behind injecting mixed CO₂-N₂ gas into a coal seam is that four positive results would accrue: the CO₂ in the injectate would adsorb on coal surfaces, causing CH₄ to desorb; the N₂ in the injectate would lower the partial pressure of CH₄ in the coal seam, inducing additional release of CH₄; the CO₂ adsorbed on coal surfaces would remain tightly bound in the seam after injection (CO₂ sequestration); and finally, the three foregoing processes would—in combination—constitute a coupled CO₂ sequestration/CBM technology that is not only economically viable, but also highly effective in reducing CO₂ emissions to the Earth's atmosphere.

Clearly, to realize the great promise of CO₂+N₂-enhanced CBM recovery, it is necessary to develop a better understanding of CO₂-CH₄-N₂ gas mixing at *P-T* conditions achieved in subterranean coalbeds. This mingling will affect not only formation pressure and mixed-gas/coal adsorption-desorption reactions, but also coal expansion and contraction as gas species adsorb onto, and desorb from, coal surfaces. In this regard, it is noteworthy that our new autoclave facility is well-suited to measurements of coal swelling and shrinkage at temperatures and gas pressures representative of those found in deep, unmineable coalbeds. Therefore, a long-term goal of our research is to determine the effects of temperature, gas pressure, and CO₂(±N₂)-CH₄ mixing on the dimensionality of small, coherent fragments of coal. Coal expansion and contraction will be measured using miniature strain gauges mounted on the surfaces of coal samples. Whenever feasible, 2-3 strain gauges will be attached to a coal fragment in orientations that facilitate determination of expansion and contraction in directions parallel and perpendicular to original bedding. This will indicate the anisotropy in coal swelling/shrinkage that develops due partly to layering of organic and mineral matter in the sample.

Acknowledgments

The research described in this paper is being sponsored by the Office of Fossil Energy, U.S. Department of Energy, National Energy Technology Laboratory, under contract number DE-AC05-00OR22725 with UT-Battelle, LLC.