

Effects of moisture and pressure cycling on sorption capacity of coals

Vyacheslav N. Romanov,* Angela L. Goodman, and Yee Soong

National Energy Technology Laboratory, U.S. Department of Energy,
Pittsburgh, Pennsylvania 15236

Abstract

Variability of the data for CO₂ absorption on coal reported by different research groups suggests that it strongly depends on experimental conditions. We investigated the effects of moisture content and pressure cycling history on temporal changes in the coal sorptive capacity for Pocahontas #3, Illinois #6, and Beulah Zap powders of Argonne premium coals. The samples were tested as received and moisture equilibrated at 96-97% RH and 55°C for 48 hours. It was demonstrated that the magnitude and dynamics of the changes are affected by the coal type (maceral) and rank. Correlation between the sample volume change (swelling/shrinkage) and the variations in absorption-desorption patterns may indicate the relationship between coal structural relaxation and kinetics of CO₂ absorption. Experimental and theoretical methods are proposed to study these effects.

* Vyacheslav N. Romanov (presenting author to whom all correspondence should be addressed): Romanov@or.netl.doe.gov

Introduction

Sequestration of CO₂ in deep unmineable coal seams is an immediately available and technologically feasible option to reduce atmospheric carbon dioxide emissions. However, there is a fundamental lack of understanding of the physical, chemical, and thermodynamic phenomena that occur when CO₂ is injected into a coal seam [White, 2003]. Being able to reliably predict carbon dioxide injectivity is important prerequisite to large-scale project investment. High precision adsorption data are required to accurately forecast the performance of such projects.

In order to be sequestered into coal seams, CO₂ has to be in supercritical state (above 32°C, 7.4 MPa). However, only recently have there been any studies of the extent of adsorption of supercritical carbon dioxide by coal. The apparent excess adsorption of carbon dioxide on dry activated carbon at 45°C reaches a maximum at about 8 MPa and then decreases linearly with increasing gas density [Sudibandriyo et al., 2003]. Coals show even more complex behavior for a few reasons. Physical properties of coal may be anisotropically altered by carbon dioxide [Larsen, 2004] and carbon dioxide or its acidic solution in water may react with the organic or mineral matter present in the coal matrix. Coal is also known to swell in the presence of CO₂ and this may be significant with respect to interpreting data.

There are two main methods currently employed for measuring isotherms on coal: volumetric/manometric and gravimetric techniques. A volumetric apparatus consists of a cell containing the coal sample, a system for controlled admission of the adsorbate gas, and manometers. As the gas is adsorbed, the pressure in the sample cell decreases. The quantity of the gas is determined by the void volume within the cell and the density of the gas that is estimated by using an equation of state (EOS) or the tables of compressibility factors (*z*). The uncertainty in sorbate compressibility value complicates the analysis of the experimental data, especially, for real gas mixtures or gases near critical point.

In gravimetric systems, the adsorbed amount is measured by a microbalance. Before the adsorption isotherm procedure, the sample volume is measured with a helium pycnometer to determine the buoyancy. By direct gravimetric gas density measurements, the

problems associated with equation of state are eliminated but the implicit assumption that the sample's volume remains constant seems absolutely unwarranted for many types of materials (rubber, polymer, coal etc.). Similarly, the volumetric method relies on assumptions about the errors associated with the sample volume changes. In fact, this is the key problem of these methods. [Ozdemir et al., 2003] In either gravimetric or volumetric apparatus, swelling of the coal sample and the corresponding volume changes cannot be directly measured during the test.

Until recently, very limited investigations have been conducted on adsorption of CO₂ on coal beyond the critical point. At the pressures above the critical point, the measured data deviate strongly from the Langmuir model of monolayer-type filling of micropores, in both volumetric and gravimetric systems. Volumetric approach often results in bimodal behavior observed in the vicinity of the critical point, with an apparent local minimum (sometimes even negative, especially for moisture-equilibrated coals [Krooss et al., 2002; Toribio et al. 2004]) around 7-9 MPa, followed by an abrupt rise in the amount of absorbed CO₂. This was interpreted as the result of a swelling effect caused by supercritical CO₂ and enhanced by water. The gravimetric results [Day et al., 2004] also confirm that adsorption by coal under supercritical conditions is in excess of what is predicted by using the Langmuir adsorption curves based on adsorption at lower pressures, indicating that a greater amount of carbon dioxide can be sequestered by coal than previously estimated. However, density-gravimetric measurements reportedly show no evidence of peculiar changes in adsorption with pressure observed in volumetric systems at ~ 8MPa.

In order to better understand these observations, we will analyze the assumptions behind the main test methods:

- Adsorption of CO₂ on coal reduces the gas pressure and increases the mass of the coal sample.
- Sample mass changes are measured by gravimetric isotherm method.
- Pressure changes are used in a volumetric isotherm method to derive the corresponding changes in gaseous mass.
- Compressibility values are tabulated (equation of state) and/or measured directly.

- All traditional methods assume homogeneous properties of the sorbate and constant volume of the sample; usually limited to single gas adsorption.

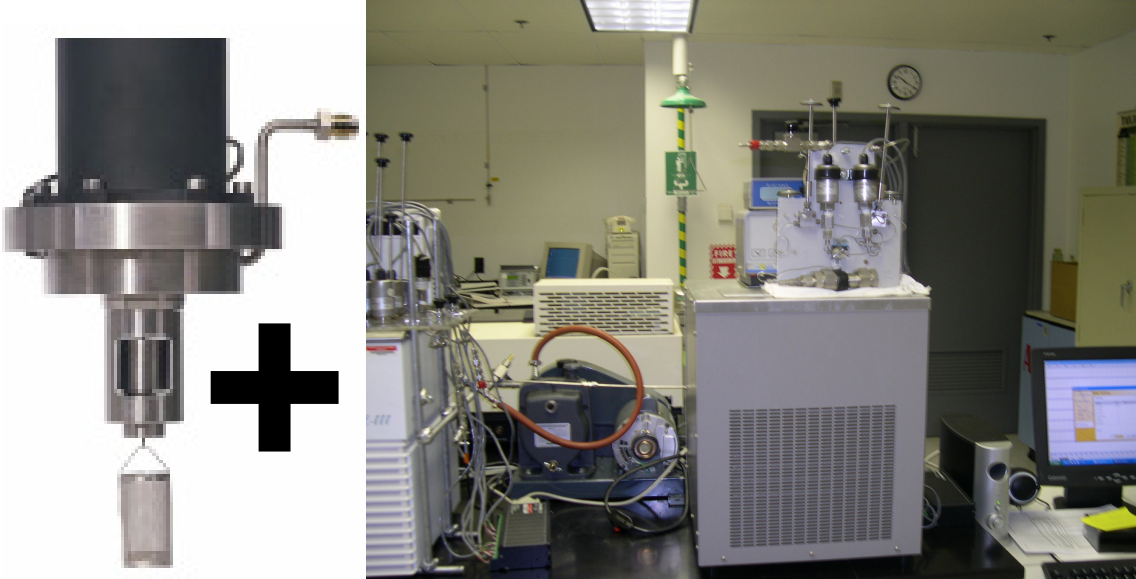


Figure 1. Basic units of the gravimetric apparatus and the manometric/volumetric apparatus.

The combination of the volumetric and gravimetric techniques (Figure 1) on the other hand utilizes the advantages of both and gives a very accurate direct method of adsorption measurement [Tomalla et al., 1994].

Conventional theoretical models used for analysis of experimental data are the Langmuir theory and the Palmer-Mansoori equation [Palmer and Mansoori, 1998].

- Langmuir equation:

$$V = V_{\infty} K_a P_e / (1 + K_a P_e), \quad (1)$$

where P_e is equilibrium pressure, K_a is absorption equilibrium constant ($1/K_a$ is Langmuir pressure), V_{∞} is CO₂ sorption capacity (Langmuir volume), and V is the equilibrium volume of adsorbed gas.

- Palmer-Mansoori model relates matrix shrinkage to porosity, uses elastic moduli to describe the effect of changing pressure on the coal volume.

The problems arising with supercritical carbon dioxide injection are:

- The volume of the coal sample is measured only before and/or after the test. During the test it is an unknown variable and is assumed to fit a certain model behavior.
- Inter-laboratory comparison [Goodman et al., 2004] has demonstrated a wide variability of the data for the same coal observed for the CO₂ pressures above the critical point. The Langmuir model is questioned in supercritical region, due to coal swelling [Ozdemir et al., 2003].
- The Palmer-Mansoori equation does not match historical data.
- Coal swelling/shrinkage is treated within rock mechanics model, ignoring the polymer-like behavior.

CO₂ sequestration in deep coal seams can be strongly affected by the coal rank and other environmental parameters. In order to understand the effects of moisture content, swelling/shrinkage properties of coal, pressure, and temperature on the CO₂ adsorption capacity and CO₂ storage stability, the main objectives of this study are:

1. To measure the sorption capacity of CO₂ on various ranks of coal under in-seam conditions including pressures up to 16 MPa and temperature of 55 °C for gaseous and supercritical CO₂;
2. To estimate the effect of the coal moisture content on the adsorption isotherms;
3. To assess the effect of coal swelling on the adsorption isotherms of CO₂ on coals;
4. To develop a method of in situ measurement of the coal volume changes during the sorption capacity measurement; and
4. To develop a mathematical model for the CO₂ sequestration process in a coal seam.

Experimental

Sorption and desorption behavior of carbon dioxide has been studied on a set of well characterized coals from the Argonne Premium Coal set (Argonne National Laboratory, USA): a low volatile bituminous (Pocahontas #3), a high volatile bituminous (Illinois #6), and a lignite (Beulah Zap). All sorption experiments were performed on approximately 0.5-2.5 grams of the powdered (100 mesh), dried (in vacuum, at 130°C for 24 hours) and moisture equilibrated (at 96% relative humidity and 55°C for 48 hours) coal samples.

The modified version of the ASTM moisture equilibration procedure D 1412 - 99 (55°C instead of 30°C) was adopted for all moist coal tests: the lignite sample that usually requires 72 hours to reach equilibrium was also equilibrated for 48 hours. This procedure was recommended in order to reproduce the moisture content under the reservoir conditions [Mavor et al., 1990]. The sample handling was performed in a positive pressure (dry nitrogen) glove bag to prevent surface oxidation.

We used the NETL-built [Ozdemir et al., 2003] high-pressure manometric/volumetric apparatus (Figure 2) to collect the CO₂ (99.999% purity, Valley Co., Pittsburgh, PA, USA) adsorption isotherm data at 55°C ($\pm 0.1^\circ\text{C}$ and $\pm 1^\circ\text{C}$) and the pressures up to 16 MPa. Gases were pressurized by the ISCO syringe pump (Model 500D). The sample and cells volume determination was done with helium (99.997% purity, Valley Co., Pittsburgh, PA, USA). Evacuation of the gas line and the reference and sample cells was done by the HayVac-2 (HayVac Products Co.) mechanical vacuum pump. Temperature was stabilized by the constant temperature bath from NesLab (Model RTE-111).

Additionally, the gravimetric adsorption isotherm measurements for dry Pocahontas #3 sample under the same conditions have been done with magnetic suspension balance of the Rubotherm GmbH at the Leipzig University, Germany.



Figure 2. High-pressure manometric/volumetric setup used in this study, including the dry nitrogen positive flow glove bag, the constant temperature bath, the syringe pump, and the CO₂ gas cylinder.

We use the excess (or Gibbs) adsorption to interpret our observations, because at high pressures, where the density of supercritical fluid approaches the density of the adsorbed phase, it is more appropriate than the absolute adsorption [Malbrunot et al., 1992; Sudibandriyo et al., 2003].

Results and Discussion

The gravimetric measurements gave a surprising result: negative adsorption values at the pressures above 10 MPa (Figure 3). This was explained by the estimated 45% swelling of the coal sample (Argonne premium Pocahontas #3 coal powder) during the test, which resulted in erroneous buoyancy term based on the He volume measurements prior to the test. The new volume that was determined immediately after the CO₂ adsorption measurements showed some residual swelling (~20%). After correction, the excess adsorption plot strongly deviates from the Langmuir model at the pressures above 8 MPa. Obviously, the above buoyancy corrections are very tentative since the volume measurements were done only before and after the test, rather than during the test. This is a common problem of pure gravimetric and pure volumetric techniques.

Gravimetric (Rubotherm) CO₂ Isotherm at 328 K

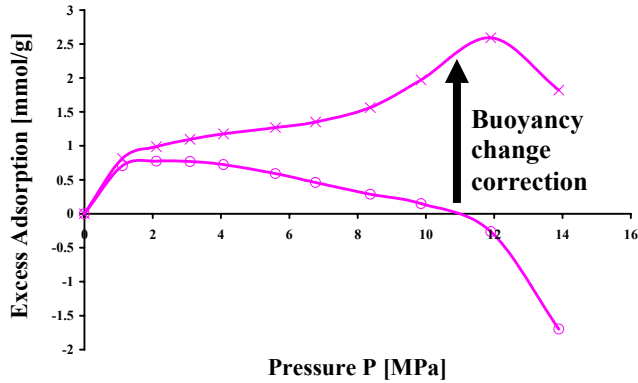


Figure 3. Alternative interpretations of the gravimetric experimental data by the Rubotherm GmbH: a) Excess absorption calculations based on the sample volume measurements before the CO₂ isotherm measurements (lower plot); b) Same isotherm interpretation based on the sample volume immediately after the experiment (upper plot).

We compared the above gravimetric data to the results of our volumetric measurements (Figure 4) for the powdered sample of the same Argonne premium coal (Pocahontas #3). The volumetric adsorption plots exhibit typical mesoporous adsorbent behavior [Gregg and Sing, 1982], similar to the corrected gravimetric data, except for a minor dip at the onset of the supercritical CO₂ pressures, at around 7-9 MPa.

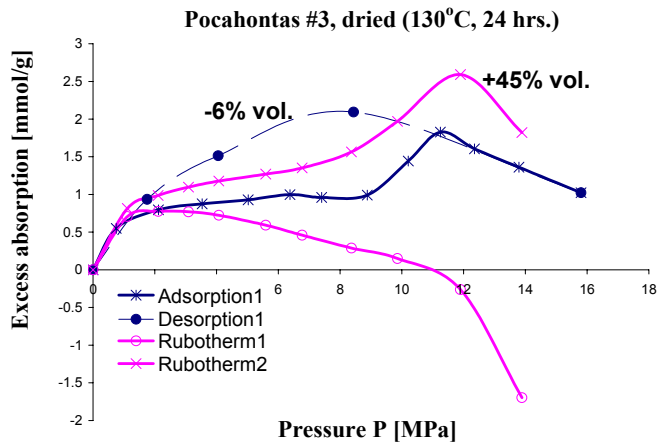


Figure 4. Comparison of the plots of the gravimetric and volumetric data for dry Pocahontas #3 coal. After the volume correction, the gravimetric isotherm is similar to the volumetric data.

Desorption of CO₂ was done in a three-step-catastrophic-expansion mode (into vacuum), similar to comminution process. After each step, the pressure was stabilized for an hour before the data were collected. The sample volume measured after desorption was ~6% smaller than the original volume, which is usually interpreted as shrinkage due to extraction of the volatile matter. Apparent sorption capacity of the coal has increased dramatically in the above procedure, which could also be attributed to either accessible

surface area increase or the void volume increase or both, since the breaking of the coal particles into smaller pieces may decrease the “dead” (envelope) volume of the sample and thus increase the accessible surface area.

Repeated adsorption measurements confirmed the correlation between the temporal sample volume changes and adsorption capacity, especially for the CO₂ pressures less than 8 MPa (Figure 5). The second and third adsorption isotherms were run immediately after the first desorption and were consistent with the first desorption data. The fourth adsorption experiment was run six weeks later, when the sample’s envelope volume measured by helium pycnometry almost relaxed to its original value. It caused the gas phase excess adsorption return to the original values as well. However, the subsequent injection of supercritical CO₂ caused the adsorption trend to break up from the original plot (first adsorption) half way to the post-comminution isotherms. We suggest that after six weeks the structural relaxation of coal was still incomplete. Partial restoration of the hydrogen-bond cross-links that contribute to elastic forces opposing the swelling of coal was sufficient to prevent carbon dioxide molecules from reaching the excessive adsorption sites. However, the supercritical carbon dioxide fluid is capable of reaching some of the hidden adsorption sites by exerting additional osmotic pressure due to thermodynamically non-equilibrium condition inherent to the injection process around the critical pressures. This can also increase the pores interconnectivity and void volume.

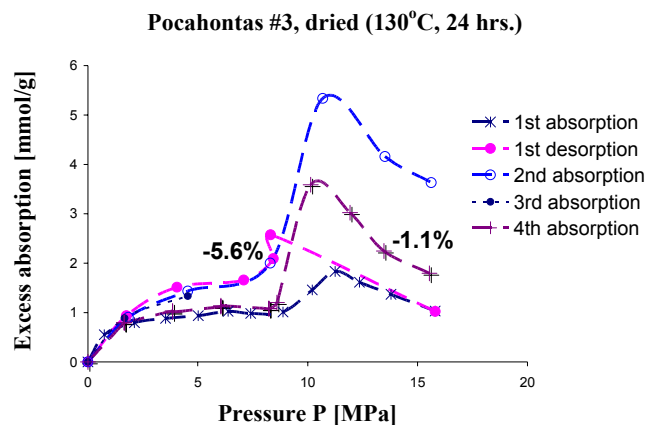


Figure 5. Effects of coal volume changes on sorption capacity. After the 1st (catastrophic) desorption, the envelop volume decreased by 5.6% and the sorption capacity increased by 50 to 150%. Six weeks later (4th absorption), the coal properties partly returned to the original values.

For volumetric study of the effects of moisture on adsorption capacity, we selected three types of Argonne premium coal powders representing a wide range of carbon content and corresponding degrees of hydrophobicity (Table 1). An additional small sample of Pocahontas #3 was used to validate the method by distinguishing between the sample specific and the instrument specific effects. Unlike the previous study, the bath temperature oscillated between 54°C and 56°C with a period of one hour.

Table 1. Parameters of the moisture equilibrated Argonne premium coal samples.

	Pocahontas #3 (small)	Pocahontas #3	Illinois #6	Beulah Zap
Mass	473 mg	2.197 g	2.164 g	2.615 g
H ₂ O	-	2% wt.	4% wt.	20% wt.
Shrink	-	<1% vol.	6% vol.	2% vol.

Desorption of the Illinois #6 sample was conducted by the three-step-catastrophic-expansion but the Pocahontas #3 and Beulah Zap samples were brought to zero CO₂ pressure by more gradual decompression. The resulting changes in the envelope volume are consistent with the non-equilibrium excessive surface area hypothesis. The moisture level does not seem to have any significant effect on the volume changes but it does affect the sorption capacity to the gas phase CO₂ (Figure 6).

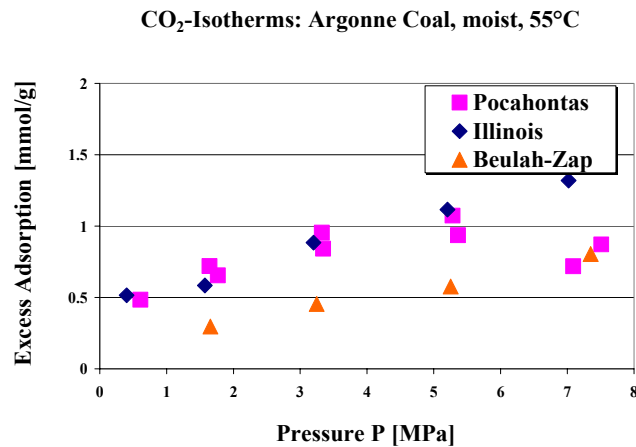


Figure 6. Gas phase CO₂ adsorption on moisture equilibrated coals.

The only coal that showed a dip near the critical pressure was Pocahontas #3 (both samples). This dip was more significant than the one previously observed for dry Pocahontas #3 at nearly constant bath temperature (Figure 7). At the same time, the following rise in the excess adsorption after transition to supercritical phase was also much steeper during the test with the larger bath temperature swings. This is another indication of non-equilibrium nature of the adsorption process.

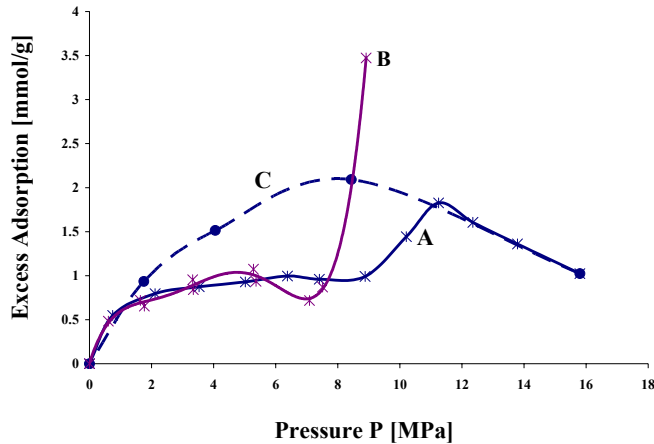


Figure 7. Anomalous adsorption behavior of the Pocahontas #3 coal powder near the critical pressure: A/C = sorption / desorption isotherms, B = sorption under the oscillating temperature conditions. The “dip” and rise become more prominent as the temperature oscillations increase.

If the pressure, temperature, temporal etc. conditions are reproduced, the excess adsorption isotherms should be the same regardless of the technique (gravimetric or volumetric) employed as long as the volume is determined by the same gas. Various types of hidden volumes are depicted in Figure 8. Should the volume V be inaccessible to helium, for instance, but become partly permeable to CO_2 , than it is treated as the sample's envelope volume in either adsorption measurement method. Any amount of CO_2 making its way to this volume is missing from the void volume in the manometric/volumetric method and is erroneously attributed to excess adsorption. By the same amount the gravimetric buoyancy is over-corrected and it is still attributed to excess adsorption. Vice versa, if this volume is accessible to helium but not to CO_2 , then the difference between the adsorbate density inside of it and the quasi-equilibrium density in the void volume of the sample cell results in equal understatement of the excess adsorption in both methods.

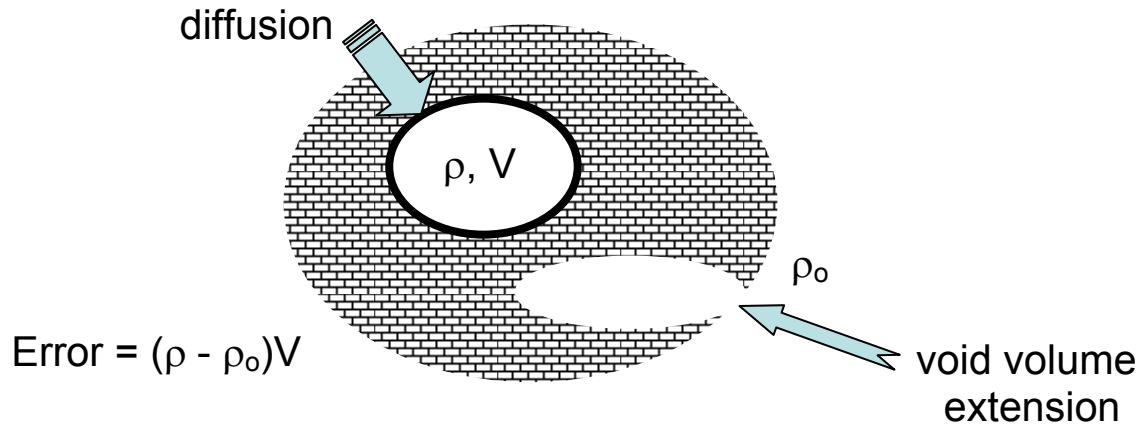


Figure 8. Illustration of the open and closed voids in the coal network.

This can be shown precisely by mathematical equations for volumetric (schematic diagram shown on Figure 9) and gravimetric methods. The excess adsorption on the sample of mass w is calculated in volumetric method as the difference between the CO₂ molar amount decrease in a reference cell (volume V_R) and the molar amount increase in the void volume of a sample cell (volume V_0), according to Equation 2. Compressibility z can be estimated from equation of state (EOS). The underlying assumption is that the void volume before and after CO₂ injection is the same. Similarly, the buoyancy correction in gravimetric method relies on the assumption that the sample's envelope volume does not change (Equation 3). The Equation 4 shows that the errors in excess adsorption determination by volumetric and gravimetric techniques caused by the uncertainty of the sample volume are identical.

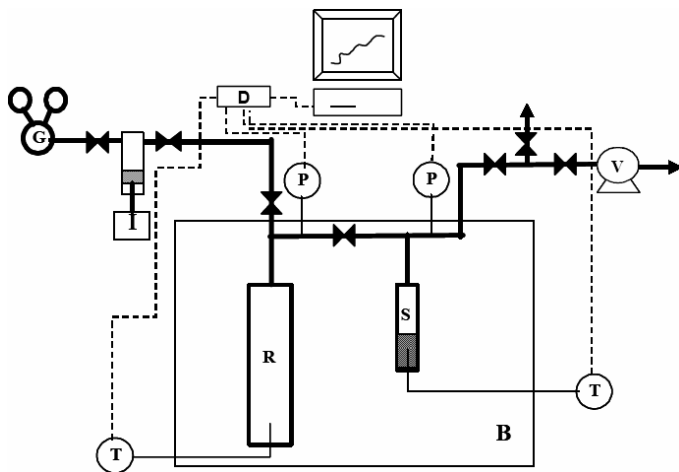


Figure 9. Schematic diagram of the manometric / volumetric apparatus: R = reference cell, S = sample cell, B = constant temperature bath, T = thermocouple, P = high accuracy pressure transducer, V = mechanical vacuum pump, G = gas regulator, D = data logger.

$$w \cdot \Delta_v n^{ex} = \left(\frac{P_{R_i}}{z_{R_i}} - \frac{P_{R_f}}{z_{R_f}} \right) \cdot \frac{V_R}{RT} - \underbrace{\left(\frac{P_{S_f}}{z_{S_f}} - \frac{P_{S_i}}{z_{S_i}} \right)}_{\text{error}} \cdot \frac{V_o}{RT} \quad (2)$$

$$w \cdot \Delta_g n^{ex} = \frac{\Delta_a m}{\mu} = \frac{\Delta_g m - \rho \cdot V_s}{\mu} \quad (3)$$

$$\frac{-\rho \cdot \Delta V_s}{\mu} = \underbrace{\frac{-P_{S_f}}{RT \cdot z_{S_f}} \cdot \Delta V_s}_{\Delta V_s \approx -\Delta V_o} \approx - \left(\frac{P_{S_f}}{z_{S_f}} - \frac{P_{S_v}}{z_{S_v}} \right) \cdot \frac{V_o}{RT} \quad (4)$$

In order to eliminate this error, we need to continuously monitor the volume changes during the test. This can be done if we combine two techniques into volume-gravimetric method and use a binary gas mixture of CO₂ and helium (Figure 10). By using the simultaneous pressure and density measurements one can determine the partial pressures of the two components as long as their molar masses are very different [Schein and Keller, 2003]. Once the helium pressure is known, the void volume and hence the sample's envelope volume can be computed by the standard volumetric procedure.

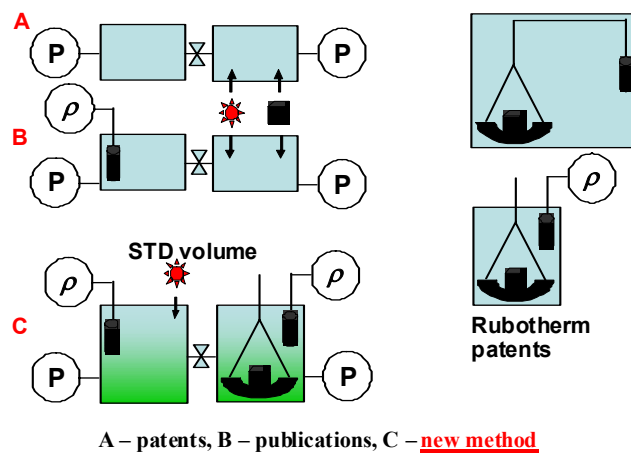


Figure 10. Development of the volume-gravimetric technique.

Since the sampled pressure and density have to be representative of the entire void volume, the volume-gravimetric apparatus inevitably requires a static mixer incorporated into the gas lines of the traditional volumetric apparatus (Figure 11). The mass measurements have to be done during shut-off periods of the mixer to avoid buoyancy errors related to flow of the CO₂/He mixture.

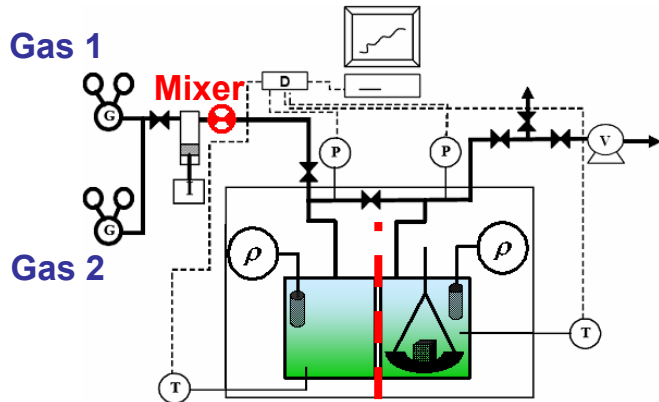


Figure 11. Schematic diagram of the volume-gravimetric apparatus. The reference and the sample cells should be separated by 0.5 m to minimize magnetic interference. The mixer is required for homogeneous mixing of the fluids.

The common issue of the volumetric techniques is the need for a very accurate EOS application to analysis of the experimental data. This becomes a problem if the physical properties of the adsorbate are not uniform or far from the equilibrium state. We suggest using the samples with significantly differing masses to calibrate the method.

In our experiments with oscillating temperature, we compared the excess adsorption isotherms of the typical (2.197 g) and small (473 mg) samples to filter out the signal contribution that was not proportional to the sample size. The corresponding equation of state was compared to Span and Wagner (1996) EOS (Figure 12).

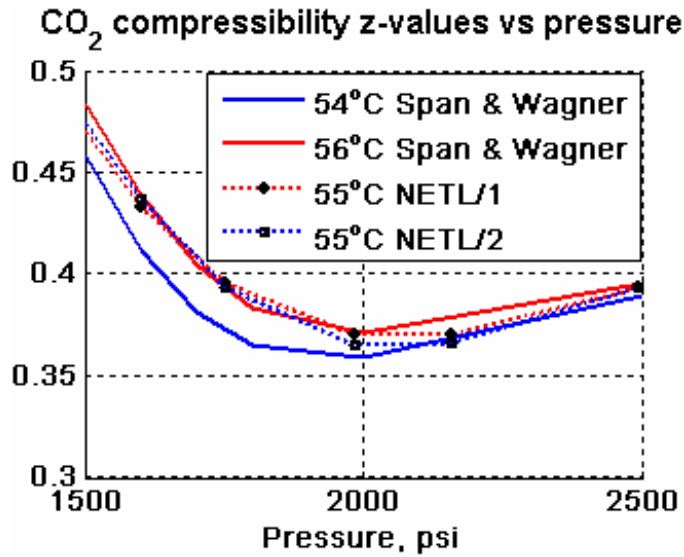


Figure 12. Experimentally determined effective equations of state corresponding to uneven size sample calibration of the system with oscillating temperature.

A possible explanation of the observed deviation from the equilibrium EOS is that at the pressures above 10 MPa the lower temperature entropic equilibrium (for simplicity, we may call it “condensation”) is reached slower than at higher temperatures (“evaporation”), resulting in slightly higher than expected effective compressibility values. Application of the effective EOS to Illinois #6 and Beulah Zap isotherms was not successful, which may indicate that the sample properties such as heat capacity, swelling, etc. are important as well. The corrected absorption isotherm for Pocahontas #3 is very similar to the corrected gravimetric isotherm for the same coal powder (Figure 13), which confirms that supercritical CO₂ region strongly deviates from the Langmuir-type isotherm. Still some research groups report that the Langmuir-type behavior (without hysteresis) can be observed at very high CO₂ pressures [Goodman et al., 2004].

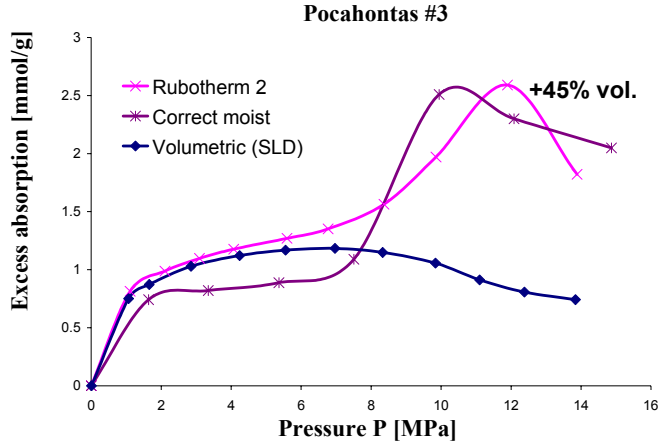


Figure 13. Volume-corrected gravimetric and temperature-corrected volumetric data versus Langmuir-type (enhanced form) isotherm [Sudibandriyo et al., 2003].

Langmuir theory assumptions:

- The entire surface has the same activity for adsorption.
- No interaction between adsorbed molecules.
- The same mechanism of adsorption for all molecules.
- Extent of adsorption is less than one complete monolayer.

However, the assumption of an energetically homogeneous surface is in doubt for coal [Clarkson and Bustin, 1997]. The assumptions of no interaction between the molecules and of a single monolayer adsorption mechanism were challenged even at pressures as high as 5 MPa [Clarkson and Bustin, 1999], where Dubinin's pore-filling model [Clarkson et al., 1997] can be a better fit for adsorption isotherm. The problems with the Langmuir isotherm model are manifested in the failure of the Palmer-Mansoori (1998) equation to match the historical data [Palmer, 2004]. This equation relies on the Langmuir term to describe the strain related to changes in porosity of the coal:

$$\frac{\Phi}{\Phi_0} = 1 + \frac{c_m}{\Phi_0} (P - P_0) + \frac{\varepsilon_1}{\Phi_0} \left(\frac{K}{M} - 1 \right) \left(\frac{P}{P_L + P} - \frac{P_0}{P_L + P_0} \right) \quad (5)$$

$$c_m = \frac{1}{M} - \left(\frac{K}{M} + f - 1 \right) \gamma \quad (6)$$

$$\frac{M}{E} = \frac{1 - \nu}{(1 + \nu)(1 - 2\nu)} \quad (7)$$

where c_m = matrix compressibility; E = Young's modulus; $f=0$ to 1 ; K = bulk modulus; M = constrained axial modulus; P = reservoir pressure; P_0 = initial reservoir pressure; P_L = Langmuir pressure constant; ν = Poisson's ratio; ε_l = strain matched to Langmuir isotherm (max at $P=0$); γ = grain compressibility; Φ = final porosity; Φ_0 = initial porosity.

Carbon dioxide is known as a good solvent. Under supercritical conditions, it can induce the transition of coal from glassy to rubbery state [Brenner, 1984]. This precludes the above rock mechanics approach. The Flory-Rehner equation derived from the equilibrium polymer swelling theory [Flory, 1953] treats coal as a loose network dissolving (mixing) in CO_2 . The Gibbs free energy of mixing is balanced by the elastic energy (rubber theory):

$$-\left[\ln(1-\nu_2) + \nu_2 + \chi_1 \cdot \nu_2^2\right] = \nu_1 \cdot n \left[\nu_2^{\frac{1}{3}} - \frac{\nu_2}{2} \right] \quad (8)$$

where $\nu_2 = 1/Q$, volume fraction of polymer in the swollen mass; ν_1 = molar volume of the solvent; χ_1 = Flory-Huggins polymer-solvent interaction parameter; $n = \rho_{dry} / \langle M_c \rangle$, $\langle M_c \rangle$ = average mol. weight between crosslink points.

The strain relaxation is driven by electro-chemical potential, $\frac{d\varepsilon}{dt} = \frac{c \cdot \Delta\mu}{\eta}$ [Cody and Botto, 1994]:

$$\varepsilon = \Pi J \left(1 - e^{-\frac{K}{\eta} t}\right) + \varepsilon(\phi^*) \quad (9)$$

where $K = \phi (\partial\Pi/\partial\phi)$, η = bulk viscosity; ϕ = volume fraction of the network; J = network compliance, Π = osmotic pressure.

This approach allows us to explain the variability of experimental data for coal adsorption isotherms by non-linear relationship between the pressure and the coal network volume changes. However, direct application of the polymer theory to coals is still under discussion, because the experimental values of $\langle M_c \rangle$ appear to be low [Veytsman and Painter, 1997].

SUMMARY

Coal swelling becomes a major factor under supercritical CO₂ conditions, but moisture effect is not so significant. Langmuir model and Palmer-Mansoori equation are no longer justified. Swelling kinetics can be quantified experimentally by density-volumetric technique and theoretically by coupling solvent diffusion to network relaxation.

The effects of coal swelling can be analyzed within polymer-like effective excluded volume network model (random phase approximation) developed by Flory and Huggins, as well as the Flory-Rehner hypothesis that the cross-terms between the elastic and the mixing parts of free energy can be ignored.

Micropore ('unoccupied' volume)



Figure 14. c^* theorem: "blob" model of a swollen densely connected network (excluded volume effects).

Excluded volume ('dangling' end)

Challenges of the polymer approach:

- Associated or colloidal structures [Takanohashi et al., 1995] (energetic response to load) versus macromolecular hypothesis or a cross-linked network [Veytsman and Painter, 1997] (at least part of response, entropic). This can be probed by examination of temperature dependence of compression modulus.
- For the swelling of lightly cross-linked networks it is not clear if the assumption of the deformation of elementary chains of the network affine with macroscopic deformation of the sample is realistic (except for small deformations).
- Topological rearrangement or disintegration of cross-link junctions and the c^* blob model of de Gennes (1979): the number of statistical segments between junction points is small and energetic terms have to be taken into account.

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