

Measurement techniques for carbon dioxide sorption capacity on various coal samples: critical review

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Abstract. Underground carbon sequestration is proposed as a geologic disposal technique for the long-term storage of CO₂ emissions to mitigate climate change and air pollution. Coal bed seams have large CO₂ adsorption capacity, long time CO₂ trapping and extra enhanced coal-bed methane recovery (CBM). However, CO₂ sorption capacity is one of significant steps required to be determined accurately in any feasibility evaluation of carbon sequestration. Hence, in lab scale, there are three methods for CO₂ adsorption capacity measurements namely manometric/volumetric, gravimetric and new capsule techniques for gas sorption on variety of sorbents. The manometric and volumetric methods require accurate determination of cell and void volumes and suitable equation of state (EoS). The gravimetric method requires a very accurate sensitive balance and less buoyancy effect and it is the best technique for small amounts (milligrams) of sorbents and the adsorption equilibrium can be mentored. Among all gas adsorption measurement techniques, the newly developed method “capsule method” exhibits the highest CO₂ adsorption capacity on Polish coal by 4.08 mmol/g because capsule method that directly measures CO₂ uptake of solid coal matrix cylinders, without the application of the equation of state (EoS) for CO₂ or volumetric corrections. The main advantage of capsule method is that it is independent of any Equation of State (EoS), and it has no volumetric effects or impurities distort the shape of the gas adsorption isotherm. The disadvantage of capsule method is time-consuming and it is not easy to implement.

1. Introduction

The major excessive emissions of green house gases (GHG_s) are emissions of carbon dioxide (CO₂) and it is one of the main causes of the global warming and air population. However, the major source of anthropogenic CO₂ emissions is the combustion of fossil fuels mainly coal to generate electricity. Therefore, mitigation and controlling CO₂ emissions are essential to address the greenhouse gases consequences [1]. Though at present separating and capturing CO₂ from the flue gas is costly and requires further research [2]. Hence, it is generally agreed that sequestering CO₂ in deep geological formations holds the most viable options for CO₂ large-scale storage of the greenhouse gas.

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Carbon sequestration are including storage of CO₂ in deep sandstone formations, deep saline aquifers, gas-rich shales, active or depleted oil and gas fields with enhanced oil recovery (EOR), deep unminable coal bed seams, methane hydrate formations, salt caverns, other geological formations, or the ocean [2-5]. Furthermore, it is a widely accepted that deep unminable coal bed seams can be used as unconventional gas reservoirs for CO₂ sequestration [6]. It is estimated that the CO₂ storage capacity of unmineable coal bed seams in the worldwide is between 140 and 3000 Gt [6], which could simultaneously displace 1.45×10^{13} m³ of methane reserve [7] and it is reported that one ton of coal can adsorb about 30–35 m³ of CO₂ at pressures in excess of 5 to 8 MPa [8].

According to G. X. Wang et al [9] predicted that coal bed seams for CO₂ storage with enhanced coal bed methane (CBM) recovery are usually at the depth of 500–1500 m, with the corresponding reservoir pressure of 5–15 MPa and temperature of 30–100°C. In 2007, N. Siemons et al. [10] reported that the target coal seams for CO₂ injection in Europe is usually at great depth, with correspondingly high reservoir pressure of 6–15 MPa and temperature of 35–50°C. In 2010, J. He et al. [11] reported that the temperatures of potential coal seams typically range from 27–52°C and the depths of the coal seams are greater than 756 m, CO₂ sequestration occurs at supercritical condition ($T_c = 31^\circ\text{C}$, $P_c = 73.8$ bar). Hence, higher pressure maintains more gas to remain adsorbed in place meanwhile higher temperature increases the kinetic energy of the system and enables gas molecules to stay in free-state rather than in the adsorbed state [1].

Economically, some of deep coal bed seams may be infeasible for mining due to inadequate coal seam thickness, poor continuity of the area, or adverse geology. However, under the proper conditions, these coal seams can provide adequate sites for CO₂ storage [11]. Hence, the starting step of evaluating the feasibility and capacity of coal bed seams for CO₂ sequestration is to simulate the coal bed seams conditions in laboratory scale. In laboratory scale, one of the significant parameters is the absolute CO₂ storage potential of the coal matrix and it is the sum of the adsorption and pore-filling capacity.

In the lab scale, there are three techniques to measure the CO₂ sorption capacity on coal samples namely manometric/volumetric, gravimetric methods and there is another newly developed method called capsule method. The manometric/volumetric method is most reliable for CO₂ adsorption capacity measurement at above supercritical pressure and temperature condition. The objectives of this work are to present the current methods for gas sorption on different sorbents and to discuss their advantages and disadvantages and to compare the gas sorption on various coal samples and the experimental results of CO₂ adsorption measurements on variety of coal specimens.

2. Methods of gas adsorption measurement

CO₂ adsorption capacity measurement is one of the major steps in assessing the CO₂ potential storage in any geosequestration reservoirs. The volumetric/ manometric and gravimetric are common techniques where have been utilized to measure gas adsorption isotherms of porous materials such as coal that are flooded with CO₂ under unconfined, isostatic conditions. These techniques are usually applied to determine the Gibbs Surface Excess (GSE), i.e. the amount of adsorbed CO₂ present in the coal in excess of the free, bulk phase present at constant pressure and temperature [22]

The manometric/volumetric method requires accurate determination of cell and void volumes. The amount of gas sorbed is recorded by pressure readings (manometric method) or pressure or volume readings (volumetric method). For high temperatures (27 – 427°C) and for corrosive gases and high pressures (50 – 300 bars) the use of metallic sealings (steel, silver) always recommended and the amount of the sample depends on the sample cell. The manometric method is most widely used for determining gas sorption capacities on coal [12, 13, 16]. The volumetric method is similar to the manometric method [14–16].

In manometric method as shown in Figure 1, the amount of sorbed gas is measured by reading gas pressure. The excess sorption mass ($m_{\text{excess}}^{\text{CO}_2}$) is the difference between the mass of gas that has been transferred into the measuring cell up to a given pressure step and the “non-sorption” reference mass [16].

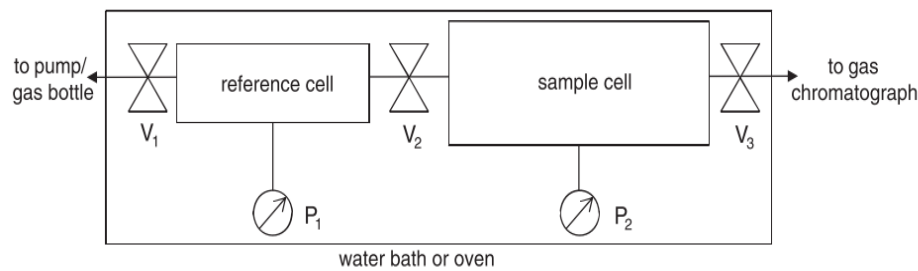


Figure 1. Schematic diagram of manometric sorption setup, V denotes valves and P denotes pressure transducers [16].

$$m_{\text{excess}}^{\text{CO}_2} = m_{\text{transferred}}^{\text{CO}_2} - V_{\text{void}}^0 \cdot \rho^{\text{gas}}(T, p) \quad (1)$$

The mass transferred from the reference cell into the measuring cell during N successive pressure steps is given by:

$$m_{\text{transferred}}^{\text{CO}_2} = \sum_{i=1}^N V_{\text{ref}} \cdot (\rho_i^{\text{gas}}(p_i, T) - \rho_{i-1}^{\text{gas}}(p_{i-1}, T)) \quad (2)$$

The void volume (V_{void}^0) of the sample cell is determined by expansion of a “non-sorbing” gas, which is typically helium. Helium densities are calculated using the equation of state (EoS) by using the Vander Waals equation with a and b parameters. This procedure also provides the skeletal volume (V_{sample}^0) and the skeletal density (ρ_{sample}^0) of the sample. For gas sorption isotherms, the void volume multiplied by the density of the gas (or supercritical) phase ($V_{\text{void}}^0 \cdot \rho^{\text{CO}_2}(T, p)$), yields the “non-sorption” reference mass, i.e. the amount of gas (supercritical fluid) that would be accommodated in the measuring cell if no sorption takes place.

In volumetric method, the amount of sorbed gas is measured by reading gas pressure or gas volume and the schematic diagram of this method is shown in Figure 2. In order to measure gas sorption amount with volumetric method, volume of measuring system has to be measured precisely at first. Then, adsorption amount is calculated from the change of gas pressure inside the measuring system by means of ideal gas equation. Sample handling is easier in volumetric method than in gravimetric method and the thermal equilibrium reaches rapidly in volumetric method. The amount of gas injected $m_{\text{gas}}^{\text{injected}}$ can be determined from the pump position as it moves forward. Therefore [16]:

$$m_{\text{gas}}^{\text{adsorbed}} = m_{\text{gas}}^{\text{injected}} - m_{\text{gas}}^{\text{unadsorbed}} \quad (3)$$

While

$$m_{\text{gas}}^{\text{injected}} = \left(\frac{p \Delta V M}{Z R T} \right)_{\text{pump}} \quad (4)$$

$$m_{\text{gas}}^{\text{unadsorbed}} = \left(\frac{p V_{\text{void}} M}{Z R T} \right)_{\text{sample cell}} \quad (5)$$

Here m denotes the mass of gas, p is pressure, T is temperature, M is the molar mass of the gas species, Z is the compressibility coefficient of the pure gas species and R is the universal gas constant. ΔV is the volume change in the pump and V_{void} is the volume of the free gas in the sample cell.

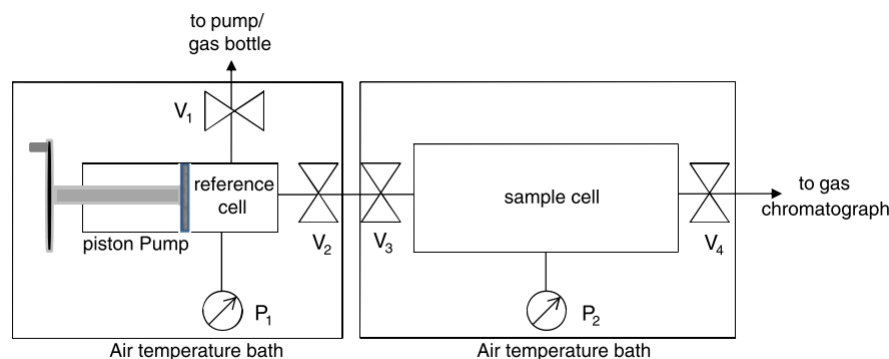


Figure 2. Schematic diagram of volumetric gas sorption setup [16, 17].

In most sorption systems, the excess sorption of the coal sample is the extra amount of gas in the cell than would be present if the coal could not interact with the gas. In volumetric technique, the measurement requires accurate values for the volume of the sample cell, the volume of coal in the sample cell and, in volumetric systems, and the temperature of the system. The volume of the coal is normally calculated from the helium density of the coal; i.e. the density of the coal that is inaccessible to helium [21].

The main advantage of volumetry/manometry is that simple easy to handle. However it needs accurate measurement of the reference and samples. The amount of sorbent material usually needed several grams if only tiny amounts (milligrams) of the sorbent are available then gravimetric measurements strongly recommended. Approach to equilibrium, gas adsorption may last for second, hours or sometime even days and months. The disadvantages of volumetric/manometric adsorption experiments do not give information on the kinetics of the process and small amounts of adsorbent (several milligrams) have shown to be ineffective. They are not practical at extreme low or high pressures as pressure measurements in these regions becomes difficult and accurate of equation of state (EoS) of the sorption gases are not always available [17]. Furthermore, swelling of the coal upon equilibration with CO₂ produces a substantial error in corrections made for the free, bulk phase present in the pores. The reliability of Helium pycnometry as a method to correct for the free, bulk phase (volumetry/manometry) may be questioned, because Helium (He) and CO₂ may not fill the same pore space in coal, and because the probe gas He itself may adsorb to the coal slightly. The thermo-physical properties of pure CO₂ near the critical point, as predicted by the equation of State (EoS), are extremely sensitive to the presence of chemical impurities, in particular to species that are extracted from coal by supercritical CO₂ [22].

In gravimetric method, the amount of sorbed gas is measured by reading sample (sorbent) gravity at constant pressure by means of an accurate balance and less buoyancy effect with the sample either suspended mechanically or by magnetic coupling across the wall of a high-pressure vessel as shown in Figure 3. The maximum amount of amount of adsorbent material is 25g and the temperature ranges 20-250°C and pressures up to 500 bar [18-20].

The excess sorption is determined from the weight change (apparent mass change) of the sample ($\Delta m = m_{\text{measured}}(T, p) - m_{\text{sample}}^0$) recorded during individual sorption steps, where m_{sample}^0 is the original sample mass.

The excess sorption is derived from its apparent weight change by a buoyancy correction based on the skeletal volume (V_{sample}^0) of the sample, corresponding to the same reference state as in the manometric procedure. The determination of the skeletal density or volume is performed with helium. The excess sorbed mass is then given by:

$$m_{\text{excess}}^{\text{gas}} = \Delta m + V_{\text{sample}}^0 \cdot \rho_{\text{gas}}(T, p), \text{ or} \quad (6)$$

$$m_{\text{excess}}^{\text{gas}} = \Delta m + \frac{m_{\text{sample}}^0}{\rho_{\text{sample}}^0} \cdot \rho_{\text{gas}}(T, p) \quad (7)$$

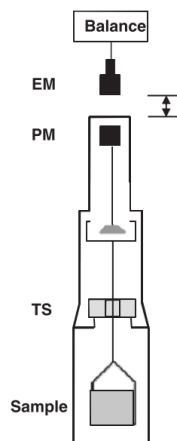


Figure 3. Schematic diagram of magnetic suspension balance (MSB). EM = electro magnet; PM = permanent magnet; TS = titanium sinker [18].

The advantage of gravimetry when compared to volumetry/manometry system is that with gravimetry it is possible to observe the approach to equilibrium during the adsorption process at the balance's data display. Therefore, one can choose arbitrarily a certain small fraction of the pure sorbent sample's mass and a certain time interval and define technical adsorption equilibrium of the system. The main disadvantages of gravimetric are the buoyancy effects, the construction of gravimetric system are costly and high sensitivity to external surrounding environment. Despite attempts made to enhance the accuracy of GSE methods in coal-CO₂ systems, these issues are extremely difficult to resolve. Thus, there is an obvious demand for an independent method to determine CO₂ uptake by coal [22].

Therefore, in 2011, Hol et al. [22] fabricated a new, direct method of measuring the uptake of CO₂ by coal (i.e. by sorption plus pore-filling). The description of the capsule method, the ductile metal capsule is placed in the compaction cell using a capsule holder as shown in Figure 4. A cylindrical coal sample, 4 mm in diameter and 4 mm in length, is jacketed in a tightly fitting, annealed gold capsule and exposed to CO₂ at constant pressure and temperature. Sorption induced swelling of the sample is accommodated by ductile deformation of the capsule. Once the coal is saturated, the capsule is sealed by mechanical loading and the external CO₂ pressure removed. This allows the CO₂ to desorb from the coal and flow into an Al-foil bag attached to the capsule. The volume of the bag, and hence the amount of CO₂ stored in the coal sample, is determined using the Archimedes method.

While the capsule method is time-consuming and not easily executed, the advantage is that it is independent of any Equation of State (EoS), and that no volumetric effects or impurities distort the shape of the isotherm.

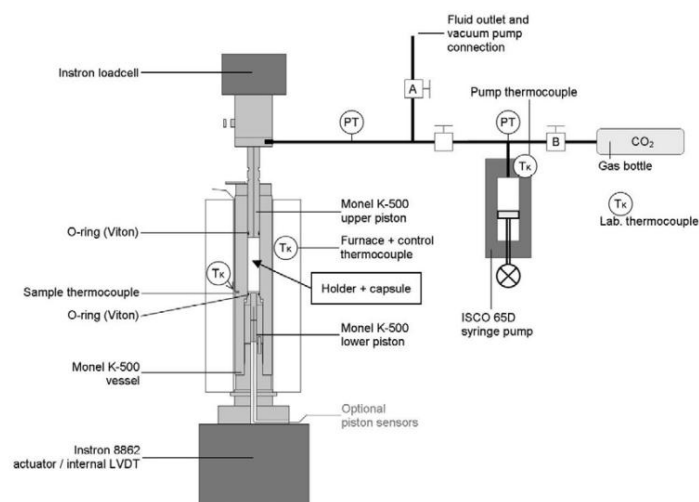


Figure 4. Schematic diagram of capsule method [22, 23].

To calculate the total CO₂ uptake of the samples, they first determined the trapped CO₂ volume by subtracting the empty capsule/ bag volume from that measured in the inflated state. The volume of CO₂ trapped in the bag at ambient conditions (V_{bag} , ml) was then multiplied by the density of pure CO₂ (ρ_{CO_2} in mmol ml⁻¹) at the ambient conditions (P, T -ambient) pertaining during weighing, and the result divided by the mass of the sample m_0 in grams, to obtain [23]:

$$N = \frac{V_{\text{bag}} \cdot \rho_{\text{CO}_2}(P, T - \text{ambient})}{m_0} \quad (8)$$

Where N is the total CO₂ uptake in $\text{mmol g}^{-1}_{\text{coal}}$ or $\text{mol kg}^{-1}_{\text{coal}}$

This newly developed technique called capsule method that directly measures CO₂ uptake of solid coal matrix cylinders, without the application of the equation of state (EoS) for CO₂ or volumetric corrections of any kind and it can determine the uptake of any adsorbate by any (swelling) adsorbent, including shale and clay cap rocks.

3. CO₂ adsorption capacity on various coal samples

In lab scale, the manometric, volumetric and gravimetric are common methods and still have being utilized by many researchers for determining gas sorption on different sorbents. In 2010, J. He et al. [24] carried out experiments to measure CO₂ adsorption/desorption isotherms on anthracite coal samples (Kyungdong, Korea) using a static volumetric method at 25°C (298 K) and 45°C (318 K), and up to 15 bar (150 atm).

The adsorption of CO₂ is favorable at low temperatures and dry coal conditions. CO₂ adsorption capacities on wet and dry coals are 1.39 and 1.49 mmol/g respectively as shown in Figure 5. In wet coal, the dissolution of H₂O in the CO₂ phase, absorption of CO₂ in the aqueous phase, and coal structure changes affected the estimation of adsorption amount, especially under supercritical condition.

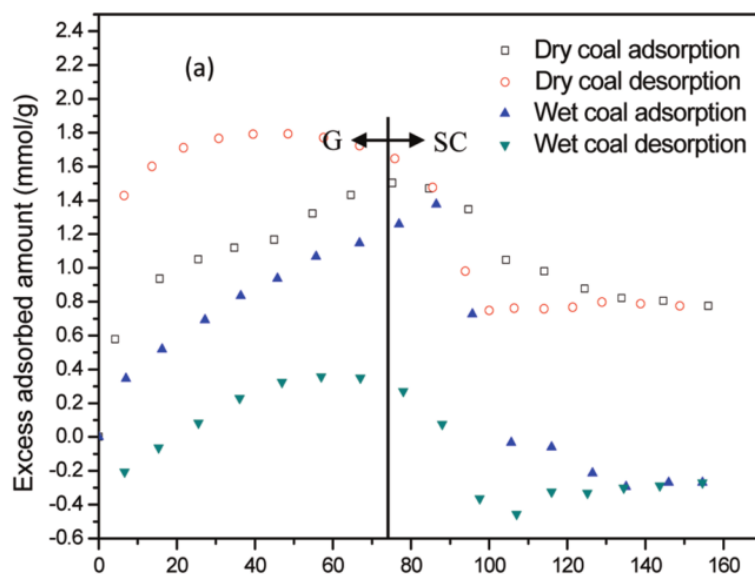


Figure 5. Comparison of adsorption and desorption of CO_2 between dry coal and wet coal (3.64%) at 45°C (318 K) with respect to pressure [24]. G: subcritical and SC: supercritical.

In 2013, H. H. Lee et al. [25] utilized a volumetric gas chromatographic method to measure the excess sorption amount of anthracite Kyungdong coal samples from South Korea and samples size range was 150–500 μm under 45°C (318K) and 65°C (338K) and up to 13 MPa. They found out that the total excess adsorbed amount and isotherm shape of mixture on dry and wet coal was similar to the results of pure CO_2 . Beyond 4 MPa (40 bar), all curves showed a similar shape due to the increased holdup ratio of the gas phase to the sorbed amount. Therefore the total excess adsorbed amount and isotherm shape of mixture on dry and wet coal were similar to the results of pure CO_2 as shown in Figure 6 and Figure 7. The moisture of the coal reduced the sorption amount compared to dry coal in the mixture system, showing a similar moisture effect on the isotherm of pure CO_2 in the same range of fluid density.

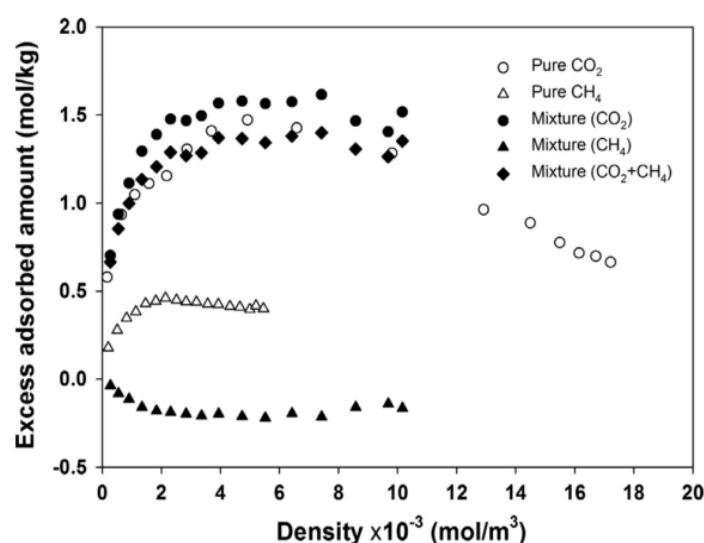


Figure 6. The highest excess adsorbed amount of CO_2 and CH_4 pure and mixture, on dry coal at 45°C (318 K) as a function of density [25].

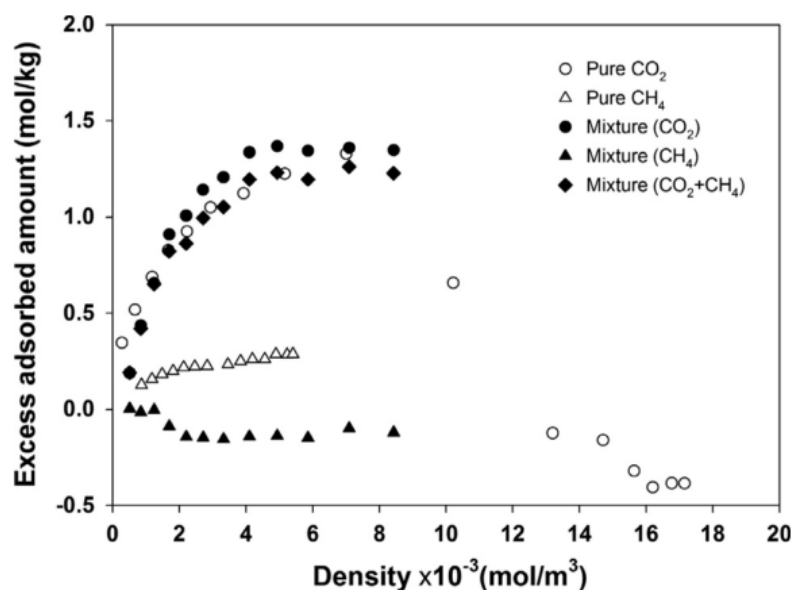


Figure 7. The highest excess adsorbed amount of pure CO₂ and CH₄, and their mixture on wet coal at 45°C (318 K) as a function of density [25].

In 2013, V.N. Romanov et al. [26] utilized manometric technique to measure CO₂ adsorption capacity of coal samples from Central Appalachian Basin, US. The CO₂ adsorption measurements were carried out at 55 °C by introducing CO₂ into the cell to build the pressure step-wise up to 12 MPa. The maximum CO₂ adsorption capacity is 0.97 mmol/g-dry-ash free (daf) as shown in Figure 8. The role of CO₂ dissolution in pore water appears to be marginal.

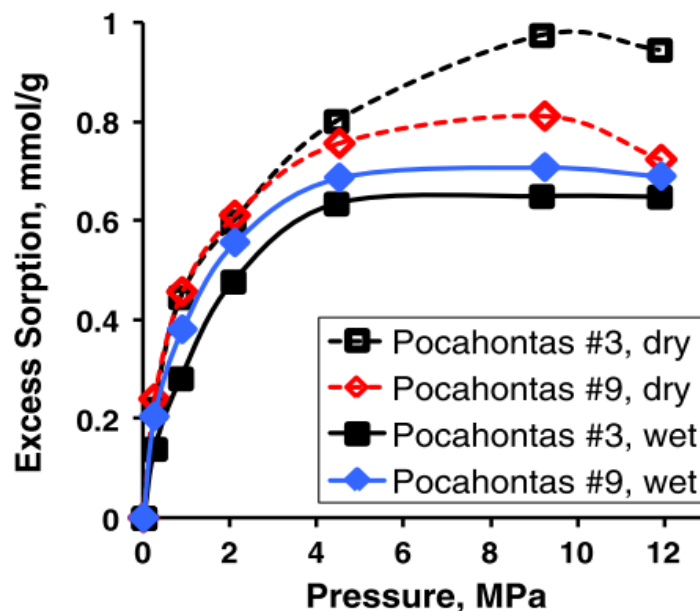


Figure 8. CO₂ excess sorption isotherms (dry basis) on wet and dry Appalachian coals [26].

In 2013, S. Hol et al. [22, 23] newly developed technique called capsule method that directly measures CO₂ uptake of solid coal matrix cylinders. The experiments were performed on high volatile bituminous coal, exposed in the Brzeszcze mine, in the Upper Silesian Basin of Poland. The samples

were saturated with CO₂ at a fixed CO₂ pressure between 0 and 16 MPa and a temperature of 40 °C. The total uptake of CO₂ measured using the capsule method continuously increases as a function of increasing CO₂ pressure, up to a value of 4.08 mmol/g coal at 18.10 MPa CO₂ of pressure meanwhile 4.08 mmol/g by using manometric technique meanwhile 3 mmol/g by using manometric technique as shown in Figure 9.

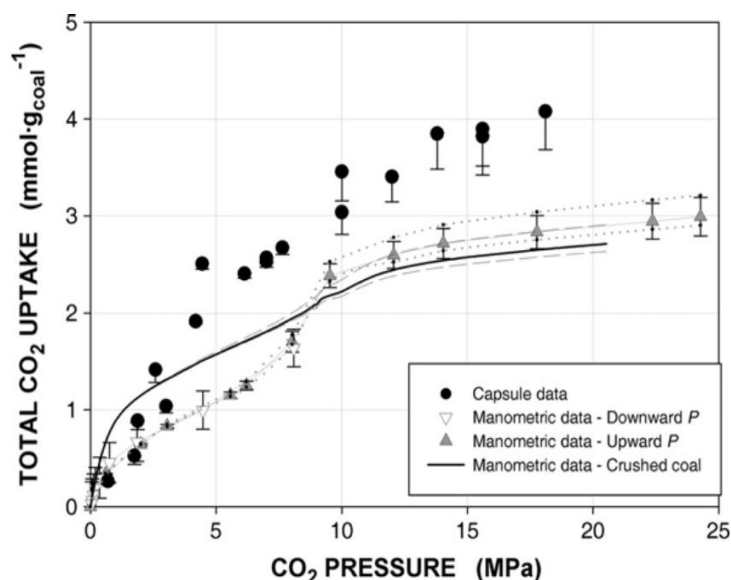


Figure 9. CO₂ comparison between single capsule method and manometric method [23].

In 2012, Weniger et al. [27] conducted the CO₂ adsorption isotherms using manometric technique to measure high-pressure CO₂ adsorption isotherms at 45 °C and at 6 to 10 MPa on as-received coal samples from the Paskov and ČSM mines from Upper Silesian Basin (Czech Republic). The excess sorption capacities of moisture-equilibrated coals ranged from 0.8 to 1.16 mmol/g-daf and the maximum excess sorption (n_{\max}) values measured on as-received coals range from 0.96 to 1.41 mmol/g for CO₂. A comparison of CO₂ adsorption isotherms measured on as-received and moisture-equilibrated coal is given in Figure 10. This reduction of CO₂ sorption capacity is due to the steep increase in the specific density of supercritical CO₂ in this pressure range [27-29].

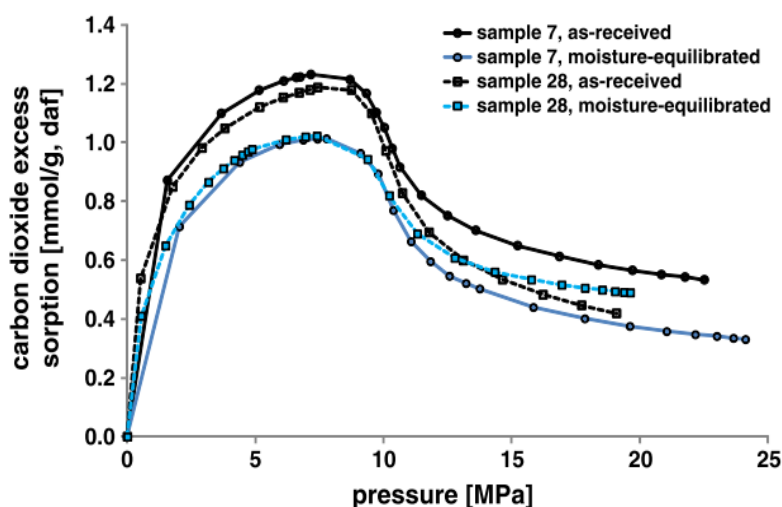


Figure 10. CO₂ sorption isotherms for as-received (open symbols) and moisture equilibrated

(solid symbols) coal from Paskov mine (squares) and ČSM mine (circles) [27].

In 2009, Kelemen and Kwiatek [30] measured CO₂ adsorption on coal samples at 30 °C, dry coal at 75°C and 1.8 MPa using gravimetric gas sorption measurements (Hiden IGA gas sorption system). The rate of gas adsorption for coal varies with the size of coal particles that are smaller than the fissure network of the coal. Gas adsorption isotherm experiments are usually conducted using powdered coal samples to assure that equilibrium is rapidly approached. As shown in Figure 11, the maximum adsorption capacity of CO₂ is 1.40 mmol/g [30, 31].

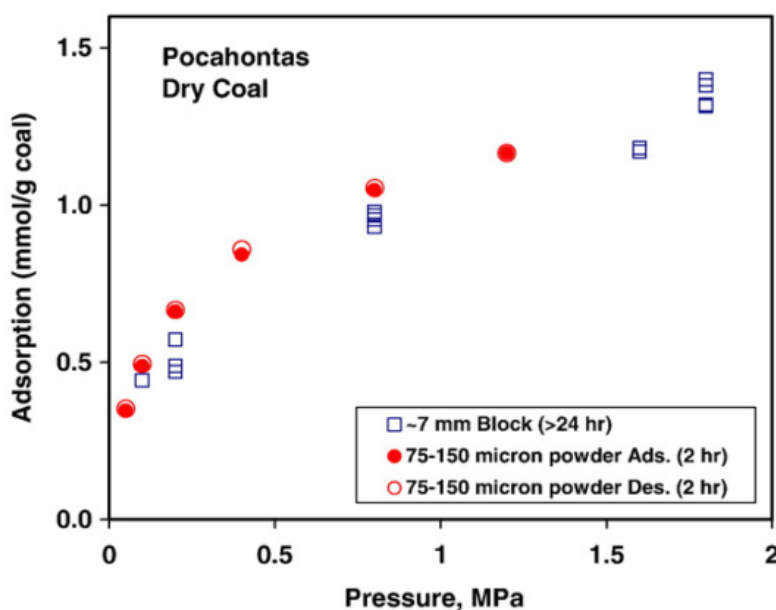


Figure 11. Comparison between CO₂ adsorption results using 75–150 µm powder and ~7 mm block dry Pocahontas Argonne Premium coal [30].

In Table 1 a summary of the maximum of CO₂ adsorption capacities on various coal samples and it is obvious that wet coal samples always have less CO₂ adsorption capacity compared to dried coal samples because the energetic active sorption sites occupied by water [15, 32]. The comparison of all dry and wet coal samples are depicted in Figure 12 and Figure 13. However it noticed that the dry Polish coal sample has the highest CO₂ adsorption on coal by 4.08 mmol/g compared to the other coal samples.

Table 1. Summary of the maximum of CO₂ adsorption capacities on various coal samples.

Coal sample	Technique	Maximum CO ₂ adsorption (mmol/g)	Ref.
Dry Polish coal	Capsule	4.08	[23]
Dry Korean coal	Volumetric	1.49	[24]
Wet Korean coal	Volumetric	1.39	
Dry Korean coal	Volumetric	1.48	[25]
Wet Korean coal	Volumetric	1.38	
Dry Appalachian coal	Manometric	0.97	[26]
Dry Czech Republic coal	Manometric	1.41	[29]
Wet Czech Republic coal	Manometric	1.16	
Dry Pocahontas coal	Gravimetric	1.40	[30]

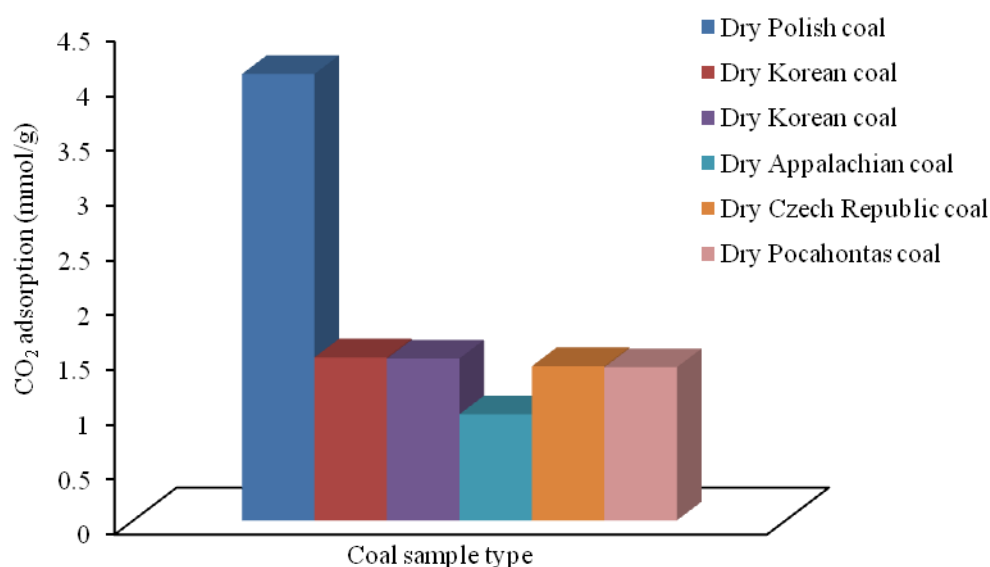


Figure 12. CO₂ adsorption of all dry samples at different conditions.

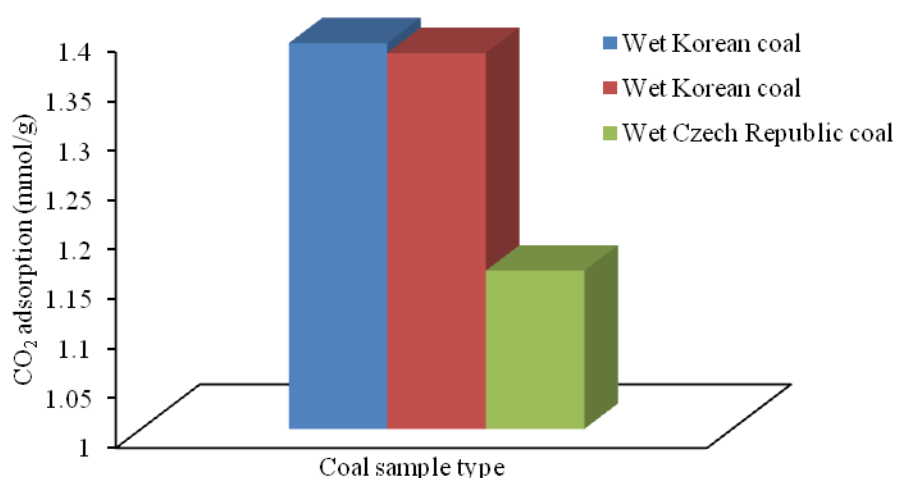


Figure 13. CO₂ adsorption of wet samples at different conditions.

4. Conclusions

The volumetric/manometric is common method for CO₂ adsorption isotherms at high pressures and temperatures on various sorbents because they easy to handle and reach thermal equilibrium rapidly. However, it requires an accurate determination of cell and void volumes and elimination of Equation of State (EoS) errors and small amounts of sorbent are ineffective. Thus, when the amounts of sorbent are small (milligrams) the gravimetric technique is strongly recommended and the approach to equilibrium during the adsorption process can be mentored. The other new capsule method is independent of any equation of State (EOS), and no volumetric effects or impurities distort the shape of the isotherm but it is time-consuming and not easily executed. Therefore, it is noticed that dried Polish coal sample using new capsule method has the highest CO₂ adsorption by 4.08 mmol/g. The

presence of moisture in coal reduces the CO₂ adsorption on coal significantly and it makes coal to swell. Hence, wet coals adsorb less CO₂ compared with the dried coals because the water molecules occupy coal's pores. The oxygen-containing functional groups are preferentially occupied by water in moist coal due to its polarity. In coal samples, the low and medium coal ranks usually have high affinity for adsorbing CO₂ than high coal rank (anthracite) due to the low and medium coals have higher surface area and higher oxygen functional groups. All CO₂ adsorption on different coal samples show that there are decline in CO₂ adsorption on coal after exceeding the CO₂ its supercritical condition. This is due to the enormous increase the specific density of CO₂. Furthermore, coal from different coal mine has different physical properties "anisotropic" hence more investigations about the interactions of subcritical and supercritical CO₂ with wet and dry coals should be conducted. In future work, CO₂ adsorption isotherms on coal using new techniques such as capsule method should be explored. Moreover, the effect of impurities such as H₂S, SO₂ and hydrocarbons on CO₂ sorption onto different coal should also be investigated.

5. References

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