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Coal sorption behavior using gas mixture

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The University of Arizona, 1992

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COAL SORPTION BEHAVIOR USING GAS MIXTURE

by

Uma Mahesh Pariti

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DEPARTMENT OF MINING AND GEOLOGICAL ENGINEERING
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For the Degree of
MASTER OF SCIENCE
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In the Graduate College
THE UNIVERSITY OF ARIZONA

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ABSTRACT

This thesis discusses an experimental study involving sorption studies using methane, carbon dioxide, and a multicomponent gas mixture representative of *in situ* gas composition. Using the isotherms for pure methane and carbon dioxide, isotherm and variation in gas composition with desorption for gas mixture were established using a numerical technique. When using gas mixture, composition of the desorbing gas at each pressure level was monitored.

Results indicate that during desorption, methane concentration decreased as the pressure was decreased while carbon dioxide concentration increased. Experimental results for sorption and variation in gas composition of the gas mixture compare very well with the theoretically obtained results. It is, therefore, possible to establish the sorption isotherm, Langmuir constants for gas mixtures and estimate the variation in gas composition with desorption theoretically, if the sorption isotherms for individual component gases are available and the *in situ* gas composition is known.

CHAPTER 1

INTRODUCTION

Methane accumulation and outburst has been a problem of vital concern in the coal mining industry. Over the past 30 years, emissions of methane into coal mines have increased significantly due to greater comminution of the coal by mechanized procedures, higher productivity, faster moving faces and a trend towards deeper workings (McPherson and Hood, 1981). In underground mines, this release of methane is considered a major hazard, and it has been a usual practice to dilute and flush the gas out to prevent gas explosions. In most cases, this is expensive and results in the wastage of large quantities of gas. Also, venting the gas to atmosphere contributes to the "greenhouse effect". It is estimated that in the United States alone, 250 million cubic feet of gas per day are lost to atmosphere from underground coal mining operations. This represents approximately 0.5 % of U.S. gas production from all sources (Black, 1990).

Recovering methane prior to mining coal reduces ventilation costs and decreases the risk of outbursts. Although initially introduced to improve mine safety and ventilation efficiency, extracting methane from coal seams has gained increasing importance during the past few years. The two major areas of coalbed methane production in the U.S. are the San Juan basin of Colorado and New Mexico with estimated resources of 84 trillion cubic feet (TCF), and Black Warrior basin of Alabama with 20 TCF (Black, 1990).

Coalbed methane gas-in-place in the U.S. is estimated to be 400 TCF, of which about 95 TCF is considered to be economically recoverable with current technology (Ayers and Kelso, 1989). This represents a significant resource since the total U.S. proved gas reserves from conventional sources are estimated to be 187 TCF.

Unlike conventional gas reservoirs, methane in coal is not stored as free gas. Most of the natural gas in coalbed methane reservoirs is in the form of adsorbed gas stored in pores and microfractures of coal. This usually accounts for 98% of the gas within a coal seam, the rest being stored as free gas (Gray, 1987). The process of desorption makes available most of the natural gas obtained from the coal seams. Study of adsorption/desorption (sorption) isotherms is, therefore, very important in determining the coal's capacity to hold gas, as well as understanding the pattern of gas release from a coalbed methane reservoir. The information provided by isotherms is used as one of the primary input parameters in simulation of coalbed reservoirs.

New methods of coalbed methane recovery are being reported involving injection of other gases to enhance methane production. Reznik *et al* (1984) reported that CO₂ injection enhanced the recovery of *in situ* CH₄ from coal beds. They showed that CO₂ injection increases the recovery of CH₄ by a factor of two or three times that achieved in simple desorption by pressure drawdown and atmospheric diffusion. Puri and Yee (1990) showed that essentially all methane sorbed on coal can be stripped by nitrogen flooding without necessarily reducing the total system pressure. All the above applications require the knowledge of at least binary sorption (mixture of two gases) behavior of coal. Also this knowledge can be used for separation of gas mixtures through preferential adsorption.

It is well known that the gas produced from many coalbeds is a multi-component gas mixture. Yet, studies of multicomponent gas sorption on coal are rare, and those which have been performed used dry coal samples. Also, the measurements have been done at only relatively low pressures (Arri *et al*, 1992). The experiments do not closely represent the *in situ* conditions where the coal is moist, pressure is high and the gas desorbed is a multi-component mixture.

It is recognized that the gas obtained from coal is a multi-component mixture usually consisting of large quantities of methane and small amounts of carbon dioxide, nitrogen and other hydrocarbons and the composition changes with the level of desorption (Stevenson et al, 1991). Since, it is the methane component of the gas that mainly contributes as a fuel, and to maintain a minimum BTU/scf for fuel supply, it is important to know the methane component and non-hydrocarbon components. The study of multi-component gas sorption on coal is, therefore, vital to the prediction of coalbed methane reserves and production. Realistic modeling and forecasting of coalbed methane wells can be done only by incorporating the results of multi-component gas sorption on coal.

For example, Pittsburgh coalbed gas samples ranged from 84 to 96 % methane, and the principal contaminant was carbon dioxide. Upper Kittanning coalbed gas samples ranged from 95 to 99 % methane, and nitrogen is the principal contaminant (Rightmire, 1984). For Fruitland Formation coals of San Juan basin the absolute BTU/lb values vary between 9,000 to 15,720. Moisture content of fresh coal ranges from 2 to 5 %. Sulfur content is usually less than 1 % (Rightmire, 1984). Analyses of gas samples collected from eight of the wells of Fruitland coal are given in Table 1. Average methane content is 88.1 %. In the non-hydrocarbon fraction, nitrogen and carbon dioxide are present in significant amounts. After allowing for minor air contamination, nitrogen averages approximately 5 % and carbon dioxide averages 3.2 %.

The purpose of this work is to obtain valuable sorption data using multi-component gas mixture. The experiments are conducted at *in situ* pressure and temperature conditions with moist coal and gas composed of a mixture of methane, carbon dioxide and nitrogen representing *in situ* gas composition. Sorption experiments are carried out at pressures to 1500 psi and temperature of 112°F with pure methane, pure carbon dioxide and a multi-component gas mixture consisting of 93 % methane,

Well number	Gas Sample Depth Interval feet	Gas Composition, %			
		CH ₄	C ₂ H ₆	N ₂	CO ₂
2	1140-1150	81.3	8.6	6.5	0.4
3	1370-1390	89.2	1.1	-	-
4	3230-3250	94.1	0.5	2.3	3.0
6	3006-3015	93.5	0.4	4.0	1.7
7	2970-2979	90.9	1.1	1.4	6.5
8	3053-3073	84.8	0.6	7.0	6.7
9	3161-3183	78.1	0.3	16.9	3.7
10	3119-3141	93.1	0.4	6.0	0.4
Average (for available data)		88.1	1.6	6.3	3.2

Table 1 Gas sample analyses of the wells of Fruitland coal (after Rightmire, 1984).

5 % carbon dioxide, and 2 % nitrogen. When using the gas mixture, a gas chromatograph is used to measure the composition of the gas at each desorbing pressure step. In a separate effort, the variation in gas composition with decreasing pressure is calculated theoretically using the sorption isotherms for pure methane and carbon dioxide. Two primary tasks have been accomplished:

1. Establishing sorption isotherms using gas mixture representative of *in-situ* gas composition. Using the sorption isotherms for pure component gases, a sorption isotherm for gas mixture is obtained theoretically. These results are then compared with the experimental results.
2. Monitoring of gas composition during the sorption experiment and comparing it with the theoretically obtained results.

Sorption isotherms and Langmuir coefficients are the basic parameters required to characterize a coalbed methane reservoir. They describe the coal's capacity to hold methane by adsorption at various pressures. They are used to predict the release of gas from the reservoir as the pressure is reduced during production. Information obtained from sorption isotherms is used as input for gas reservoir simulation. They are also used in long term flow rate prediction from methane gas reservoirs. Also, using the sorption isotherms, an estimate of recovery percentage for the coalbed methane well can be obtained.

Chapter 2 provides background about the formation of methane and its storage in coal. Chapter 3 discusses theories about sorption of gas, sorption isotherms and factors affecting the sorption of gas. Work done by previous researchers involving multicomponent gas mixture on coal is also highlighted. Sample procurement, preparation and the experimental procedure employed are discussed in Chapter 4. Experimental results and numerical analyses are discussed in Chapter 5. Results of

extended Langmuir isotherm is also presented. Chapter 6 provides a brief conclusion of the research work and recommendations for future research.

CHAPTER 2

BACKGROUND

2.1 Natural Gas and its Occurrence

Natural gas forms an important source of energy accounting for about 20% of world energy supplies (Hagoort, 1988). Natural gas is a mixture of hydrocarbon gases with some impurities, mainly nitrogen, carbon dioxide and hydrogen sulfide. The hydrocarbon gases are methane, ethane, propane, butanes, pentanes, and small amounts of hexanes, heptanes and some heavier fractions (Beggs, 1984). In gas used for fuel, methane is the largest component, usually 95 to 98%.

Natural gas provides a clean and very flexible source of heat. It burns with a clear flame when mixed with the correct proportion of air and its combustion products are non-corrosive and non-polluting (Tiratsoo, 1979). It is used primarily as a fuel for space heating and for generating steam for electric power plants, although its use as a feedstock for petrochemical plants is increasing rapidly (Beggs, 1984). Because of the necessity of using very high pressure to store significant quantities of natural gas in small spaces, its use as a fuel for motor vehicles is very limited. However, as the supply of liquid fuels such as gasoline diminishes, it is likely that technology will be developed to overcome this problem. Natural gas is of special value for domestic heating and cooking applications. Commercial applications for natural gas include heating and air-conditioning in shops, offices and swimming pools. Natural gas is widely used in the industry for space heating, product drying and steam generating.

There are several sources of unconventional natural gas. The United States is well endowed with such unconventional sources of gas as western tight sands, Devonian shale, methane in coal seams, and geopressured aquifers (water-bearing rocks)

(Oppenheimer, 1980). The work described in this thesis is related to the area of coalbed methane, which owes its existence to the chemical conversions by which coal is formed.

2.2 Formation of Coal

Coal is composed of fossilized remains of land vegetation that flourished millions of years ago. It is an organic substance, primarily carbon and varying proportions of hydrogen, oxygen, nitrogen, and sulfur (Lindbergh & Provorse, 1980). The initial step in the formation of coal is the process by which green plants extract organic compounds from air and water for use in building their own tissues. Subjected to tremendous pressure and heat over a length of time, these carbon compounds, in the form of compressed plant debris transform to coal. The chemical change of cellulose produces carbon dioxide, marsh gas (methane), water and peat (most primitive form of coal). Though burial under layers of silt halts most bacterial decaying action in peat, some further decay is caused by anaerobic bacteria, which works in the absence of oxygen. However, as water is gradually forced out of the peat, this secondary decay also ceases. The by-product of anaerobic decay, a volatile matter consisting of gaseous hydrocarbons (natural gas), remains trapped in pockets and fissures of coal seam.

2.3 Methane Generation

Methane is generated by two mechanisms during the coalification process: biogenic and thermogenic. During the early stages, at temperatures below 50°C, biogenic methane is formed by microbial decomposition of the organic material (Rightmire, 1984). As temperature increases above 50°C through increased depth of burial or the increasing geothermal gradient, the coal rank increases. Rank increase is related to the time that the material is maintained in a given thermal regime. This time

temperature relationship dictates the level of maturity of the coal that, among other things, controls the volume of methane generated. The principal product gases generated under this regime are methane, carbon dioxide, and nitrogen.

Nitrogen and carbon dioxide form the two major contaminants in methane from coal beds.

2.4 Methane Retention

Methane is retained in coals in one of three states: as adsorbed molecules on the coal surface, as free gas within the pores or fractures, and/or dissolved in groundwater within the coal bed (Rightmire, 1984). The primary mechanism of methane retention in coalbeds is the adsorption on the coal surface within the matrix pore structure accounting for approximately 98 % of coalbed methane. The majority of gas is contained as a monomolecular adsorbed layer within the coal structure (Harpalani and McPherson, 1986). Figure 2.1 shows the representation of methane molecules inside a coal pore. The amount of gas stored in the coals is dependent on depth of burial and its related pressure, rank of coal and its related porosity distribution, and a time-maturity relationship.

Coal, being a solid colloid, possesses a certain porosity. It is to this porosity that it owes some of its properties, e.g. the capacity to adsorb gases and vapors, swell in vapors and liquids and develop heat on wetting (Van Krevelen, 1981). The pore surface, also called the internal surface, is primarily responsible for these properties. Coal has a dual porous system: a macropore system and a micropore system. The micropores have a dimension ranging from 5 to 10 Å and exist in the coal matrix between the seam's cleats. The macropore system is made up of the volume occupied by the cleats of widths varying from a few Å to microns (King, 1985).

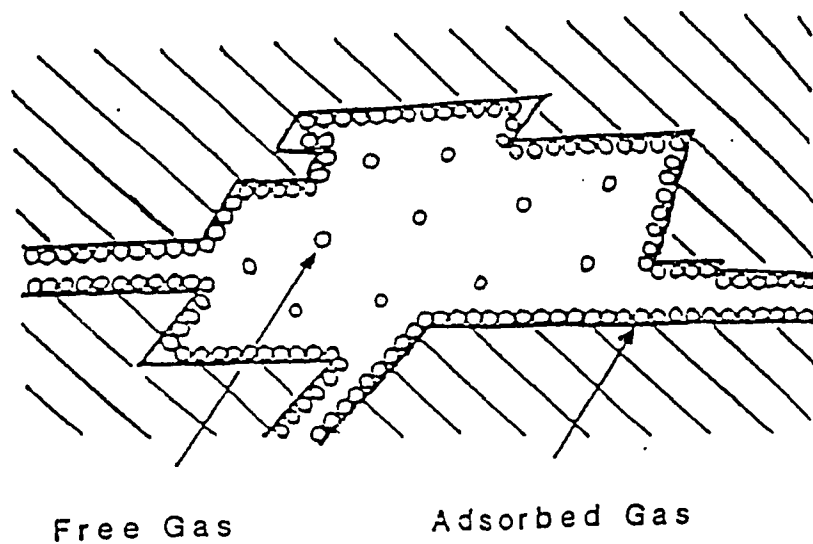


Figure 2.1 Pictorial representation of methane molecules inside a coal pore (after McPherson, 1975).

The micropore system is inaccessible to water due to the dimension of the pores. Hence, this serves as the storehouse for large quantities of methane held within the porous matrix by adsorption mechanism that is controlled by the reservoir pressure. The macropore system, on the other hand, is water saturated prior to production.

Figure 2.2 shows basic structure of coal where it is made of small blocks separated by fractures called 'cleats'. The spacing of the fractures determines how far the gas has to diffuse before reaching the fracture, and the dimension of the fracture decides the quantity of gas that can flow (Harpalani & Schraufnagel, 1990). It is for this reason that coal is considered a dual porosity system and flow through it a dual process. Figure 2.3 shows the three distinct processes involved in the transport of coalbed methane, starting with desorption from the internal coal surfaces. Gas then diffuses through the matrix and micropores towards the cleats, fractures (King, 1985). Once in the natural fracture network, flow of gas is eased significantly and follows Darcy's law.

2.5 Gas Transport in Coal

Most U.S coals are characterized by very high water saturations (Tandon, 1991). The coalbeds, therefore, must be dewatered before gas flow can begin. Dewatering reduces the hydrostatic head that holds the gas in an adsorbed state on the coal pore and fracture surfaces and gas is released. With decreasing water saturation, the permeability to gas increases and methane begins to flow towards the wellbore. As shown in Figure 2.4, desorption and flow of gas follow three main stages (Koenig et al, 1989):

- 1) Single-phase flow, where only water is produced and reservoir pressure drop is small.

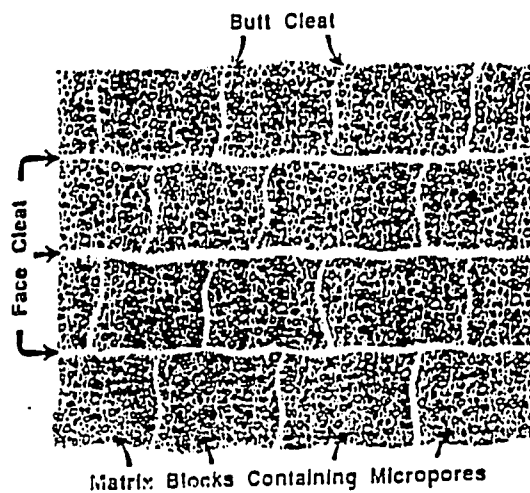


Figure 2.2 Basic structure of coal (after Sawyer et al, 1987).

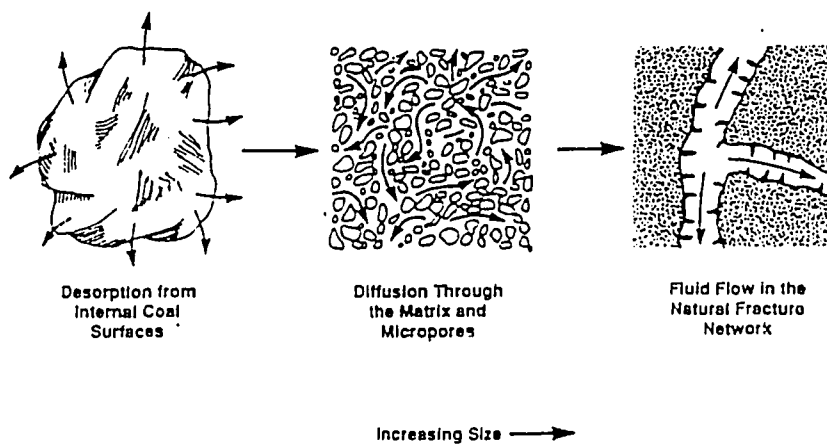


Figure 2.3 Processes involved in the transport of coalbed methane (after King, 1985).

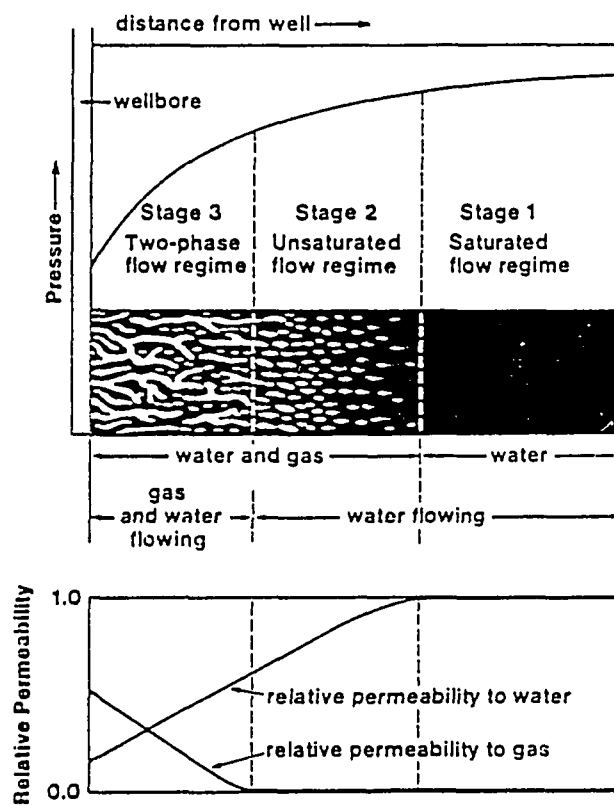


Figure 2.4 Three stages of coalbed methane production (after Koeing et al, 1989).

- 2) Unsaturated single-phase flow, where both gas and water are present, but only the water phase is mobile. At this stage, the decrease in reservoir pressure is insufficient for methane desorption to begin. Isolated gas bubbles form, decreasing the relative permeability to water. But since the gas bubbles are not connected, no gas flow occurs.
- 3) Two-phase flow, where both gas and water are present and mobile. With continued pressure decrease and desorption, gas saturation increases to where individual bubbles connect and form continuous pathway to the wellbore. Two phase flow begins where the relative permeability to gas becomes non-zero.

As the reservoir pressure is further reduced and water saturation declines, the relative permeability to gas increases at the expense of relative permeability to water. This sequence of regimes progresses outward from the wellbore into the formation over time and gas is produced.

Two basic mechanisms appear to govern gas migration, once the two-phase flow starts (Tandon, 1991). The first of these is the free-phase gas flow through fractures and the pore system (macropores or cleats) according to Darcy's law and the operative relative permeability relationship for the coal. Response of coalbed methane reservoir to this flow type is similar to that in conventional reservoirs. The second mechanism is flow by diffusion through the microporosity of the solid coal which follows the Fick's law for diffusion. Since most of the adsorbed gas exists within the matrix micropore system, this second mechanism is more important in terms of long-term production. The diffusion mechanism is more important because the gas molecules must first diffuse through the micropores and reach the cleats before the gas flow is eased in the cleats due to Darcy's flow.

CHAPTER 3

SORPTION OF GAS AND PREVIOUS STUDIES

3.1 Adsorption and Desorption

When a gas is allowed to come to equilibrium with a solid or liquid surface, the concentration of gas molecules is always found to be greater in the immediate vicinity of the surface than in the free gas phase. The process by which this surface excess is formed is termed adsorption (Young and Crowell, 1962). Adsorption is accompanied by a decrease in the free energy (total enthalpy and entropy) of the system. As energy is released during adsorption, it is always an exothermic process. The decrease in the heat content of the system is defined as the heat of adsorption. Adsorption is of two types, physical adsorption and chemical adsorption. Physical adsorption involves the Van der Waals forces of molecular interaction. Chemical adsorption may be considered to be a chemical reaction between an adsorbate molecule and the surface array of adsorbent atoms.

Methane is stored in coal by a sorption process usually identified as physical adsorption of the gas onto internal coal surfaces. Desorption is the reverse process of adsorption causing the release of gas from the surface of the adsorbent. The process of desorption makes available most of the natural gas obtained from the coal seams. Study of adsorption/desorption (sorption) isotherms is, therefore, very important in determining the coal's capacity to hold gas, as well as understanding the pattern of gas release from a coalbed methane reservoir.

3.2 Theories of Adsorption

There have been several attempts to evolve a theoretical basis for the adsorption

phenomena. A brief outline of major theories proposed to explain the adsorption phenomenon is given here.

Freundlich's exponential equation is one of the oldest attempted explanations of adsorption. According to it, as adsorption at higher pressures is approached, the volume adsorbed becomes proportional to a power of the gas pressure smaller than unity. It is expressed as:

$$v = kp^{1/n}$$

where n is greater than 1. Isotherms having such shapes are referred to as Langmuir isotherms, since the adsorption mechanism postulated by Langmuir leads to this type of isotherm (Mantell, 1951).

Langmuir proposed a theory in 1915 based on the belief that adsorption was a type of chemical combination or process and that the adsorbed layer was unimolecular. About the same time, Polanyi suggested that adsorption was a physical process, electrical in nature, and that the adsorbed phase was many layers thick (Mantell, 1951). Polanyi theory has also been known as the potential theory. The adsorbent is believed to exert strong attractive forces. These attract gas molecules in the vicinity and reach out to such an extent that many adsorbed layers can form. These layers are under pressure, partly because of layers on top and because of the attractive force of the surface of the adsorbent.

Patrick (1920) brought forward the suggestion that all physical adsorption was the result of capillary condensation, from which a more generalized theory and mathematical development arose. Magnus (1929) proposed a theory of unimolecular adsorption on the assumption that the forces of interaction between the surface of the adsorbent and gas were electrostatic in nature, and not chemical as assumed by Langmuir (Mantell, 1951). He supposed that the molecules held on the surface of the adsorbent behaved like a two-dimensional imperfect gas whose actions conformed to the van der

Waals equation of state. This assumption is realistic since real imperfect gases deviate from ideal behavior, which is explained by van der Waals equation of state.

3.3 Langmuir Model

Of the sorption models available, the simplest one is that of Langmuir for a monolayer adsorption. This is the one most commonly used. The adsorption isotherm which determines the volume of adsorbed gas, V , in equilibrium with free gas at pressure, P , is defined as:

$$V = \frac{V_L P}{P + P_L}$$

where,

V_L = Langmuir Volume - total sorptive capacity of coal,

P_L = Langmuir Pressure - pressure when the volume adsorbed is half the total sorptive capacity,

V = sorbed volume,

P = absolute pressure.

3.4 Factors Affecting Sorption of Gas

Several researchers have studied the sorption behavior of coal and the effect of temperature, moisture and particle size on sorption. Joubert and others (1973, 1974) studied the effect of moisture on the sorption capacity of bituminous coal at a temperature of 30°C and pressure up to 900 psi. For all coals studied, the capacity of coal to adsorb methane decreased with increasing moisture content up to a certain value characteristic of the coal type. Moisture present in excess of the critical value had no effect on methane sorption. At values of moisture content m (wt %), below the critical

value m_c , an empirical equation developed by Ettlinger represents the methane sorption data quite well:

$$\frac{V_d}{V_w} = C_0 m + 1$$

where V_d and V_w are volumes of methane adsorbed on dry and moist coal respectively, and C_0 is the correlating coefficient (Joubert et al, 1974), with a value of 0.31 often used for bituminous coal. When coal is saturated with moisture, i.e., at or above the critical saturation value, m_c , methane sorption can be described by:

$$\left(1 - \frac{V_w}{V_d}\right)_{\max} = C_1 X_0 + C_2 \quad (m \geq m_c)$$

where X_0 is the coal oxygen content in wt % (moisture free basis). The reduction in methane sorption capacity with increasing moisture is more significant for high oxygen coals due to their high moisture capacities. The exact knowledge of moisture content is important because experiments must be conducted at *in situ* moisture content for the results to be accurate and useful.

The dependency of sorption capacity on moisture content was also studied by Bell (1986) and results similar to those reported by Joubert and others were reported. One interesting observation of the study was that at pressures above 700 psi, the moisture content had no effect on sorption capacity.

Bell (1986) reported a hysteresis between adsorption and desorption isotherms. However, an error in calculating the sorbed volumes was realized and later work by Bell (1989) reported no hysteresis. Also, Bell reported laboratory gas content being about 50% higher than that measured in the field, and attributed the discrepancy to a possible effect of stress on adsorption equilibrium.

The effect of particle size on the sorption capacity was studied by Ruppel and others (1974). The amount of methane adsorbed on crushed and dried coal was measured

as a function of pressure. Isotherms were measured at 30°C for the Illinois coal and at 0, 30, 50°C for the others. Most measurements were made to 150 atm pressure, but a few to 240 atm. Isotherms were repeated using 6-8, 80-100 and 270-325 mesh coal. The conclusion of the study was that particle size in the range of 6 and 325 mesh has no effect on equilibrium adsorption.

In the same study, temperature effect on the sorption capacity of coal was reported. There was a distinct decrease in the amount of adsorbed gas with increase in temperature from 0 to 50°C. A similar dependence was again reported by Yang and others (1985). Ettinger (1958) developed an empirical equation where, if the methane adsorption isotherm of a coal at 30°C is known, the isotherm at any other temperature can be established by:

$$V_t = V_{30} \frac{e^{n_{30}}}{e^{n_t}}$$

where V_t and V_{30} are the methane adsorption capacity of dry coal at temperature t and 30°C, respectively, and n_t and n_{30} are the indices of the degree of the temperature coefficient at these temperatures (Yalcin et al, 1991). Another relationship commonly used for bituminous coal was presented by Boxho (1980). Starting at 23°C, the volume of adsorbed gas falls at a rate of 0.8% per degree.

The effect of temperature and moisture content on sorption capacity of coal is shown in Figure 3.1. It shows that when temperature and/or moisture content increases the sorption capacity of coal decreases. Figure 3.2 shows the effect of coal rank on adsorption. It is apparent that anthracite, a higher ranking coal, has a higher sorption capacity than lower ranking bituminous coal. This is because higher ranking coals have higher internal surface area and greater carbon content, both contributing to higher sorption capacity.

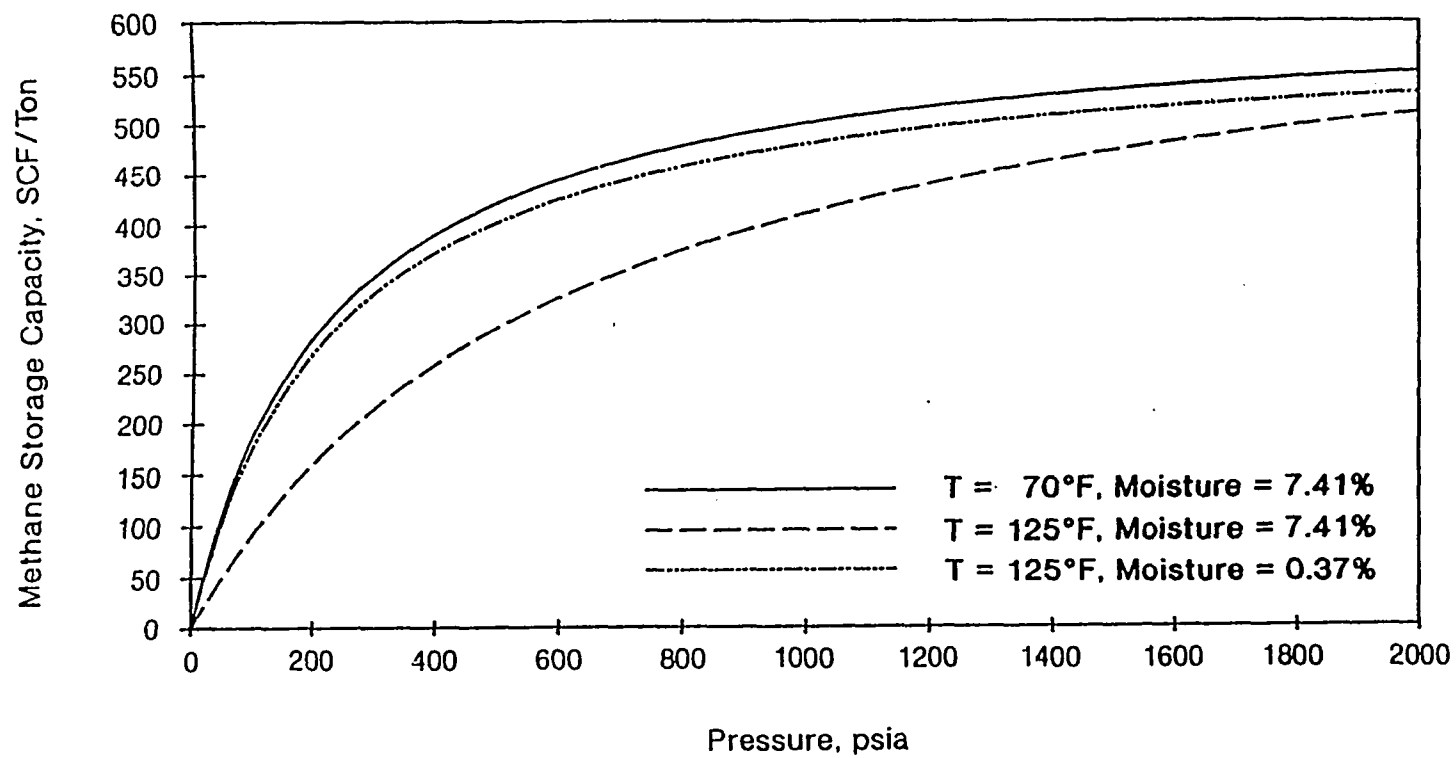


Figure 3.1 Effect of temperature and moisture content on sorption capacity of coal (after Mavor et al, 1990).

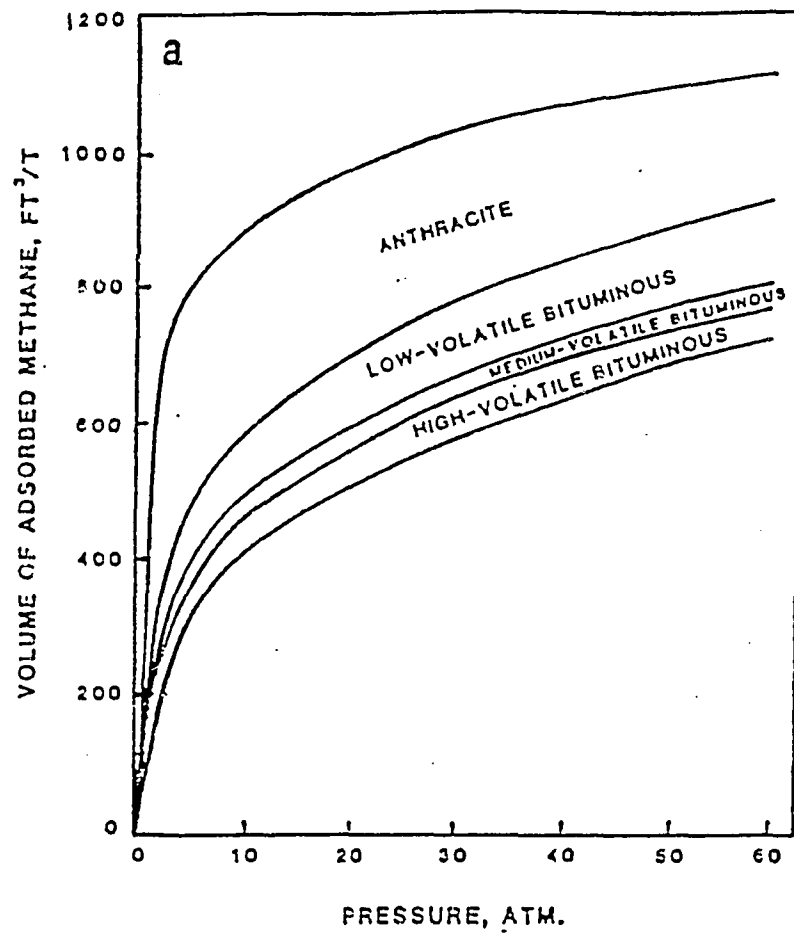


Figure 3.2 Effect of coal rank on adsorption (after Jones et al, 1987).

The effect of presence of a second adsorptive gas, along with methane, was investigated by Ruppel and others (1972). They calculated the binary adsorption characteristics of methane and ethane on dry coal from individual methane and ethane isotherms. The pure gas isotherms were experimentally determined at 0, 30 and 50°C. Presence of ethane reduced the volume of adsorbed methane, although the total quantity of adsorbed gas increased.

The effect of gas sorption on the strength of coal was studied by Ates and Barron (1988) primarily because of some unexpected outbursts in coal mines. The conclusion of the study was that the strength of coal is significantly reduced due to the presence of adsorbed gas - more than what can be explained by the law of effective stress.

One comment about most of the work carried out in the past is the practice of oven drying of coal either because dry coal was used for the experimental work, or drying prior to equilibrating with moisture. Drying the coal by exposing it to air or heat alters the structure of coal since the internal surface area of coal is affected, and hence, its sorption capacity is influenced. Dried coal, therefore, should not be used when measuring properties of coal (Nelson, 1989).

Based on the information presented above, any experimental work to measure sorption isotherms must consider the following factors:

- 1) Moisture content should be equal to the critical moisture content, although a higher moisture content would not affect the results adversely.
- 2) Temperature must be maintained constant throughout the experiment at the level encountered *in situ*.
- 3) Equilibrium must be attained at each pressure step before starting the subsequent step.

3.5 Previous Studies with Gas Mixtures

The reservoir conditions of most U.S. coal seams require that binary sorption measurements be made with moist coal samples at high pressure (Arri et al, 1992). This is because the gas obtained from coal seams is not pure methane, but is a gas mixture consisting of major non-hydrocarbon contaminants like nitrogen and carbon dioxide. Yet, studies of multicomponent gas sorption on coal are rare. This represents a serious limitation to the development of coalbed gas drainage numerical simulators capable of modeling mixed gas adsorption/desorption processes (Stevenson, 1991). Following are the major studies that looked into the area of multicomponent gas sorption.

Myers and Prausnitz (1965) described a simple technique for calculating the adsorption equilibria for components in a gaseous mixture, using only data for the pure-component adsorption equilibria at the same temperature and on the same adsorbent. Their technique is based on the concept of an ideal adsorbed solution (IAS) and, using classical surface thermodynamics, an expression analogous to Raoult's law is obtained. *The essential idea of their calculation lies in the recognition that in an ideal solution the partial pressure of an adsorbed component is given by the product of its mole fraction in the adsorbed phase and the pressure which it would exert as a pure adsorbed component at the same temperature and spreading pressure as those of the mixture.* The predictions of the IAS theory are in quantitative agreement with the experimental data for a wide variety of gas mixtures and for different heterogeneous adsorbents.

Four major studies have previously looked into the area involving the sorption of gas mixtures on coal. The first three involved the use of dry coal for the sorption experiments. Ruppel *et al* (1972) calculated the binary adsorption characteristics of methane and ethane on dry coal for pressures to 40 atm from individual methane and ethane isotherms. The adsorption was purely physical. The binary adsorption characteristics were calculated by employing the IAS theory of Myers and Prausnitz and

experimentally-determined pure gas isotherms at 0, 30 and 50°C. The coal used in their investigation was high-volatile 'A' bituminous from the Pennsylvania Pittsburgh seam. Isobars on the resulting binary equilibrium diagram exhibited an unexpected phenomenon of intersecting each other. The IAS theory appeared to describe the methane/ethane/coal system realistically.

Saunders *et al* (1985) employed a static system to measure the adsorption of H₂-CH₄ mixtures. Experimental data were obtained at temperatures from 22 to 207°C and pressures upto 4.1 MPa on PCB activated carbon, Pittsburgh bituminous coal, Pittsburgh coke, Montana lignite and Montana char. The IAS theory of Myers and Prausnitz did not compare well for the two raw coal samples but gave excellent predictions for the rest. Except for the two raw coals, the temperature and pressure dependencies of the selectivity ratio agreed with the theoretical predictions. The selectivity ratio is a useful parameter indicating the degree of preferential adsorption under a set of specific conditions, and it is important for separation processes. The CH₄-H₂ selectivity ratio is defined as:

$$S_{CH_4/H_2} = \frac{X_{CH_4}/Y_{CH_4}}{X_{H_2}/Y_{H_2}}$$

Stevenson *et al* (1991) measured adsorption isotherms for binary and ternary mixtures of CH₄, CO₂ and N₂ on coal at 30°C and pressures to 5200 KPa. Measurements were reported for the pure components, for the binary systems CO₂-CH₄, CH₄-N₂ and CO₂-N₂ and for the CH₄-CO₂-N₂ ternary system. Here, too, dry coal samples were used. Their measurements show that equilibrium gas and adsorbate phase compositions differ considerably and that the total amount of gas mixture adsorbed is strongly dependent on composition and system pressure. The experimental measurements were used to test the applicability of models based on adsorbate solution

theory to the prediction of multicomponent adsorption data from pure component isotherms at pressures of interest in coalbed gas applications. IAS theory, which assumes ideality of the adsorbed phase, provides good predictions for adsorption of binary and ternary mixtures.

Arri *et al* (1992) examined the binary sorption of methane-nitrogen and methane-carbon dioxide mixtures on coal and modified a reservoir simulator to include the extended Langmuir isotherm to describe the free and sorbed gas composition. A moist Fruitland coal sample from the San Juan Basin of Colorado was used. Binary sorption measurements were carried out at 115°F and total pressures of 500, 1000 and 1500 psia. The results showed that each gas did not sorb independently, instead both gases were competing for the same sorption sites. A simple extended Langmuir isotherm using only pure gas sorption constants provided a reasonable fit to the experimental data. A compositional reservoir simulator was modified using the extended Langmuir isotherm as the equilibrium relationship between the free and sorbed gas. The modified compositional simulator was successfully tested for the cases of primary recovery of a single sorbing component and the enhanced recovery by nitrogen injection.

3.6 Importance of Sorption Isotherms

Sorption isotherms and Langmuir coefficients are the basic parameters required to characterize a coalbed methane reservoir. These describe the coal's capacity to hold methane by adsorption at various pressures and are used to predict the release of gas from the reservoir as the pressure is reduced during production.

As shown in Figure 3.3, an estimate of recovery percentage can be made based upon the reservoir abandonment pressure. Abandonment pressure is the pressure at which the well is abandoned due to economic and technical reasons. Critical desorption pressure is the pressure to which the reservoir must be lowered to for gas flow to take

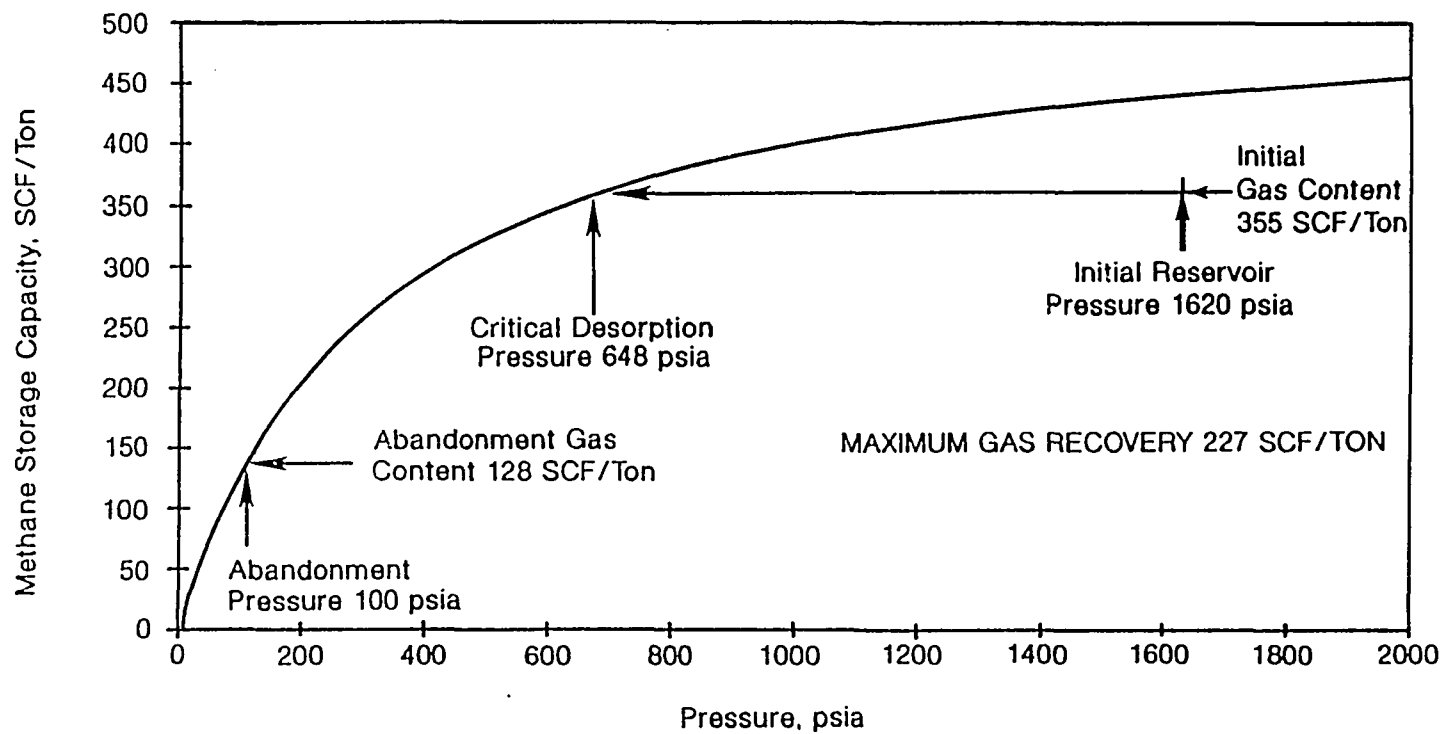


Figure 3.3 Sorption isotherm example (after Mavor et al, 1990).

place. Above this pressure, mostly water flow takes place. This value is obtained from the field. Using the critical desorption pressure and the reservoir abandonment pressure, the initial gas content and abandonment gas content are determined from the sorption isotherms. Using these values the recovery percentage is computed as a ratio of the decrease in gas content to the initial gas content.

The gas sorbed on coal is not always pure methane. In fact, the composition can vary significantly depending on the coal basin. Coal can also contain appreciable amounts of carbon dioxide, nitrogen and heavier hydrocarbons. In these cases, a description of multicomponent gas sorption is needed to predict methane gas-in-place, rates and reserves (Arri, 1992).

CHAPTER 4

EXPERIMENTAL WORK

The experimental work discussed in this chapter comprises mainly of sample preparation, measurement of the amount of sorbed gas, and monitoring of gas composition when using a gas mixture.

4.1 Sample Procurement and Handling

Samples from the San Juan basin were used for the experimental work discussed in this thesis. For the sorption experiments, powdered samples were prepared from the cores. Special care was taken in handling and preservation of coal.

Coal should be kept in contact with water to prevent drying, and contact of coal with air should be avoided (Gash, 1991). Also, weathering (drying by exposing to air and heat) alters the structure of coal (Nelson, 1989). When drying of the cores was required to facilitate grinding to specifications, care was taken to use only vacuum drying and thus preventing drying by exposing to heat or air. Also, the powdered samples were re-moistened using ASTM procedure.

4.2 Sample Preparation

It is a common practice to use powdered samples for sorption experiments in order to reduce the time for the experiments by minimizing the distance that the gas molecules must diffuse through the matrix. The size reduction speeds up the diffusion of gas molecules and hence the sorption of gas. This greatly reduces the equilibrium time for each pressure step and speeds up the experiment.

Proper sample preparation is a critical part of an adsorption/desorption experiment. Sample preparation consists of the following steps:

1. Sample selection
2. Pulverization
3. Equilibrium moisture content

For this study, powdered samples were prepared from the coal cores obtained from the sources. The sample was first vacuum dried (at room temperature) just before crushing. Drying was necessary to facilitate grinding to specification in the ball mill. It was then broken into small lumps approximately 1 cm in size in a jaw crusher. The small lumps of coal were ground in a ball mill. The resulting powdered coal was sieved to obtain the desired sample size of 40-200 mesh (0.0425 - 0.0075 cm).

One of the major concerns is the effect of crushing the coal samples on the experimental results. It is feared that crushing increases the surface area of coal and therefore the amount of gas adsorbed. Crushing the coal changes the surface area for gas adsorption by very little which is not believed to affect the accuracy of the gas storage capacity determination. Calculations for the change in surface area due to crushing are shown in Appendix A.

After crushing, the ASTM procedure was followed to ensure that the sample had equilibrium moisture content. Approximately 200 grams of sample was collected and divided into two parts and weighed. They were then kept in a vacuum desiccator containing a saturated solution of potassium sulfate. The desiccator was evacuated to a pressure of 30 mm Hg, and maintained at a temperature of 30°C. The potassium sulfate solution was used to maintain a relative humidity of 97%. It took approximately 48 hours for the coal to become fully moist. This was determined by weighing the coal sample periodically. The stabilized weight of the moist coal sample was noted. One part was taken and dried at a temperature of 70°C. The dry weight of the sample was

determined. The exact moisture content was calculated as the percentage ratio of the weight of moisture in coal to the weight of dry coal. The other part was used in the sorption experiment.

4.3 Experimental Setup

The experimental setup design is based on the volumetric method using the gas expansion technique to measure the quantity of adsorbed gas. This technique utilizes the Boyle's law for ideal gases. At a given temperature, the volume of a fixed mass of gas varies inversely with absolute pressure. At high pressures, a compressibility factor is usually taken into account to allow for the non-ideal behavior of real gases and the relationship becomes:

$$\frac{P_1 V_1}{Z_1} = \frac{P_2 V_2}{Z_2}$$

where,

P_1 is the initial pressure,

V_1 is the initial volume,

P_2 is the final pressure,

V_2 is the final volume,

Z_1 & Z_2 are the compressibility factors at initial and final conditions

respectively. Figure 4.1 shows the compressibility factors for methane.

The experimental setup principally consists of a stainless steel fixed volume cylinder (FV), 150 cm³ in volume, to hold a known mass of gas, and a stainless steel sample container (SC), approximately 250 cm³ in volume. The setup is shown in Figure 4.2. The sample container holds the powdered coal. Since the sorption isotherms are very sensitive to temperature, the entire setup is placed in a constant temperature

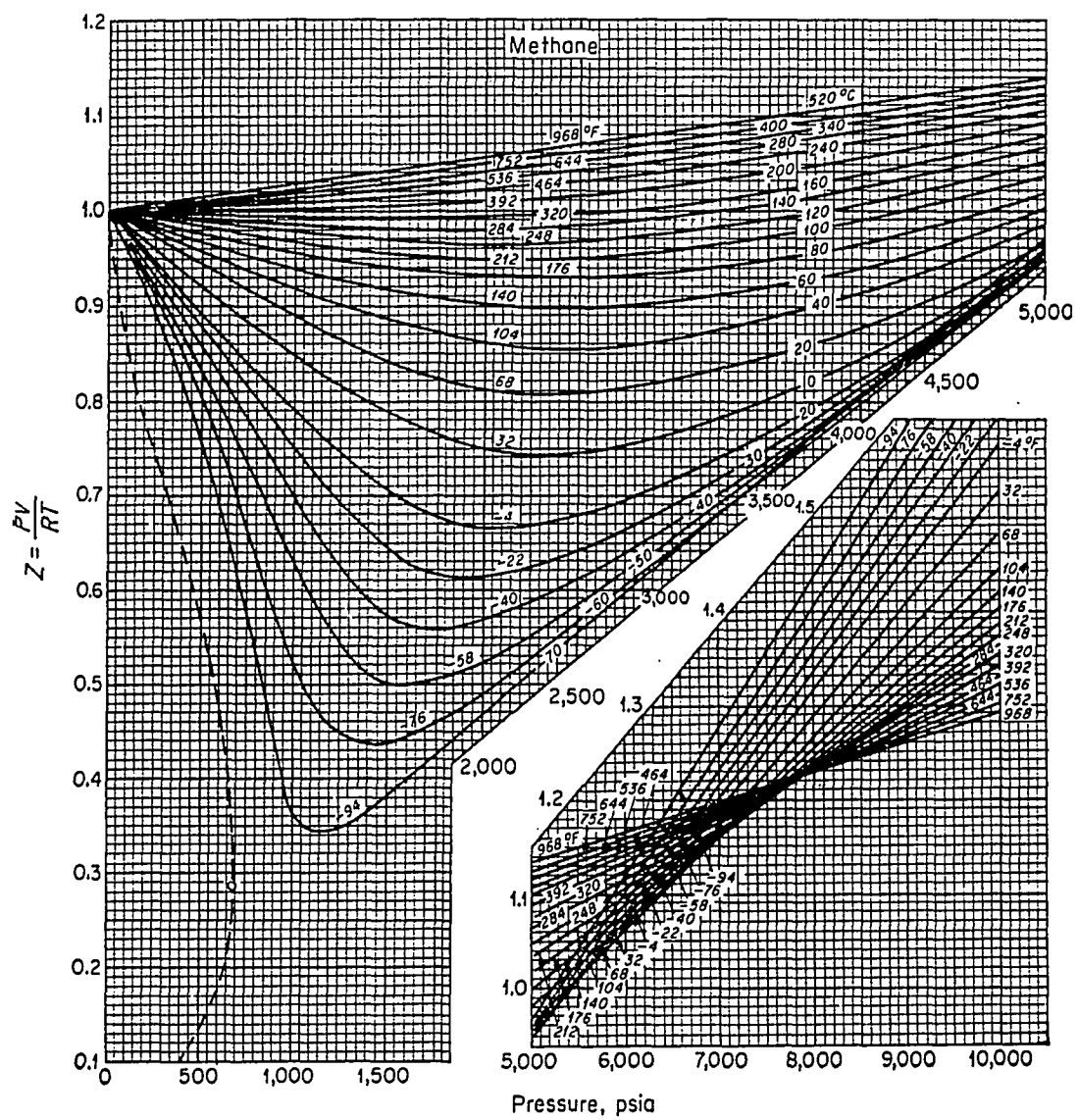


Figure 4.1 Compressibility factors for methane (after Brown et al, 1948).

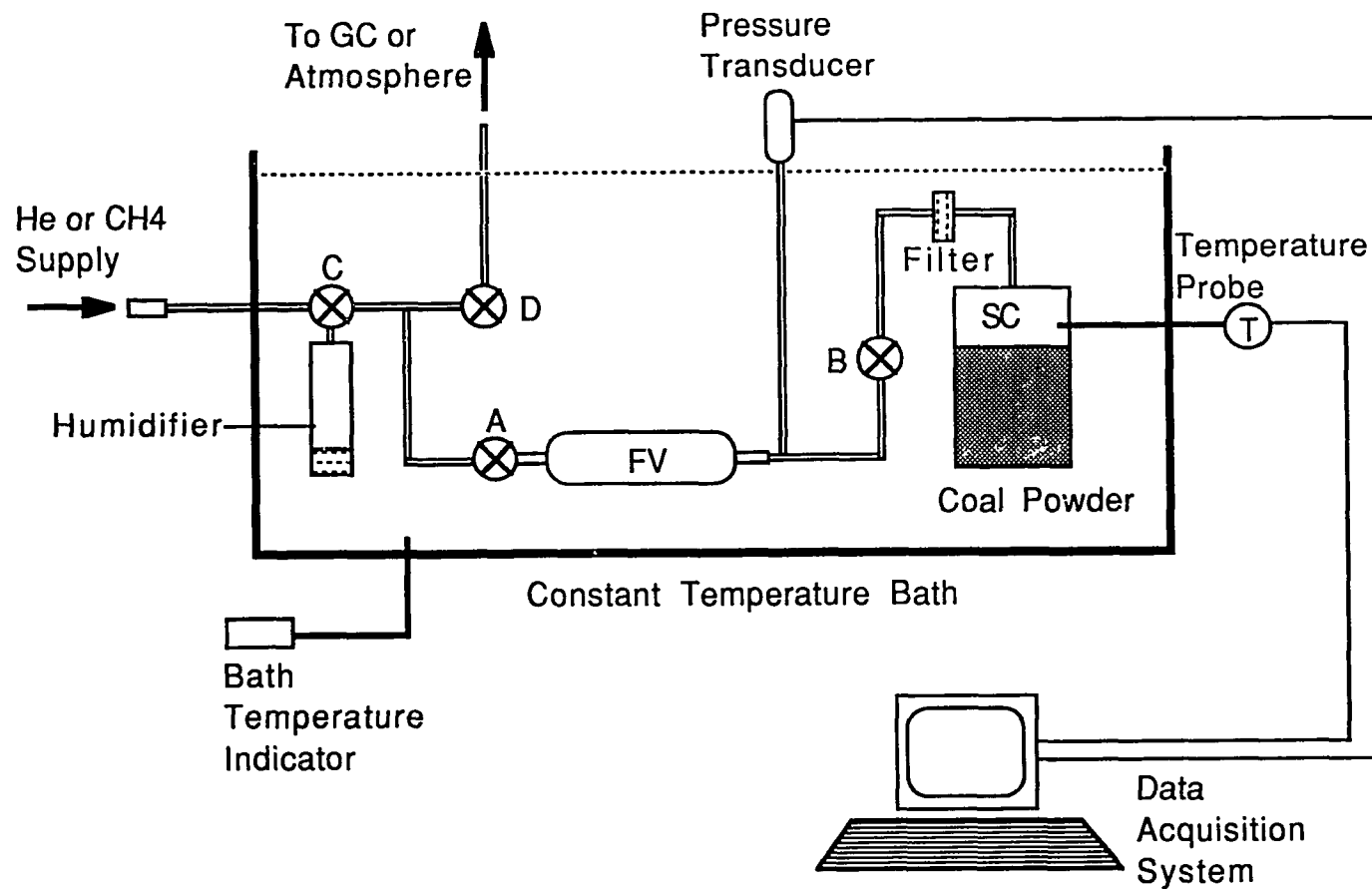


Figure 4.2 Experimental setup for adsorption/desorption tests.

bath which maintains a constant temperature to within $\pm 0.1^{\circ}\text{C}$. A temperature indicator indicates the bath temperature throughout the experiment. A pressure transducer is attached to the FV cylinder and a temperature probe (T) is installed in the sample container. A filter is provided to prevent any coal particles from being blown away from the sample container into the fixed volume cylinder. A three way valve, C, is provided at the top to let dry gas into the humidifier and let out the humidified gas to the FV cylinder. Valve B is placed between FV and SC. It allows gas to expand into/from SC. Valve A lets gas into/out of FV. Valve D is used during desorption steps to bleed the gas to atmosphere. All the cylinders, tubing and valves are rated to a pressure much higher than that used in the experiments.

4.4 Experimental Procedure

For sorption isotherm experiments, the procedure consisted mainly of three parts:

1. Calibration
2. Measurement of adsorbed gas volume
3. Measurement of desorbing gas volume

Calibration of the setup involved determining the void volume in the sample container after placing the moist powdered sample in it. The sample container was first purged with helium. To ensure that the moisture content of the sample did not decrease, the sample container was not evacuated. The test, therefore, started with atmospheric pressure. With valve B closed, helium (non-adsorptive gas) was injected into the fixed volume, and pressure, P_1 , was measured. Valve B was then opened and helium allowed to expand into the sample container. Gas pressure, P_2 , was recorded. Using Boyle's law, the volume of the void space in the sample container was calculated. This procedure was repeated three times to minimize experimental error.

Establishing the adsorption isotherm for a sample consisted of first venting the entire setup to atmosphere. Opening the three way valve, C, methane was then let into the humidifier, where it was allowed sufficient time. With valve B closed, valves C and A were opened, and the FV cylinder was filled with humidified gas from the humidifier and pressure, P_1 , was recorded. Next, valve B was opened to allow expansion of the gas into the SC. Once gas pressure stabilized, pressure, P_2 , was measured. The above steps were repeated for increasing pressure levels to obtain a complete adsorption isotherm for pressures upto 1500 psi.

Once the highest pressure for the adsorption isotherm was reached, the desorption isotherm was established. Although the two isotherms should be identical if the experiment is performed correctly (Mavor *et al*, 1990), it is important to repeat the experiment for decreasing pressure to ensure that the two, in fact, are in agreement. Also, estimating changes in gas content in the sample during the desorption isotherm enables calculation of the diffusion coefficient for the powdered sample.

The quantity of desorbing gas was determined by closing valve B, and opening valves A and D to let gas out of the FV cylinder. Pressure, P_1 , was recorded. Valves A and D were closed, and valve B was opened to allow expansion of the gas from the SC. Once the gas pressure stabilized, pressure, P_2 , was measured. These steps were repeated for decreasing pressure until the pressure reached near atmospheric, and a complete desorption isotherm was obtained.

The same procedure was used when using carbon dioxide gas except that experiments were conducted to pressures of 700 psia. This was done because carbon dioxide liquefies at a pressure of 940 psia at room temperature (Compressed Gas Association, 1990). Since vital sorption information for carbon dioxide can be obtained by 700 psia, and to be at a safe range from the liquefaction pressure of carbon dioxide, the experiments were conducted upto pressures of 700 psia.

4.5 Monitoring the Gas Composition

One modification was made to the standard procedure to enable monitoring the composition of the desorbing gas during the desorption part of the experiment when using a gas mixture. A gas chromatograph was included and the gas could either be vented to atmosphere or let into the gas chromatograph for analysis. After equilibrium was attained and the equilibrium pressure recorded, a sample of the gas was passed through the GC and the composition of the gas for the particular pressure estimated. This was repeated three times before the subsequent pressure step. At the end of the experiment, along with the sorption isotherm, the gas composition variation (as a function of pressure) was also obtained. After completing the desorption part of the experiment, moisture content of the sample was again determined.

CHAPTER 5

RESULTS AND DISCUSSION

For purposes of calculation, the partial pressure of methane was considered, rather than the total pressure, to account for the fact that the total volume included a small fraction of helium.

5.1 Adsorption

Using P_1 and P_2 , S.T.P. volume of gas that left the fixed volume was calculated. Using the void volume in the sample container, S.T.P. volume of free gas in this space was determined. The S.T.P. volume of adsorbed gas at pressure, P_2 , was the difference between the volume of gas that left the fixed volume and that appearing as free gas. This calculation was repeated for all pressure steps. A sample calculation is shown in Appendix B.

5.2 Desorption

Using P_1 and P_2 , S.T.P. volume of gas that entered the fixed volume was calculated. Using the void volume in the sample container, S.T.P. volume of free gas in this space at P_2 was determined. The difference between this and the previous volume of free gas gave the volume of free gas leaving the SC. The S.T.P. volume of desorbed gas at pressure, P_2 , was the difference between the volume of gas that entered the fixed volume and the free gas component as calculated in the last step. Using this, the remaining adsorbed gas at pressure, P_2 , was calculated. The procedure was repeated for stepwise decrease in gas pressure.

Using the measured values of pressure, the amount of gas adsorbed and desorbed was calculated for each equilibrium pressure. Error caused due to experimental uncertainty was calculated using errors in the instrumental measurements. For the temperature indicator with the thermocouple the accuracy was 0.3°F and for the pressure indicator with the transducer the span drift was 0.01 %/°F. For the results of the experiments presented in this section, error was calculated for each pressure step. For any one step, the maximum error was 0.3 %.

5.3 Pure Gases

The sorption experimental results were analyzed using the Langmuir form. Hence, a pressure versus pressure/volume plot was drawn, as shown in Figure 5.1. Using the slope and intercept of the best fitting straight line, Langmuir coefficients were obtained. Figure 5.2 shows the sorption isotherm based on this equation, along with the experimental results. The experimental temperature was 86°F. The following values were obtained

$$P_L = 306 \text{ psia}$$

$$V_L = 19.2 \text{ scc/g (614 standard cubic feet/ton)}$$

The values of P_L and V_L for similar coal (basal coal in the San Juan Basin) are 330 and 345 psi, and 562 scf/ton (Bell, 1989). The isotherm clearly indicates that at 1500 psi monomolecular saturation is not attained for this sample, although the rate of increase in the volume of adsorbed gas is extremely slow. It is also apparent that there is no hysteresis between the adsorption and desorption results.

Several improvements that have been made are summarized below:

1. Moist coal samples were used for experiments with pure gases as well as gas mixture to simulate the *in situ* conditions. Known procedures were used to moisten the coal sample.

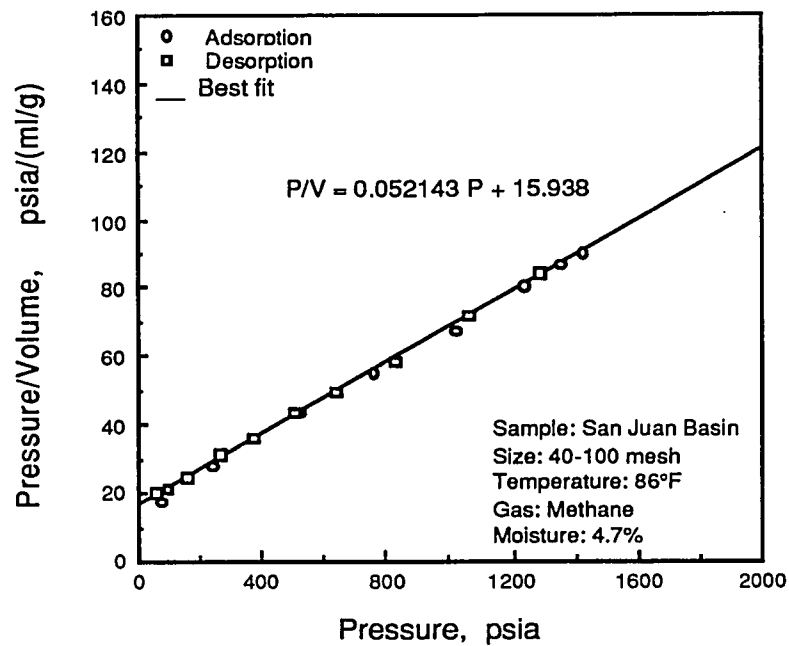


Figure 5.1 Langmuir plot of sorption data for basal coal in the San Juan basin.

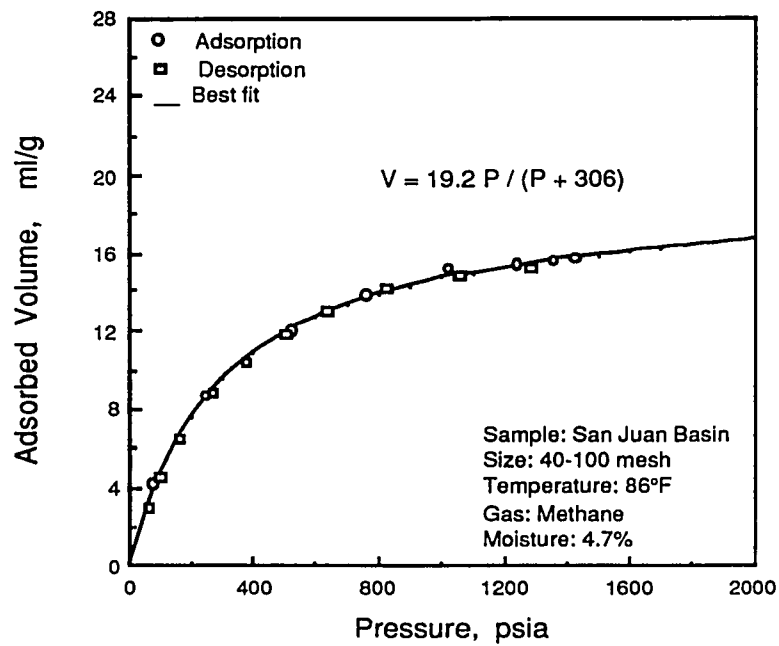


Figure 5.2 Sorption isotherm for basal coal in the San Juan basin.

2. A filter was placed between the fixed volume cylinder and the sample container. It serves the purpose of preventing coal dust from blowing from the sample container into the fixed volume cylinder. This also ensures that the weight of coal in the SC remains the same throughout the experiment.
3. Since sorption process is very sensitive to temperature, the entire setup was immersed in a water bath with sensitive temperature control.

Figures 5.3 and 5.4 show the results for pure methane at a temperature of 112°F. Following values were obtained:

$$P_L = 299 \text{ psia}$$

$$V_L = 11.6 \text{ scc/g (371 scf/ton)}$$

The results for the sorption experiment using pure carbon dioxide at 112°F are shown in Figures 5.5 and 5.6. Following values were obtained for pure carbon dioxide:

$$P_L = 116 \text{ psia}$$

$$V_L = 17.1 \text{ scc/g (547 scf/ton)}$$

Figure 5.7 shows the comparison of the sorption isotherms for pure methane and pure carbon dioxide. It can be seen from the figure that carbon dioxide is more adsorptive than methane on coal. The Langmuir volume of carbon dioxide, 17.1 scc/g, is almost 1.5 times that of methane, 11.6 scc/g. Also, carbon dioxide sorbs more quickly, its Langmuir pressure being 116 psia compared to 299 psia for methane.

5.4 Gas Mixture

Figures 5.8 and 5.9 show the results for a sample from the Fruitland coal of the San Juan Basin. The sample was obtained from a well preserved core provided by AMOCO. The recommended temperature and moisture content were 112°F and 1.7 - 1.9 % respectively. A multicomponent gas mixture consisting of 93 % methane, 5 % carbon dioxide and 2 % nitrogen was used. The first run gave the following results:

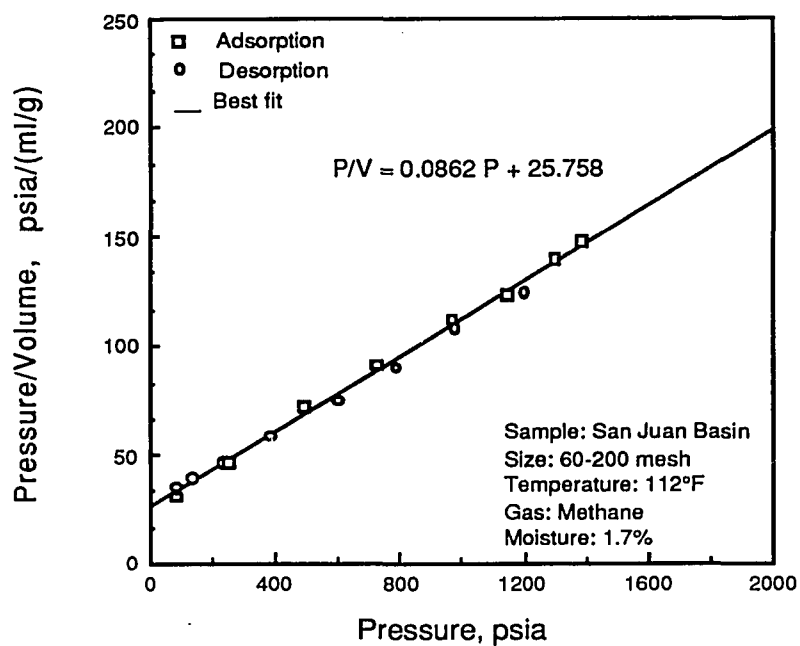


Figure 5.3 Langmuir plot for pure methane on coal from San Juan basin.

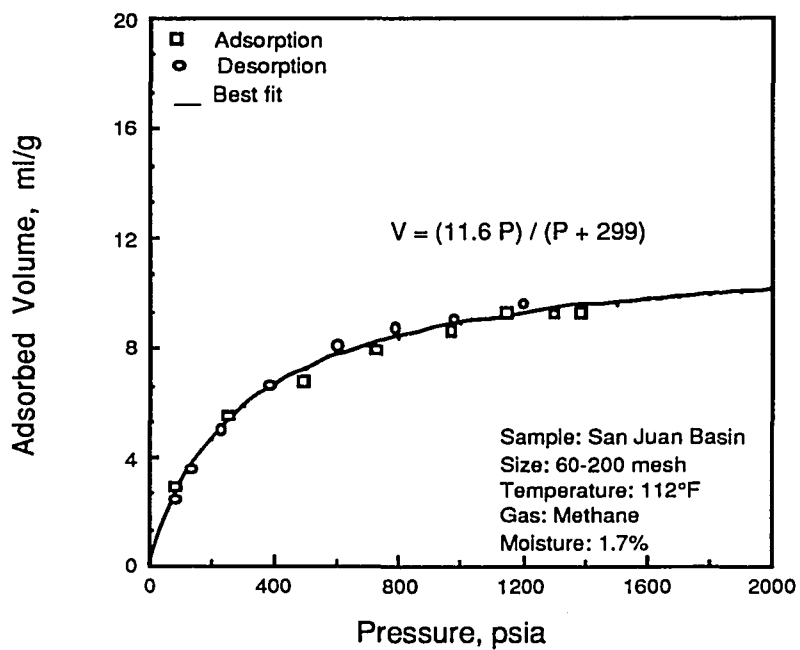


Figure 5.4 Sorption isotherm for pure methane on coal from San Juan basin.

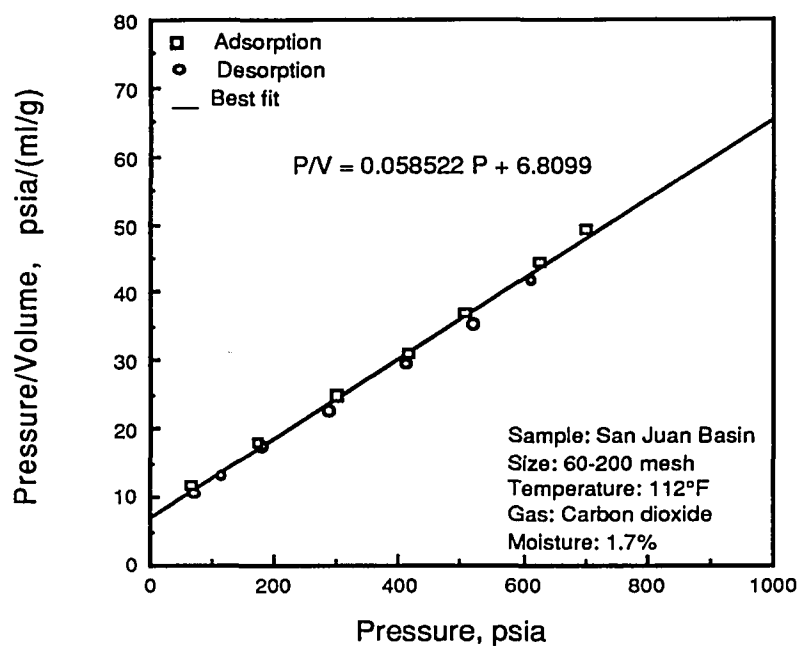


Figure 5.5 Langmuir plot for pure carbon dioxide on coal from San Juan basin.

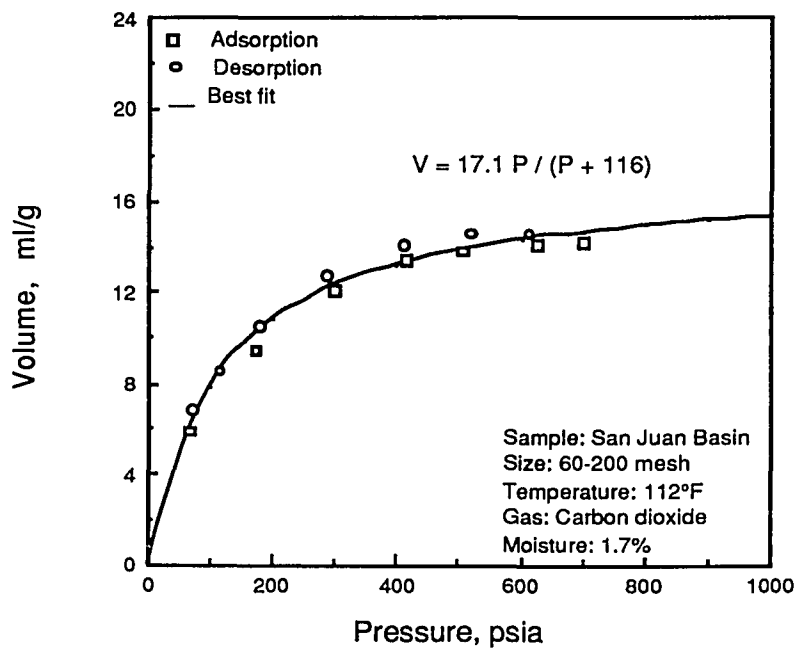


Figure 5.6 Sorption isotherm for pure carbon dioxide on coal from San Juan basin.

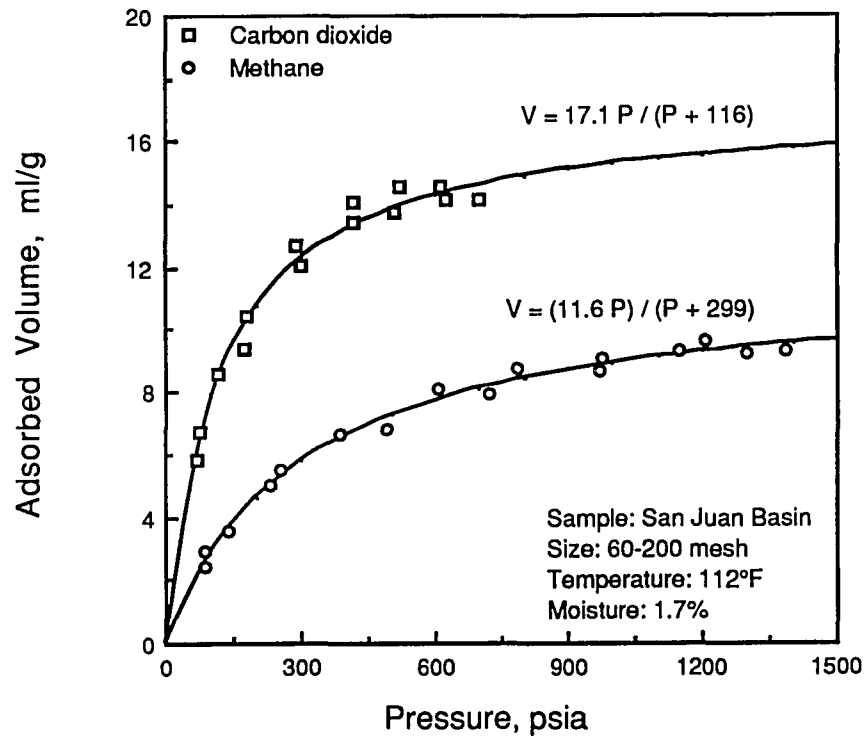


Figure 5.7 Comparison of the sorption isotherms for pure methane and carbon dioxide.

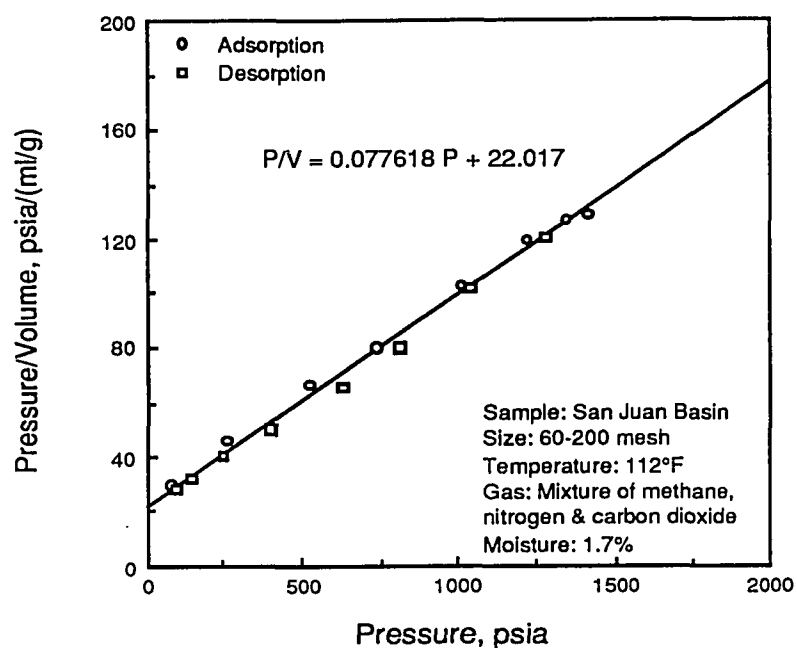


Figure 5.8 Langmuir plot for gas mixture on coal from San Juan basin.

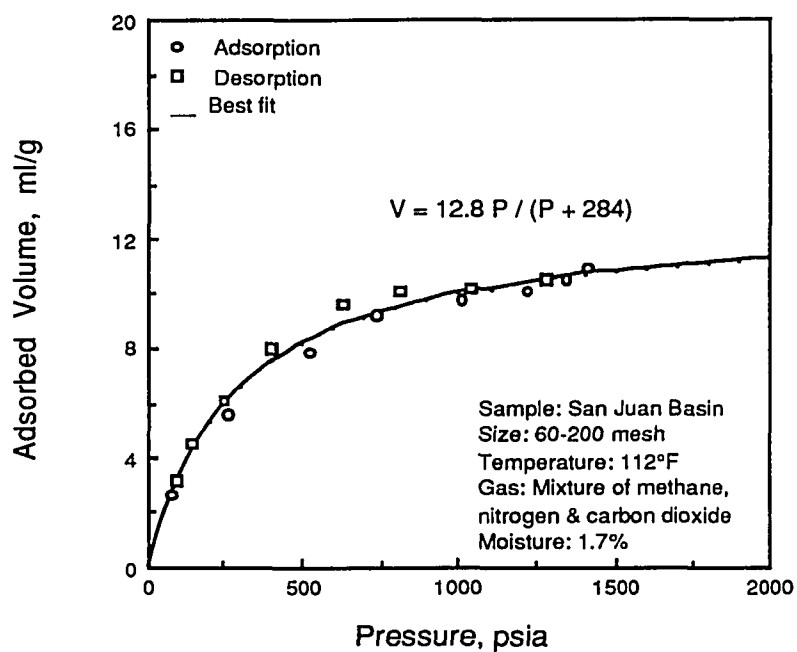


Figure 5.9 Sorption isotherm for gas mixture on coal from San Juan basin.

$$P_L = 284 \text{ psia}$$

$$V_L = 12.8 \text{ scc/g (412 scf/ton)}$$

Figure 5.10 shows the plot of methane and carbon dioxide concentrations measured for the desorption part of the experiment. Figure 5.11 shows the sorption isotherms for pure methane, pure carbon dioxide and gas mixture. It is evident that the isotherm for the gas mixture lies in between the isotherms for pure methane and pure carbon dioxide. The Langmuir volume of gas mixture, 12.8 ml/g, is approximately 10 % higher than that of pure methane, 11.6 ml/g, due to the presence of carbon dioxide which is more adsorptive. Also, the Langmuir pressure of gas mixture, 284 psia, is 5 % lower than that of pure methane, 299 psia, again, due to the presence of faster sorbing carbon dioxide.

5.5 Numerical Analysis

As discussed earlier, several researchers have utilized the ideal adsorbed solution (IAS) theory of Myers and Prausnitz to come up with the sorption behavior of binary and ternary gas mixtures on coal. For the current work, a numerical analysis method suggested recently by Scott (1992) was used to compute the composition of gas mixture from the sorption results of individual gases. The numerical analysis deals with computing the composition of the methane-carbon dioxide gas mixture at each desorbing pressure step using the individual methane and carbon dioxide sorption results. These numerically computed gas composition results are then compared to the experimentally obtained data.

The multi-component gas mixture used in the sorption experiments consisted of 93 % methane, 5 % carbon dioxide and 2 % nitrogen. Since the nitrogen component remained almost constant, it was not used in the calculations to simplify the procedure.

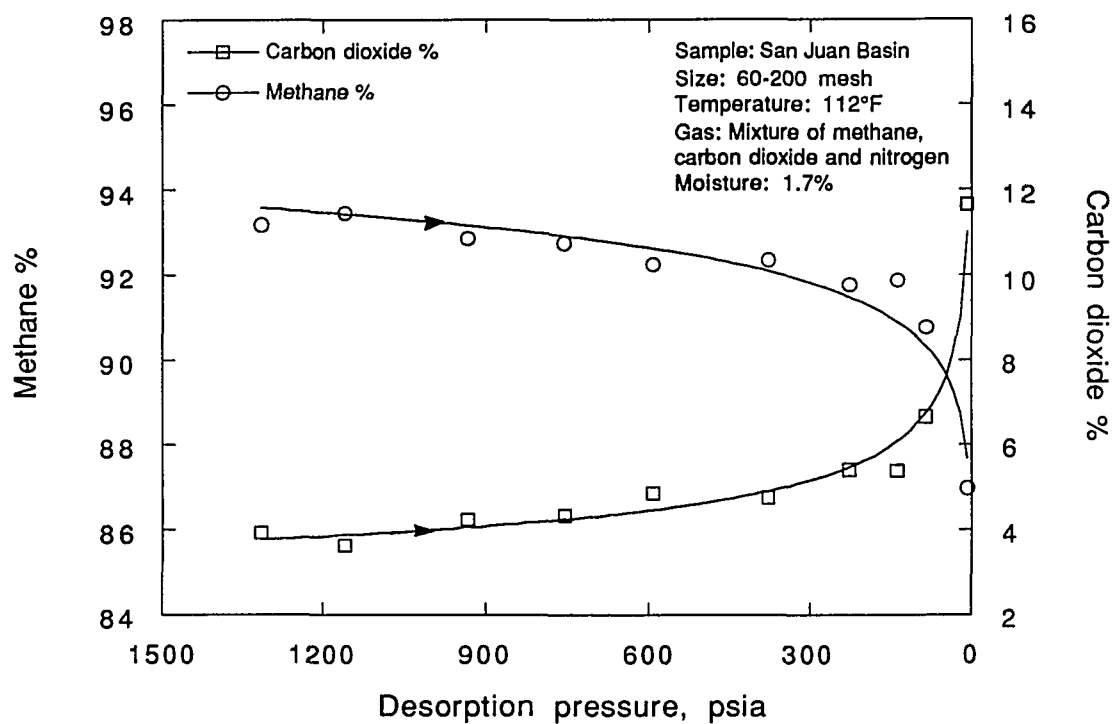


Figure 5.10 Variation in gas composition with pressure decline.

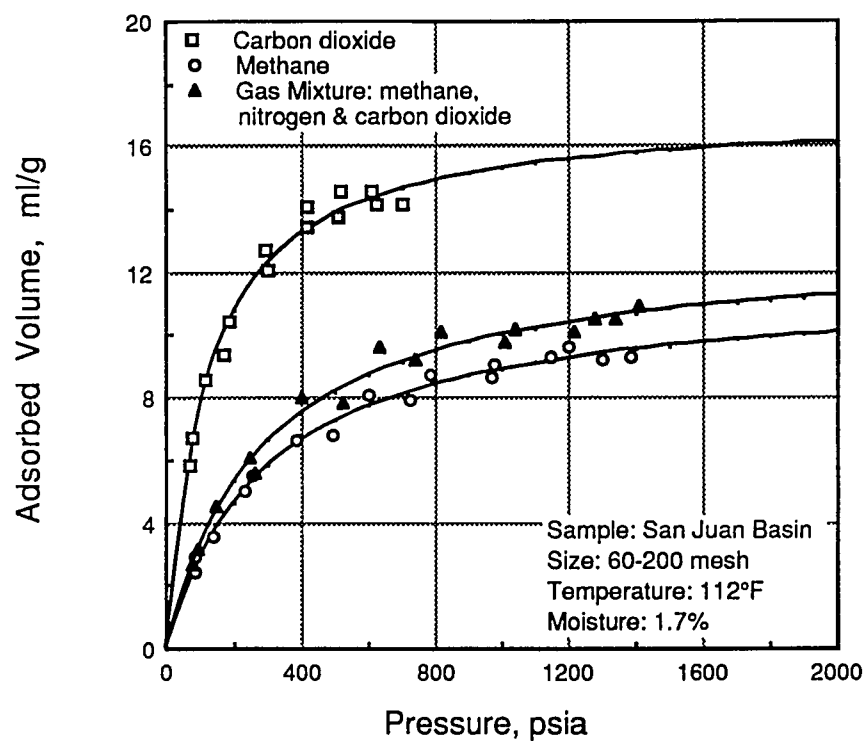


Figure 5.11 Comparison of sorption isotherms for pure methane, pure carbon dioxide and gas mixture.

The methane and carbon dioxide percentages were normalized and a binary composition of 94.9 % methane and 5.1 % carbon dioxide was obtained. All the experimental results of gas composition for various pressure steps obtained by using the gas chromatograph were normalized accordingly to obtain binary composition of methane and carbon dioxide as shown in Table 2.

The numerical analysis method was then utilized for theoretical calculations of gas composition at various pressure steps using the sorption data from pure methane and pure carbon dioxide experiments. The first step was obtaining the adsorbed volumes of methane and carbon dioxide for various pressures using their respective Langmuir equations. The next step was to multiply the volume of methane adsorbed at each pressure step with its normalized percentage, 94.9 %. The same was done for carbon dioxide, its normalized percentage being 5.1 %. The loss in methane for each pressure step was then obtained by subtracting the normalized volume of methane from the respective original volume of methane. The same was done for carbon dioxide. By adding the two, the total loss was obtained for each pressure step. The percentage component of methane at each pressure step was obtained as the ratio of loss of methane to the respective total loss expressed in percentage. Similarly, the percentage of carbon dioxide was obtained for each pressure step. These percentages represent the composition of the methane-carbon dioxide gas mixture at various pressure steps. The calculations are shown in Table 2.

Using the numerically obtained composition of the gas mixture, a plot was obtained as shown in Figure 5.12 indicating the percentages of methane and carbon dioxide components at each pressure step. Figure 5.13 shows the comparison of the experimental data to the numerically computed values.

It is evident from Figure 5.13 that during desorption, methane concentration decreased with decrease in pressure while carbon dioxide concentration increased during

Pressure psia	CH4 ml/g	CO2 ml/g	x CH4 % B x 94.9%	x CO2 % C x 5.1%	Total gas ml/g	Loss CH4 9.072-D	Loss CO2 0.8047-E	Total loss G+H	CH4 % (G/I) x100	CO2 % (H/I) x100
A	B	C	D	E	F	G	H	I	J	K
1400.0	9.5596	15.7786	9.0720	0.8047	9.8767	0.0000	0.0000	0.0000		
1317.2	9.4550	15.7028	8.9728	0.8008	9.7737	0.0992	0.0039	0.1030	96.26	3.74
1160.5	9.2247	15.5326	8.7542	0.7922	9.5464	0.3178	0.0125	0.3303	96.20	3.80
933.5	8.7872	15.1958	8.3390	0.7750	9.1140	0.7330	0.0297	0.7627	96.10	3.90
756.6	8.3157	14.8120	7.8916	0.7554	8.6470	1.1804	0.0493	1.2297	95.99	4.01
593.3	7.7145	14.2878	7.3211	0.7287	8.0498	1.7509	0.0760	1.8269	95.84	4.16
378.9	6.4853	13.0748	6.1546	0.6668	6.8214	2.9174	0.1379	3.0553	95.49	4.51
227.7	5.0166	11.3102	4.7607	0.5768	5.3375	4.3113	0.2279	4.5392	94.98	5.02
138.5	3.6737	9.2873	3.4864	0.4737	3.9600	5.5856	0.3310	5.9167	94.40	5.60
84.8	2.5642	7.2044	2.4334	0.3674	2.8009	6.6386	0.4373	7.0758	93.82	6.18
8.5	0.3208	1.1634	0.3045	0.0593	0.3638	8.7675	0.7454	9.5129	92.16	7.84
Experimental Results										
Pressure psia	CH4 %	CO2 %	Total %	Normalised CH4 %	Normalised CO2 %	Initial gas composition CH4 % CO2 % N2 % 93 5 2				
1317.2	93.18	3.92	97.10	95.96	4.04	Normalised gas composition CH4 % CO2 % 94.9 5.1				
1160.5	93.45	3.62	97.07	96.27	3.73					
933.5	92.85	4.23	97.08	95.64	4.36					
756.6	92.75	4.32	97.07	95.55	4.45					
593.3	92.24	4.85	97.09	95.00	5.00					
378.9	92.34	4.75	97.09	95.11	4.89					
227.7	91.77	5.40	97.17	94.44	5.56					
138.5	91.88	5.38	97.26	94.47	5.53					
84.8	90.76	6.66	97.42	93.16	6.84					
8.5	86.97	11.64	98.61	88.20	11.80					

Table 2 Numerical isotherm and gas composition calculations.

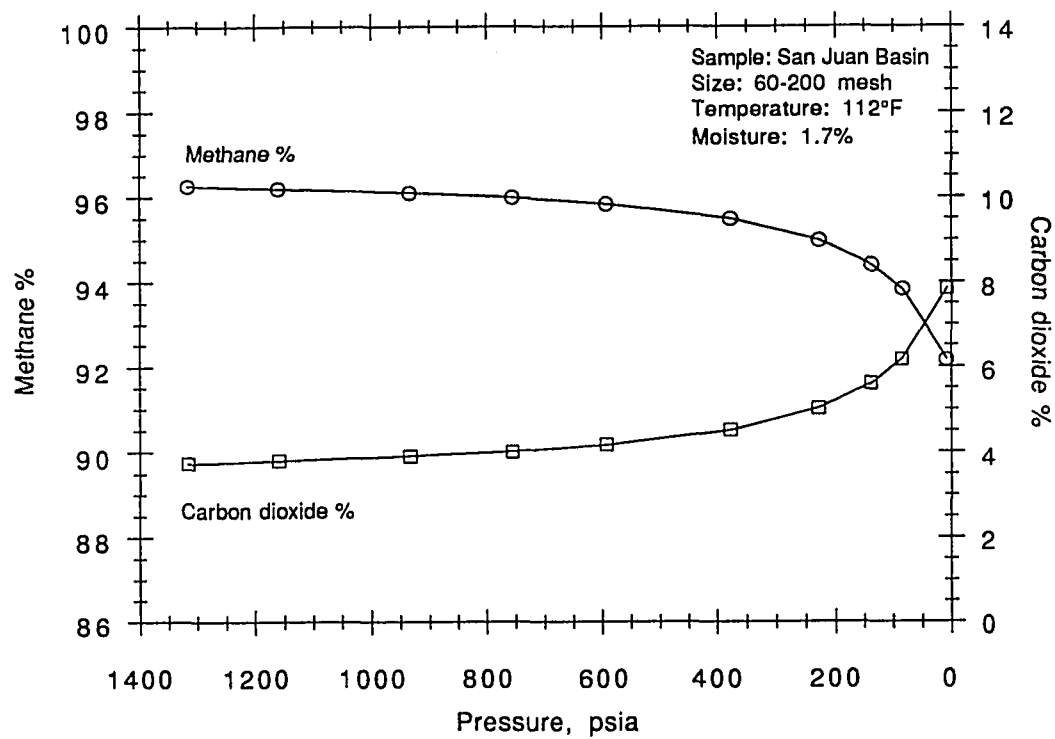


Figure 5.12 Numerically obtained plot of change in gas composition with declining pressure.

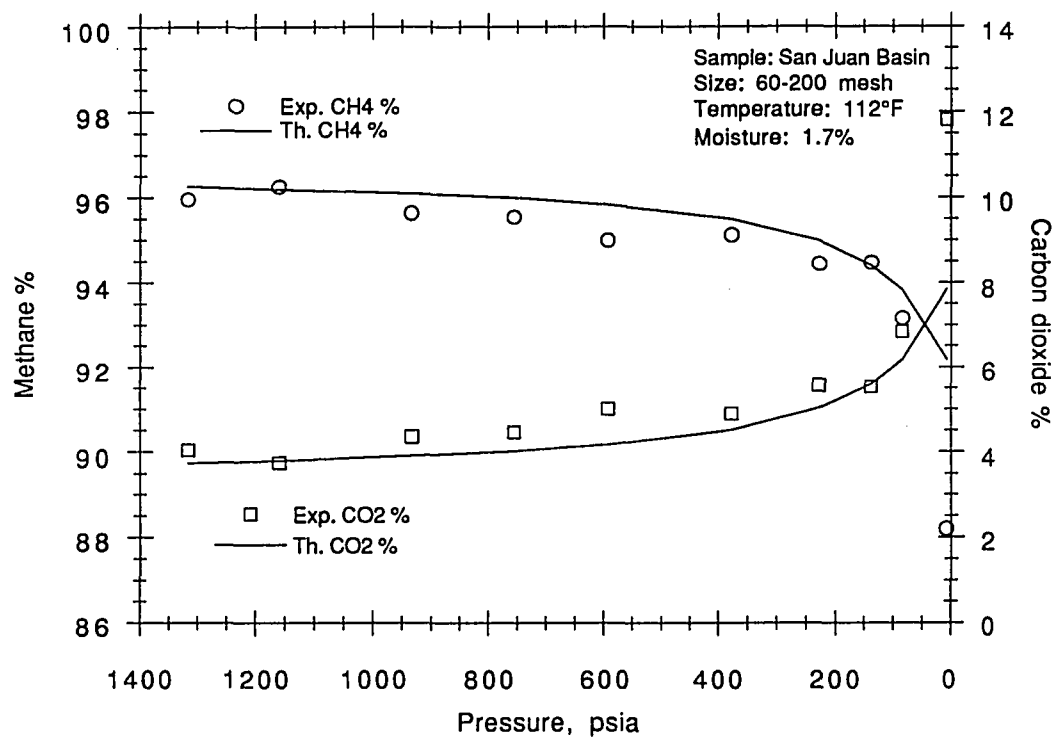


Figure 5.13 Comparison of experimental and numerical gas composition plots.

the same period. This is true for both experimental and theoretical values. Also, it is seen that the change is fairly significant for gas pressure below 400 psia. Methane concentration dropped from 96 % to 92 % as the pressure was decreased from 1400 psia to 50 psia. During the same period, carbon dioxide concentration increased from 4 to 8 %. The numerically computed values compare very well with the experimental results. The numerically obtained values are in agreement to experimental results within 0.4 % gas concentration.

From Table 2, numerically computed sorption data of pressure versus total gas adsorbed was obtained. Langmuir plot of this sorption data is shown in Figure 5.14. Figure 5.15 shows the sorption isotherm for the numerically computed data.

Figure 5.16 shows the comparison of the sorption isotherms obtained by the numerical analysis method versus the experimentally obtained sorption isotherm for the gas mixture. It is evident that the two compare very well. The Langmuir volume of the numerical isotherm, 11.8 ml/g, is less than that of experimental isotherm, 12.8 ml/g, by approximately 8 %. Also, the Langmuir pressure of the numerical isotherm, 273 psia, is less than that of experimental isotherm, 284 psia, by approximately 4 %. The numerically obtained values are, therefore, within 8 % of the values obtained from experimental isotherm.

5.6 Extended Langmuir Isotherm

The Langmuir isotherm for single-gas adsorption can be readily extended to a multi-component gas mixture. The extended Langmuir equation has been discussed by previous researchers (Ruthven, 1984 and Yang, 1987). The extended Langmuir equation for an n-component mixture is given by:

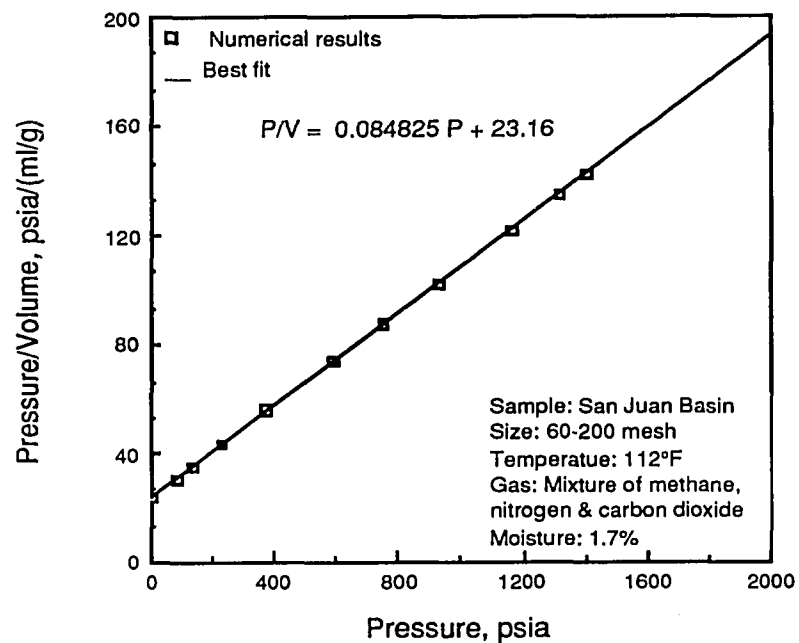


Figure 5.14 Langmuir plot of numerically computed sorption data.

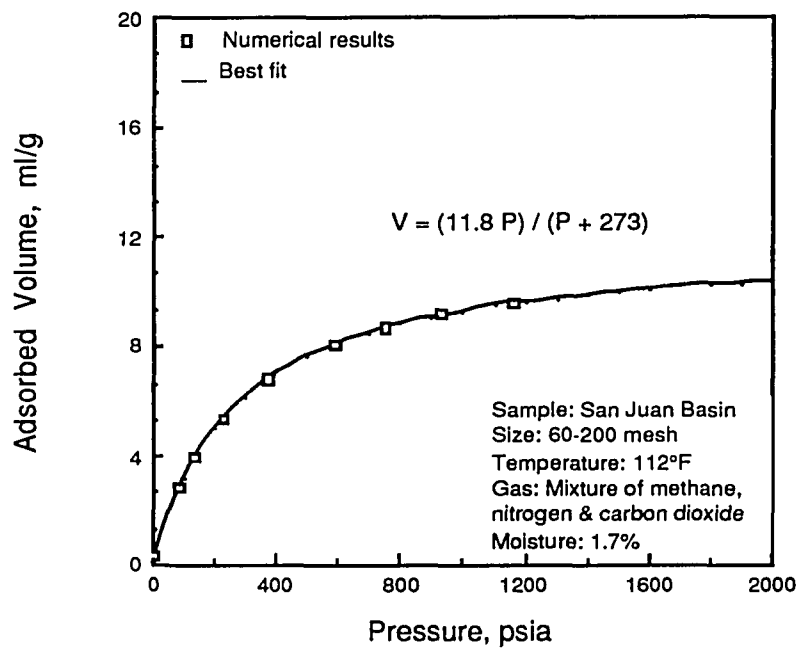


Figure 5.15 Sorption isotherm for numerically computed data.

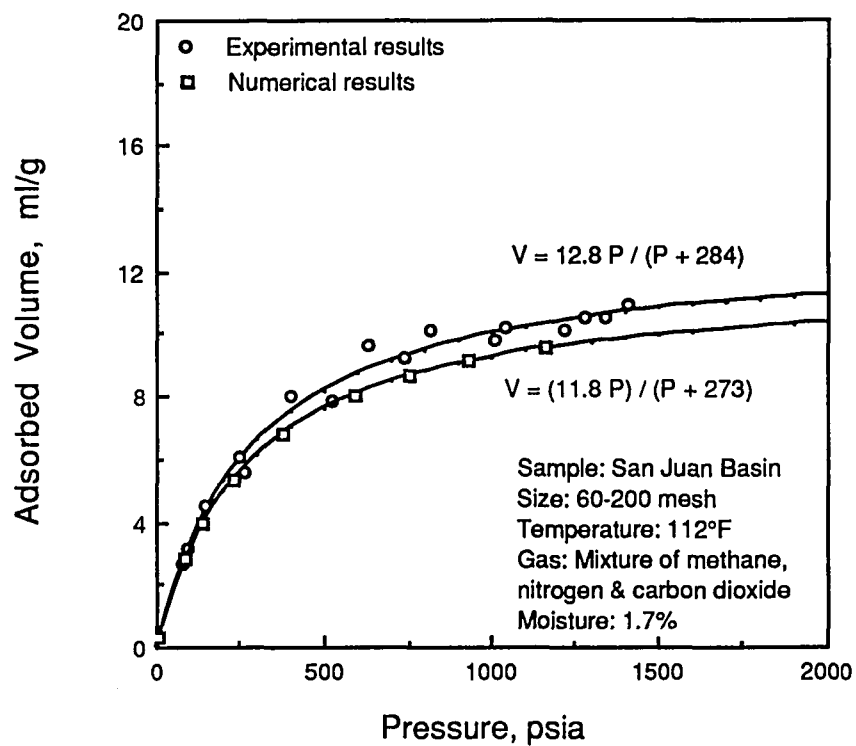


Figure 5.16 Comparison of experimental and numerical sorption isotherms.

$$V_i = \frac{V_{m_i} B_i P_i}{1 + \sum_{j=1}^n B_j P_j}$$

where, V_i = amount adsorbed for component i in the mixture

V_{m_i} = monolayer amount for i (V_L for i)

$B_i = 1/P_L$ for i

P_i = Partial Pressure for i

n = number of components in the mixture

Using this equation, the volumes adsorbed for methane and carbon dioxide have been computed as shown in Table 3. Total volume of gas mixture adsorbed is the sum of the volumes of methane and carbon dioxide components adsorbed. Figures 5.17 and 5.18 show the Langmuir plot and sorption isotherm of the data obtained from the extended Langmuir equation.

It is evident from Figure 5.19 that the Langmuir volume for the extended isotherm, 12.3 ml/g, is less than that of experimental isotherm, 12.8 ml/g, by approximately 4 %. The Langmuir pressure of the extended isotherm, 277 psia, is less than that of experimental isotherm by around 3 %.

Figure 5.20 shows the comparison of extended Langmuir isotherm versus numerical isotherm. The Langmuir volume of extended isotherm is greater than that of numerical isotherm by approximately 4 %. The respective difference in Langmuir pressures is around 1 %.

Pressure	Par Pr CH4	Par Pr CO2	1+B1P1+B2P2	Vol CH4	Vol CO2	Total Vol
P, psia	P1, psia	P2, psia	D	V1, ml/g	V2, ml/g	V, ml/g
P	P x 94.9 %	P x 5.1 %	1+B1P1+B2P2	Vm1B1P1/D	Vm2B2P2/D	V1 + V2
1400.0	1328.6000	71.4000	6.0641	8.5139	1.7295	10.2434
1317.2	1250.0228	67.1772	5.7646	8.4265	1.7117	10.1383
1160.5	1101.3145	59.1855	5.1978	8.2337	1.6726	9.9063
933.5	885.8915	47.6085	4.3767	7.8657	1.5978	9.4635
756.6	718.0134	38.5866	3.7368	7.4668	1.5168	8.9836
593.3	563.0417	30.2583	3.1461	6.9546	1.4127	8.3673
378.9	359.5761	19.3239	2.3706	5.8944	1.1974	7.0918
227.7	216.0873	11.6127	1.8236	4.6046	0.9354	5.5400
138.5	131.4365	7.0635	1.5010	3.4028	0.6912	4.0941
84.8	80.4752	4.3248	1.3067	2.3932	0.4861	2.8793
8.5	8.0665	0.4335	1.0307	0.3041	0.0618	0.3659
Methane		Carbon dioxide				
Vm1 = 11.6 ml/g		Vm2 = 17.1 ml/g				
B1 = 0.00335		B2 = 0.00859				
Conc. = 94.9 %		Conc. = 5.1 %				

Table 3 Extended Langmuir isotherm calculations.

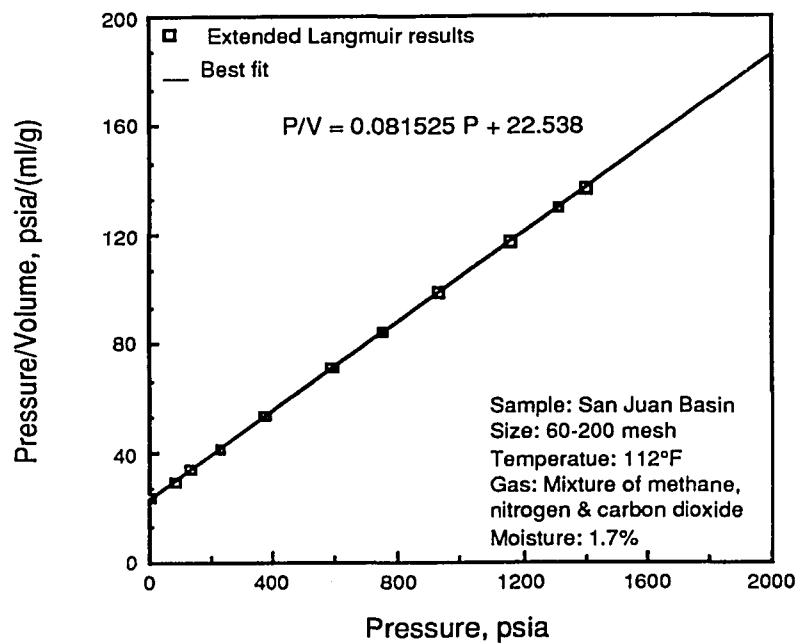


Figure 5.17 Langmuir plot of extended Langmuir sorption data.

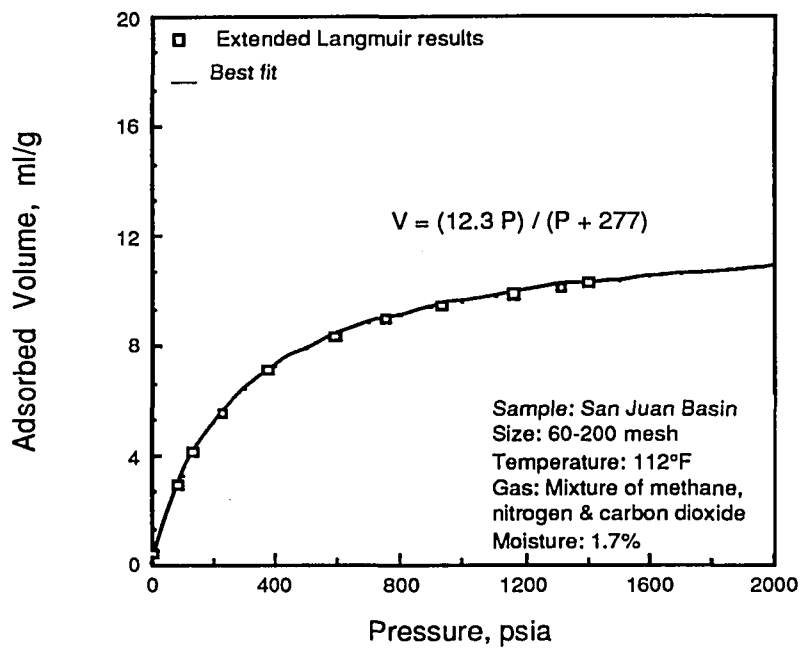


Figure 5.18 Sorption isotherm for extended Langmuir sorption data.

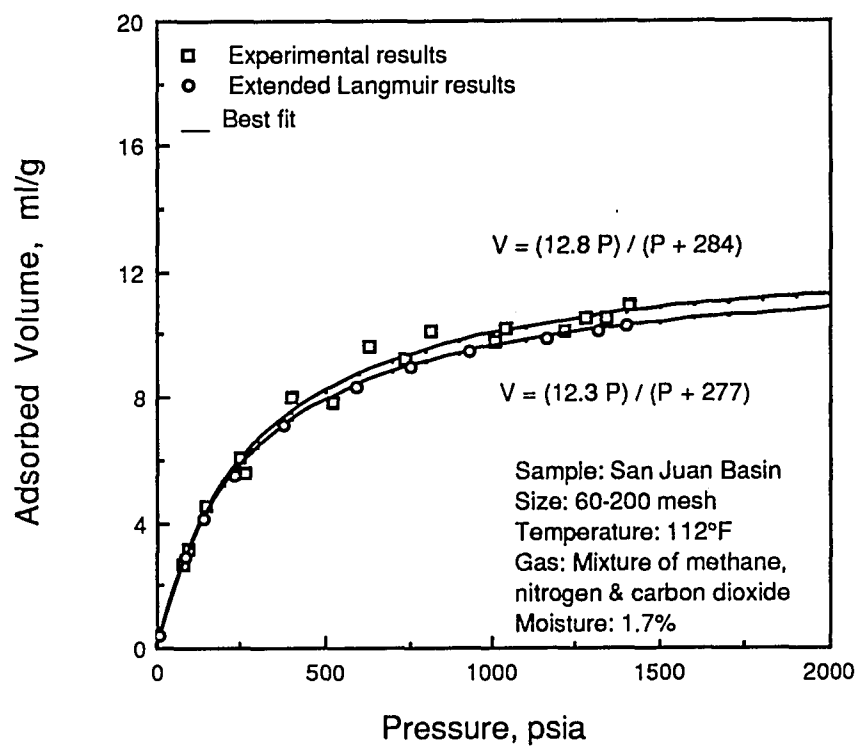


Figure 5.19 Comparison of experimental and extended Langmuir sorption isotherms.

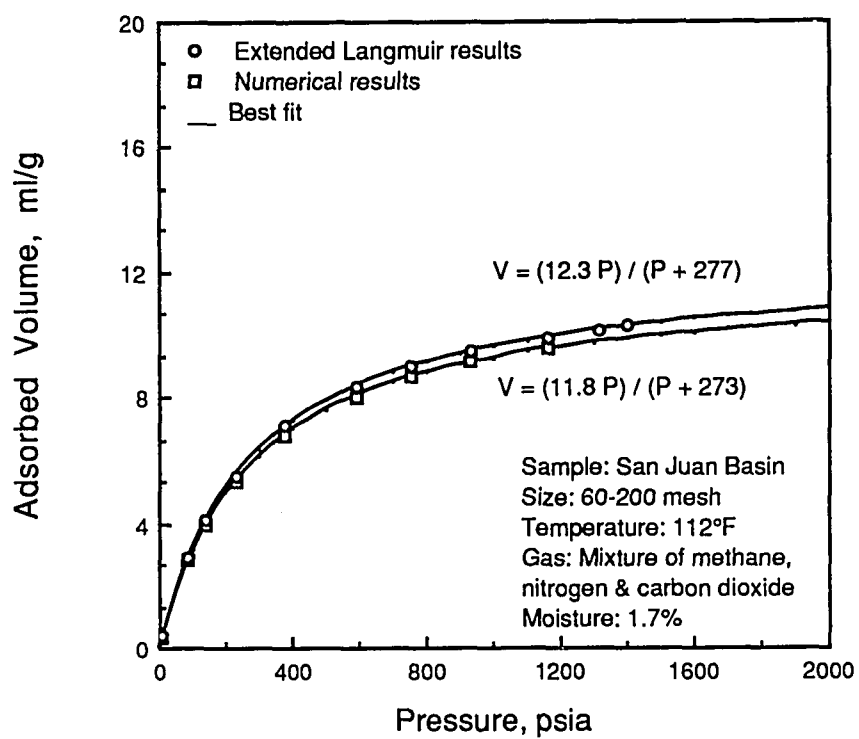


Figure 5.20 Comparison of numerical and extended Langmuir sorption isotherms.

CHAPTER 6

CONCLUSIONS

6.1 Conclusions

Experimental results indicate that during desorption, methane concentration decreased as the pressure was decreased while carbon dioxide concentration increased during the same period. The change is fairly significant for gas pressure below 400 psia. Since the nitrogen component was only 2 %, the change in its concentration was insignificant for calculation purposes. Methane concentration dropped from 96 % to 92 % as the pressure was reduced from 1400 psia to 50 psia. During the same period, carbon dioxide concentration increased from 4 % to 8 %. This information is useful because the reservoir pressure decreases during gas production, and it is possible to predict with reasonable accuracy the decline in concentration and production of methane. Since, it is the methane component of the natural gas that contributes as a fuel and to maintain a minimum BTU/scf for fuel supply, it is important to know the methane component for economic operation of the well.

Furthermore, the theoretically calculated values of gas composition obtained by using the numerical analysis method provide a good fit to the experimental results. The numerically obtained values are in agreement to experimental results within 0.4 % gas concentration.

Sorption results for the gas mixture obtained by the numerical analysis method compares very well with the sorption isotherm obtained from experimental results. The Langmuir volume of the numerical isotherm, 11.8 ml/g, is less than that of experimental isotherm, 12.8 ml/g, by approximately 8 %. Also, the Langmuir pressure of the numerical isotherm, 273 psia, is less than that of experimental

isotherm, 284 psia, by approximately 4 %. The numerically obtained values are within 8 % of the values obtained from experimental isotherm. A part of this difference in the experimental and theoretical values could be due to instrumental errors. At higher temperatures, the difference could be higher.

Also, the extended Langmuir isotherm values are within 4 % of the experimental results. The results of numerical and extended Langmuir isotherms compare very well with the experimental isotherm. The extended Langmuir isotherm provides a better theoretical prediction compared to the numerical method. It is, therefore, recommended that the extended Langmuir isotherm be used for the theoretical prediction of the results.

Under the given conditions of temperature and pressure, it is possible to come up with the sorption isotherm and the Langmuir constants for the gas mixture and the variation in gas composition over the life of a producing well theoretically, if the sorption isotherms for individual component gases are available and the *in situ* gas composition is known. The complicated procedure using gas mixtures and measuring the concentration of various gases is not necessary.

Another conclusion from this work is regarding the sorption isotherms for pure gases. Carbon dioxide is more sorptive on coal, its Langmuir volume being 1.5 times that of methane. Also, carbon dioxide sorbs more quickly on coal, its Langmuir pressure being 116 psia, compared to methane, 299 psia.

The isotherm for the gas mixture lies between those of methane and carbon dioxide. The Langmuir volume of gas mixture, 12.8 ml/g, is approximately 10 % higher than that of pure methane, 11.6 ml/g, due to the presence of carbon dioxide which is more adsorptive. Also, the Langmuir pressure of gas mixture, 284 psia, is 5 % lower than that of pure methane, 299 psia, again, due to the presence of faster sorbing carbon dioxide.

6.2 Comments

Sorption isotherms are very sensitive to parameters like temperature, moisture content, gas composition etc. It is important to know the parameters accurately for the coalbeds from which samples are obtained. Results of the experiments conducted at *in situ* conditions can be used for realistic modeling and forecasting of coalbed methane wells.

6.3 Recommendations for Future Work

It is recommended that further experiments be carried out using gas mixtures to determine the binary (two gases) and ternary (three gases) behavior of coal using a complete range of composition of different gases.

APPENDIX A

Calculation of Change in Surface Area of Coal due to Crushing

The internal surface area of 100 grams of bituminous coal (in which most coal bed reservoirs occur) ranges from 75,000 to 220,000 cm² (Jones *et al*, 1988). The external surface area of 100 grams of spherical coal particles (1.25 g/cc density) 0.025 cm in diameter (60 mesh) is 240 cm² (Mavor *et al*, 1990).

60 mesh = 0.025 cm dia., $r_1 = 0.0125$ cm

200 mesh = 0.0075 cm dia., $r_2 = 0.00375$ cm

Volume of a particle of 60 mesh diameter = $\frac{4}{3} \pi r_1^3$

Volume of a particle of 200 mesh diameter = $\frac{4}{3} \pi r_2^3$

Number of 200 mesh particles in a 60 mesh particle = $\frac{\frac{4}{3} \pi r_1^3}{\frac{4}{3} \pi r_2^3} = \frac{r_1^3}{r_2^3}$

External surface area of a 60 mesh particle = $4\pi r_1^2$

External surface area of equivalent 200 mesh particles = $\frac{r_1^3}{r_2^3} 4\pi r_2^2 = \frac{r_1}{r_2} 4\pi r_1^2$

External surface area of 100 gm of spherical 60 mesh particles = 240 cm²

External surface area of 100 gm of spherical 200 mesh particles = $\frac{r_1}{r_2} 240$
 $= \frac{0.0125}{0.00375} (240)$
 $= 800 \text{ cm}^2$

Change in surface area due to crushing for 60 mesh particles = 0.1 % to 0.3 %

Change in surface area due to crushing for 200 mesh particles = 0.36 % to 1 %

Crushing 100 grams of coal to 200 mesh size changes the surface area for gas adsorption by 0.36 % to 1 % which is not believed to affect the accuracy of the gas storage capacity determination.

APPENDIX B

Sample Calculations of Gas Volumes Adsorbed/Desorbed

SAMPLE CALCULATIONS

Following parameters are required for calculations:

Volume of FV, $V_{FV} = 172.0$ ml

Void volume in SC, $V_{SC} = 204.73$ ml

Sample Weight (dry) = 107.9 g

Sample Weight (moist) = 113 g

Moisture content = 4.73%

Temperature = 30°C = 303 K

Partial pressures of methane have been used in the calculations.

Adsorbing Gas

The first values of P_1 and P_2 were 202.3 psia and 74.1 psia. The volume of gas in FV is converted to standard condition using Real Gas Law.

$$\begin{aligned}
 V_{FST} \text{ (at } P_1) &= \frac{V_{FV} \cdot T_{ST} \cdot P_1}{T \cdot P_{ST} \cdot Z_1} \\
 &= \frac{172 \times 273 \times 202.3}{303 \times 14.7 \times 0.98} \\
 &= 2176.21 \text{ ml}
 \end{aligned}$$

After the gas was allowed to expand, the pressure of gas in FV was 74.1 psia. At standard conditions,

$$\begin{aligned}
 V_{FST} \text{ (at } P_2) &= \frac{172 \times 273 \times 74.1}{303 \times 14.7 \times 0.993} \\
 &= 786.68 \text{ ml}
 \end{aligned}$$

The volume of gas that left FV is the difference

$$2176.21 - 786.68 = 1389.53 \text{ ml}$$

At pressure P_2 , the volume of gas in the void space in SC at standard condition is,

$$\begin{aligned}
 V_{VST} \text{ (at } P_2) &= \frac{V_V \cdot T_{ST} \cdot P_2}{T \cdot P_{ST} \cdot Z_2} \\
 &= \frac{204.73 \times 273 \times 74.1}{303 \times 14.7 \times 0.993} \\
 &= 936.40 \text{ ml}
 \end{aligned}$$

Of the 1389.53 ml of methane that left the FV, 936.40 ml appeared as free gas.

The quantity of adsorbed gas is, therefore, the difference

$$\begin{aligned}
 V_{ads} &= 1389.53 - 936.40 \\
 &= 453.13 \text{ ml}
 \end{aligned}$$

This volume is divided by the mass of the sample (107.9 g) giving the standard volume of methane adsorbed per unit mass of coal at the equilibrium pressure (74.1 psia).

$$Q_{ads} = \frac{453.13}{107.9} = 4.20 \text{ ml/g}$$

Similarly, for the second value of P_1 and P_2 ,

$$V_{FST} \text{ (at } P_1) = 5317.61 \text{ ml}$$

$$V_{FST} \text{ (at } P_2) = 2632.31 \text{ ml}$$

$$\text{The volume (st) that left FV} = 5317.61 - 2632.31 = 2685.30 \text{ ml}$$

$$V_{VST} \text{ (at } P_2) = 3133.27 \text{ ml}$$

The gas (st) that was already in SC

$$V_{VST} \text{ (old)} = 936.40 \text{ ml}$$

$$\begin{aligned}
 V_{VST} \text{ (entered)} &= 3133.27 - 936.40 \\
 &= 2196.87 \text{ ml}
 \end{aligned}$$

Of the 2685.30 ml that left the FV, 2196.87 appeared as free gas.

$$V_{ads} = 2685.30 - 2196.87$$

$$= 488.43 \text{ ml}$$

$$Q_{\text{ads}} = \frac{488.43}{107.9} = 4.53 \text{ ml/g}$$

The standard volume of methane adsorbed per unit mass of coal at equilibrium pressure 243.7 psia is, therefore, the sum of this and the volume already adsorbed at previous pressure (4.20 ml/g).

$$4.53 + 4.20 = 8.73 \text{ ml/g}$$

This procedure was continued for every value of P_1 and P_2 , and the adsorption isotherm was obtained.

Desorbing gas

The volume of gas at P_1 and P_2 (1112.8 psia and 1281.7 psia) are converted to standard conditions:

$$V_{\text{FST}} (\text{at } P_1) = \frac{V_{\text{FV}} \cdot T_{\text{ST}} \cdot P_1}{T \cdot P_{\text{ST}} \cdot Z_1}$$

$$= \frac{172 \times 273 \times 1112.8}{303 \times 14.7 \times 0.895}$$

$$= 13107.66 \text{ ml}$$

$$V_{\text{FST}} (\text{at } P_2) = 15337.04 \text{ ml}$$

The quantity of gas that came out of SC is the difference between these two volumes.

$$15337.04 - 13107.66 = 2229.38 \text{ ml}$$

The volumes of free gas in SC before and after opening valve B (at 1420.6 psia and 1281.7 psia) are converted to standard conditions:

$$V_{\text{VST}} (\text{before opening B}) = \frac{204.73 \times 273 \times 1420.6}{303 \times 14.7 \times 0.873}$$

$$= 20419.70 \text{ ml}$$

$$V_{VST} \text{ (after opening B)} = 18255.86 \text{ ml}$$

The quantity of free gas that left SC is the difference between these two volumes (st):

$$20419.70 - 18255.86 = 2163.84 \text{ ml}$$

Of 2229.38 ml that left SC, 2163.84 ml was free gas. The quantity of desorbed gas is, therefore, the difference:

$$\begin{aligned} V_{des} &= 2229.38 - 2163.84 \\ &= 65.54 \text{ ml} \end{aligned}$$

The standard volume desorbed per unit mass of coal at the equilibrium pressure 1281.7 psia is given by:

$$Q_{des} = \frac{65.54}{107.9} = 0.61 \text{ ml/g}$$

Since the total amount of gas adsorbed was 15.8 ml/g at 1420.6 psia, the remaining gas in adsorbed form at 1281.7 psia is:

$$15.8 - 0.61 = 15.19 \text{ ml/g}$$

This procedure was continued, and a complete desorption isotherm was obtained.

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