Adsorption of Pure Methane, Nitrogen, and Carbon Dioxide and Their Mixtures on San Juan Basin Coal

Topical Report

January, 2001 – March, 2002

K. A. M. Gasem
R. L. Robinson, Jr.
S.R. Reeves

Contract No. DE-FC26-00NT40924

May, 2002

Oklahoma State University
School of Chemical Engineering
Stillwater, Oklahoma 74078-0537

and

Advanced Resources International
9801 Westheimer, Suite 805
Houston, TX 77042

U.S. Department of Energy Disclaimer

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United Sates Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United Sates Government or any agency thereof.

Oklahoma State University Disclaimer

The Principal Investigators agreed to undertake this research on a best effort basis. Neither Oklahoma State University and the Principal Investigators, nor any of their employees, make any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed or represents that its use would not infringe privately owned rights.

Advanced Resources International Disclaimer

The material in this Report is intended for general information only. Any use of this material in relation to any specific application should be based on independent examination and verification of its unrestricted applicability for such use and on a determination of suitability for the application by professionally qualified personnel. No license under any Advanced Resources International, Inc., patents or other proprietary interest is implied by the publication of this Report. Those making use of or relying upon the material assume all risks and liability arising from such use or reliance.

Abstract

The major objectives of this project were to (a) measure the adsorption behavior of pure methane, nitrogen, CO_2 and their binary and ternary mixtures on wet Tiffany coal at 130°F and pressures to 2000 psia; (b) correlate the equilibrium adsorption isotherm data using the extended Langmuir model, the Langmuir model, the loading ratio correlation and the Zhou-Gasem-Robinson equation of state; and (c) establish sorption-time estimates for the pure components. Specific accomplishments are summarized below regarding the complementary tasks involving experimental work and data correlation.

- Representative coal samples from BP Amoco Tiffany Injection Wells #1 and #10 were prepared, as requested. The equilibrium moisture content and particle size distribution of each coal sample were determined. Compositional coal analyses for both samples were performed by Huffman Laboratories, Inc.
- Pure gas adsorption for methane on wet Tiffany coal samples from Injection Wells #1 and #10 was measured separately at 130°F (327.6 K) and pressures to 2000 psia (13.7 MPa). The average expected uncertainty in these data is about 3% (9 SCF/ton). Our measurements indicate that the adsorption isotherms of the two coal samples exhibit similar Langmuir-type behavior. For the samples from the two wells, a maximum variation of about 5% in the amount adsorbed is observed at 2000 psia.
- Gas adsorption isotherms were measured for **pure** methane, nitrogen and CO_2 on a wet, mixed Tiffany coal sample. The coal sample was an equal-mass mixture of coals from Well #1 and Well #10. The adsorption measurements were conducted at 130°F at pressures to 2000 psia. The adsorption isotherms have average expected experimental uncertainties of 3% (9 SCF/ton), 6% (8 SCF/ton), and 7% (62 SCF/ton) for methane, nitrogen, and CO_2, respectively.
- Adsorption isotherms were measured for methane/nitrogen, methane/CO_2 and nitrogen/CO_2 **binary mixtures** on wet, mixed Tiffany coal at 130°F and pressures to 2000 psia. These measurements were conducted for a single molar feed composition for each mixture. The expected uncertainties in the amount adsorbed for these binary mixtures vary with pressure and composition. In general, average uncertainties are about 5% (19 SCF/ton) for the total adsorption; however, the expected uncertainties in the amount of individual-component adsorption are significantly higher for the less-adsorbed gas at lower molar feed concentrations (e.g., nitrogen in the 20/80 nitrogen/CO_2 system).
- Adsorption isotherms were measured for a single methane/nitrogen/CO_2 **ternary mixture** on wet, mixed Tiffany coal at 130 °F and pressures to 2000 psia. The nominal molar feed composition was 10/40/50. The average expected uncertainty for the total adsorption and CO_2 adsorption is about 5%

(16 SCF/ton). However, the low adsorption of nitrogen and methane in this ternary yield average experimental uncertainties of 14% (9 SCF/ton) and 27% (9 SCF/ton), respectively.

- Limited binary and ternary gas-phase compressibility factor measurements at 130°F and pressures to 2000 psia involving methane, nitrogen, and CO_2 were conducted to facilitate reduction of our ternary adsorption data. These newly acquired data (and available data from the literature) were used to improve the Benedict-Webb-Rubin (BWR) equation-of-state (EOS) compressibility factor predictions, which are used in material balance calculations for the adsorption measurements. In general, the optimized BWR EOS represents the experimental compressibility factor data within 0.5% AAD.

- The Langmuir/loading ratio correlation (LRC) and the Zhou-Gasem-Robinson (ZGR) two-dimensional EOS were used to analyze the newly acquired adsorption data. Model parameters were obtained for the systems studied.

- The LRC and ZGR EOS were used to **correlate** the adsorption data for methane, nitrogen, and CO_2 and their mixtures on wet Tiffany coal. The model parameters were determined by minimizing the sum of squares of weighted errors in the calculated amounts of gas adsorbed. The results demonstrate the ability of the LRC and ZGR EOS to represent the total pure, binary and ternary systems within their expected experimental uncertainties. Specifically, representations with average absolute percentage errors (AAD) of 1-3% (2-15 SCF/ton), 1-8% (1-25 SCF/ton), and 2-10% (7-37 SCF/ton) were obtained for the pure, total binary, and total ternary adsorption isotherms, respectively. However, the quality of fit for the individual–component adsorption varies significantly, ranging from 3% for the more-adsorbed methane or CO_2 to 32% for the less-adsorbed nitrogen.

- The LRC and ZGR EOS are capable of **predicting** binary adsorption isotherms based solely on pure-fluid adsorption parameters within twice their experimental uncertainties (1-50 %AAD, 5-40 SCF/ton). In comparison, the ternary predictions based on pure-fluid parameters yield three times the experimental uncertainties (4-56 %AAD, 2-60 SCF/ton). The quality of the model predictions indicate that although the two models are capable of predicting total adsorption isotherms adequately, they predict individual-component adsorption in mixtures poorly, especially when dealing with the less-adsorbed component of the mixture.

- Sorption-time estimates for pure methane, nitrogen, and CO_2 were represented with average errors of about 8%.

TABLE OF CONTENTS

List of Tables

List of Figures

A. Executive Summary

The major objectives of this project were to (a) measure the adsorption behavior of pure methane, nitrogen, CO_2 and their binary and ternary mixtures on wet Tiffany coal at 130°F and pressures to 2000 psia; (b) correlate the equilibrium adsorption isotherm data using the extended Langmuir model, the Langmuir model, the loading ratio correlation and the Zhou-Gasem-Robinson equation of state; and (c) establish sorption-time estimates for the pure components. Specific accomplishments are summarized below regarding the complementary tasks involving experimental work and data correlation.

Experimental Work

- Representative coal samples from BP Amoco Tiffany Injection Wells #1 and #10 were prepared, as requested. The equilibrium moisture content and particle size distribution of each coal sample were determined. Compositional coal analyses for both samples were performed by Huffman Laboratories, Inc.
- Pure gas adsorption for methane on wet Tiffany coal samples from Injection Wells #1 and #10 was measured separately at 130°F (327.6 K) and pressures to 2000 psia (13.7 MPa). The average expected uncertainty in these data is about 3% (9 SCF/ton). Our measurements indicate that the adsorption isotherms of the two coal samples exhibit similar Langmuir-type behavior. For the samples from the two wells, a maximum variation of about 5% in the amount adsorbed is observed at 2000 psia.
- Gas adsorption isotherms were measured for **pure** methane, nitrogen and CO_2 on a wet, mixed Tiffany coal sample. The coal sample was an equal-mass mixture of coals from Well #1 and Well #10. The adsorption measurements were conducted at 130°F at pressures to 2000 psia. The adsorption isotherms have average expected experimental uncertainties of 3% (9 SCF/ton), 6% (8 SCF/ton), and 7% (62 SCF/ton) for methane, nitrogen, and CO_2, respectively.
- Adsorption isotherms were measured for methane/nitrogen, methane/CO_2 and nitrogen/CO_2 **binary mixtures** on wet, mixed Tiffany coal at 130°F and pressures to 2000 psia. These measurements were conducted for a single molar feed composition for each mixture. The expected uncertainties in the amount adsorbed for these binary mixtures vary with pressure and composition. In general, average uncertainties are about 5% (19 SCF/ton) for the total adsorption; however, the expected uncertainties in the amount of individual-component adsorption are significantly higher for the less-adsorbed gas at lower molar feed concentrations (e.g., nitrogen in the 20/80 nitrogen/CO_2 system).
- Adsorption isotherms were measured for a single methane/nitrogen/CO_2 **ternary mixture** on wet, mixed Tiffany coal at 130 °F and pressures to 2000

psia. The nominal molar feed composition was 10/40/50. The average expected uncertainty for the total adsorption and CO_2 adsorption is about 5% (16 SCF/ton). However, the low adsorption of nitrogen and methane in this ternary yield average experimental uncertainties of 14% (9 SCF/ton) and 27% (9 SCF/ton), respectively.

- Limited binary and ternary gas-phase compressibility factor measurements at 130°F and pressures to 2000 psia involving methane, nitrogen, and CO_2 were conducted to facilitate reduction of our ternary adsorption data. These newly acquired data (and available data from the literature) were used to improve the Benedict-Webb-Rubin (BWR) equation-of-state (EOS) compressibility factor predictions, which are used in material balance calculations for the adsorption measurements. In general, the optimized BWR EOS represents the experimental compressibility factor data within 0.5% AAD.

Data Correlation

- The Langmuir/loading ratio correlation (LRC) and the Zhou-Gasem-Robinson (ZGR) two-dimensional EOS were used to analyze the newly acquired adsorption data. Model parameters were obtained for the systems studied.

- The LRC and ZGR EOS were used to **correlate** the adsorption data for methane, nitrogen, and CO_2 and their mixtures on wet Tiffany coal. The model parameters were determined by minimizing the sum of squares of weighted errors in the calculated amounts of gas adsorbed. The results demonstrate the ability of the LRC and ZGR EOS to represent the total pure, binary and ternary systems within their expected experimental uncertainties. Specifically, representations with average absolute percentage errors (AAD) of 1-3% (2-15 SCF/ton), 1-8% (1-25 SCF/ton), and 2-10% (7-37 SCF/ton) were obtained for the pure, total binary, and total ternary adsorption isotherms, respectively. However, the quality of fit for the individual–component adsorption varies significantly, ranging from 3% for the more-adsorbed methane or CO_2 to 32% for the less-adsorbed nitrogen.

- The LRC and ZGR EOS are capable of **predicting** binary adsorption isotherms based solely on pure-fluid adsorption parameters within twice their experimental uncertainties (1-50 %AAD, 5-40 SCF/ton). In comparison, the ternary predictions based on pure-fluid parameters yield three times the experimental uncertainties (4-56 %AAD, 2-60 SCF/ton). The quality of the model predictions indicate that although the two models are capable of predicting total adsorption isotherms adequately, they predict individual-component adsorption in mixtures poorly, especially when dealing with the less-adsorbed component of the mixture.

- Sorption-time estimates for pure methane, nitrogen, and CO_2 were represented with average errors of about 8%.

B. Introduction

The specific objectives of the adsorption measurements and correlations for BP Amoco Tiffany coal were to:

- Prepare representative coal samples from Injection Well #1 and Injection Well #10.
- Determine (a) equilibrium moisture content, (b) particle size distribution, (c) compositional analyses, and (d) vitrinite reflectance analysis for each coal sample.
- Measure the adsorption behaviors of pure methane, nitrogen, CO_2 and their binary and ternary mixtures on a Tiffany equal-mass, mixed-coal sample from Injector Wells #1 and #10 at 130°F and pressures to 2000 psia. The nominal molar feed compositions for the methane/nitrogen, methane/CO_2, and nitrogen/CO_2 binary mixtures were specified at 50/50, 40/60, and 20/80, respectively. The nominal molar feed composition for the methane/nitrogen/CO_2 ternary mixture was 10/40/50.
- Correlate the equilibrium adsorption isotherm data using the extended Langmuir model, the Langmuir model, the loading ratio correlation and the Zhou-Gasem-Robinson equation of state.
- Establish sorption-time estimates for the pure components.

C. Experimental Work

1. Experimental Facility

The experimental apparatus was developed in previous work for Amoco Corporation and the Oklahoma Center for the Advancement of Science and Technology. As a precursor to the present data acquisition, the apparatus was thoroughly re-tested and revised as necessary. The equipment is described in detail elsewhere [1,2].

Recently, we enhanced our experimental facility to include the ability to measure adsorption kinetics for systems encountered in coalbed methane production and sequestration of CO_2. Brief descriptions of experimental methods and procedures are given in the following section.

2. Experimental Methods and Procedures

(a) Adsorption Measurements

Our experimental technique employs a mass balance method, utilizing volumetric accounting principles. The experimental apparatus, shown schematically in

Figure 1, has been used successfully in previous measurements [1, 2]. Brief descriptions of the experimental apparatus and procedures follow.

The entire apparatus (both Pump and Cell sections) is maintained in a constant temperature air bath. The equilibrium cell (EC, Figure 1) is filled with the coal to be studied, and the cell is placed under vacuum prior to gas injection. The void (gas) volume, V_{void}, in the equilibrium cell is then determined by injecting a known quantity of helium from a calibrated injection pump. Since helium is not adsorbed, the void volume can be determined from measured values of the temperature, pressure and amount of helium injected into the cell. The void volume equations are

$$V_{void} = n_{He}(Z_{He}RT\,/P)_{cell} \quad (1)$$

$$n_{He} = (PV/Z_{He}RT)_{pump} \quad (2)$$

In these equations, n_{He} is the number of moles of helium injected into the cell, V is the volume of gas injected from the pump, Z_{He} is the compressibility factor of helium, R is the universal gas constant, T is the temperature, P is the pressure, and the subscripts "cell" and "pump" refer to conditions in the cell and pump sections of the apparatus, respectively.

The amount of gas (methane, for example) adsorbed at a given pressure can be calculated based on the preliminary calibrations done above. First, a given quantity of methane, n_{inj}, is injected into the cell. This amount is determined by an equation analogous to Equation 2, above. A magnetic recirculating pump is used to circulate methane over the adsorbent until equilibrium is reached, where no further methane is adsorbed. The amount of unadsorbed methane, n_{unads}, is then determined based on the fact that any unadsorbed methane will remain in the void volume (determined from the helium calibration). The expression for this quantity is

$$n_{unads} = (PV_{void}/Z_{methane}RT)_{cell} \quad (3)$$

where the pressure P is measured after equilibrium is reached in the cell. In addition, we estimate the amount of gas dissolved in water, n_{dis}, using correlations for gas solubility [2]. The amount of adsorbed methane, n_{ads}, is then calculated by difference as

$$n_{ads} = n_{inj} - n_{unads} - n_{dis} \quad (4)$$

These steps are repeated at sequentially higher pressures to yield a complete adsorption isotherm.

In mixture studies, a gas mixture of known composition is injected, so the total amount of each gas fed into the cell is known. The amount of unadsorbed gas at each pressure is calculated by Equation 3 with $Z_{methane}$ replaced by Z_{mix}, the gas mixture compressibility factor. The composition of the gas mixture in the void volume is determined by chromatographic analysis using a microliter-size sample captured in a sampling valve (SV1). This permits the total amount of unadsorbed gas to be apportioned among the various components according to their mole fractions in the gas. Equation 4 can be then applied to each component in the gas mixture. For methane/nitrogen/CO_2 mixtures, the mixture Z factors (Z_{mix}) are determined accurately from the BWR EOS, as described below.

The estimated uncertainties in each of the experimentally measured quantities are as follows: temperature 0.2°F, pressure 1.0 psia, injected gas volumes 0.02 cc, bulk gas-phase composition 0.001 in mole fraction. The expected uncertainties in the amount adsorbed are estimated using error propagation in all the measured variables and confirmed by replicate runs.

Compressibility Factors

As indicated by Equations 1-3, accurate gas-phase compressibility (Z) factors are required for methane, nitrogen and carbon dioxide and their mixtures to properly analyze our experimental adsorption data. The compressibility factors for **pure** methane, nitrogen and CO_2 were determined from highly accurate equations of state [3-5]. However, a careful evaluation of the current literature led us to conclude that an adequate predictive capability for the **mixture** Z factors does not exist. Therefore, we elected to develop such a capability using the Benedict-Webb-Rubin (BWR) equation of state.

Specifically, we used available pure-fluid and **binary** mixture data to refit the BWR equation and improve its accuracy significantly; in general, the new BWR EOS parameters yield deviations in the Z factor within 0.2%. This allowed us to address our compressibility factor needs for binary adsorption mixtures.

To facilitate our **ternary** adsorption measurements, we conducted a limited number of binary and ternary compressibility factor measurements involving methane, nitrogen, and CO_2 at 130°F and pressures to 2000 psia. These newly acquired data and available data from the literature were used to improve the BWR EOS compressibility factor predictions. In general, the optimized BWR EOS represents the compressibility factor data within 0.5% AAD [11].

Relationship between Gibbs and Absolute Adsorption

By definition, Gibbs adsorption considers the gas-phase volume as the sum of the gas (V_{gas}) and adsorbed phase (V_{ads}) volumes (ignoring the reduction in gas-phase volume due to presence of the adsorbed phase.) Expressing Gibbs adsorption in terms of vapor volume (V_{gas}) and adsorbed-phase volume (V_{ads}), and using the specific molar volume (v_{gas} and v_{ads}), we obtain:

$$n_{ads}^{Gibbs} = n_{inj} - \left[\frac{V_{gas} + V_{ads}}{v_{gas}} \right] \quad (5)$$

For absolute adsorption, the amount adsorbed within the equilibrium cell is given as:

$$n_{ads}^{Abs} = n_{inj} - \left[\frac{V_{gas}}{v_{gas}}\right] \text{ (6)}$$

By combining Equations 5 and 6, the Gibbs adsorption expression can be rewritten as:

$$n_{ads}^{Abs} = n_{ads}^{Gibbs} + \left[\frac{V_{ads}}{v_{gas}}\right] \text{ (7)}$$

Since

$$V_{ads} = n_{ads}^{Abs} v_{ads} \qquad \text{and} \qquad v_{ads} = \frac{1}{\rho_{ads}}$$

Then

$$n_{ads}^{Abs} = \frac{n_{ads}^{Gibbs}}{\left[1 - \left(\frac{\rho_{gas}}{\rho_{ads}}\right)\right]} \text{ .(8)}$$

where ρ is density. At low pressures, the density-ratio correction is negligible, but at higher pressures it becomes significant.

A common approximation for the density of an adsorbed phase is to use the liquid density at the atmospheric pressure boiling point, as done by Yee [6]. However, more accurate estimates for the adsorbed-phase density are required when the adsorbed-phase density approaches the bulk gas density.

For multicomponent systems, the adsorbed-phase density, $?_{ads}$, in Equation 8 is replaced with the mixture adsorbed-phase density, which is assumed to be the adsorbed mole fraction weighted average of the pure-component phase volumes ($1/\rho_{ads,i}$), i.e.:

$$\rho_{ads} = \frac{1}{\sum \frac{x_i^{Abs}}{\rho_{ads,i}}} \text{ (9)}$$

Component Absolute Adsorption

The component mole fraction in the adsorbed phase, x_i^{Abs}, is calculated based on the following derivation. Note that abbreviated subscripts are used for volumes to simplify documentation (g=gas, a=ads, and c=void).

$$n_{inj}(i) = \frac{V_g}{v_g} y_i + \frac{V_a}{v_a} x_i^{Abs} \quad (10)$$

Since

$$V_c = V_g + V_a = V_{void}$$

and substituting for n_{ads}^{Abs} then

$$n_{inj}(i) = \left[\frac{(V_c - V_a)}{v_g}\right] y_i + \left[\frac{n_{ads}^{Gibbs}}{1 - \frac{v_a}{v_g}}\right] x_i^{Abs} \quad (11)$$

or

$$n_{inj}(i) = \frac{V_c}{v_g} y_i - \frac{V_a}{v_g} y_i + \left[\frac{n_{ads}^{Gibbs}}{1 - \frac{v_a}{v_g}}\right] x_i^{Abs} \quad (12)$$

Noting that

$$n_{ads}^{Gibbs} = \frac{V_a}{v_a}\left[1 - \frac{v_a}{v_g}\right] = \left(\frac{V_a}{v_a} - \frac{V_a}{v_g}\right),$$

which upon rearrangement leads to

$$\frac{V_a}{v_g} = \frac{n_{ads}^{Gibbs}}{\left(1 - \frac{v_a}{v_g}\right)} - n_{ads}^{Gibbs} = \left[\frac{1}{\left(1 - \frac{v_a}{v_g}\right)} - 1\right] n_{ads}^{Gibbs} = \left[\frac{\frac{v_a}{v_g}}{\left(1 - \frac{v_a}{v_g}\right)}\right] n_{ads}^{Gibbs}$$

Therefore, Equation 12 becomes

$$n_{inj}(i) - \frac{V_c}{v_g} y_i = -\left[\frac{\frac{v_a}{v_g}}{\left(1 - \frac{v_a}{v_g}\right)}\right] n_{ads}^{Gibbs} y_i + \left[\frac{n_{ads}^{Gibbs}}{1 - \frac{v_a}{v_g}}\right] x_i^{Abs} \quad (13)$$

or

$$\left(n_{inj}(i)-\frac{V_c}{v_g}y_i\right)\left(1-\frac{v_a}{v_g}\right)=\left[x_i^{Abs}-y_i\left(\frac{v_a}{v_g}\right)\right]n_{ads}^{Gibbs} \quad (14)$$

By definition

$$x_i^{Gibbs}=\frac{n_{ads}^{Gibbs}(i)}{n_{ads}^{Gibbs}}$$

Then

$$x_i^{Gibbs}=\frac{\left(n_{inj}(i)-\frac{V_c}{v_g}y_i\right)}{n_{ads}^{Gibbs}}$$

Then Equation 14 can be written as

$$x_i^{Gibbs}\left(1-\frac{v_a}{v_g}\right)=x_i^{Abs}-y_i\left(\frac{v_a}{v_g}\right) \quad (15)$$

For a binary system, Equation 15 becomes two equations:

$$x_1^{Gibbs}=x_1^{Abs}+(x_1^{Gibbs}-y_1)\left[\frac{v_{a1}}{v_g}x_1^{Abs}+\frac{v_{a2}}{v_g}x_2^{Abs}\right] \quad (16)$$

and

$$x_2^{Gibbs}=x_2^{Abs}+(x_2^{Gibbs}-y_2)\left[\frac{v_{a1}}{v_g}x_1^{Abs}+\frac{v_{a2}}{v_g}x_2^{Abs}\right] \quad (17)$$

Given the Gibbs adsorbed-phase compositions $(x_1^{Gibbs},x_2^{Gibbs})$ and the experimental gas-phase compositions (y_1,y_2), absolute adsorbed-phase compositions are obtained by solving Equations 16 and 17 simultaneously. Once these compositions are obtained, the absolute adsorption of each individual component is calculated as follows:

$$n_{ads}^{Abs}(i)=x_i^{Abs}n_{ads}^{Abs} \quad (18)$$

(b) Determination of Coal Particle Size Distribution

A sieve analysis was use to determine the macro-particle size distribution. A series of meshes was selected: They were No. 3.5, 8, 10, 12, 20, 30, 40, 50 and

60 with respective openings of 5.66, 2.38, 2.00, 1.70, 0.85, 0.60, 0.425, 0.300, 0.250 mm. The analysis was performed on a pre-weighed in-situ coal sample. The sieves were stacked in order of mesh size. After sufficiently shaking the sample, we measured the weight of the contents remaining in each sieve to determine the respective proportion of the coal particle size distribution.

(c) Determination of Coal Moisture Content

A pre-weighed, as-received wet coal sample was placed into a pre-weighed container. The container was subjected to a continuous vacuum in a 215-220°F oven. Vacuum was applied overnight to remove moisture. After the moisture was removed, the container was re-weighed, and the difference was assumed to be from the moisture loss.

Another wet sample was placed on a flat pan in a 35.0°C air atmosphere at 97-99% relative humidity. The sample weight was determined periodically to gauge the constancy of weight, which indicates the approach of the sample to equilibrium moisture content. Once a constant sample weight was achieved, the sample was assumed to be at its “equilibrium moisture content” or EMC.

The equilibrium sample was then placed in a continuous vacuum at 215-220°F. The moisture loss determined by weight difference was used to calculate the EMC. For the Tiffany samples considered in this study, the moisture content of the as-received samples was found to be higher than the EMC.

(d) Sorption-Time Measurements for Pure Gases

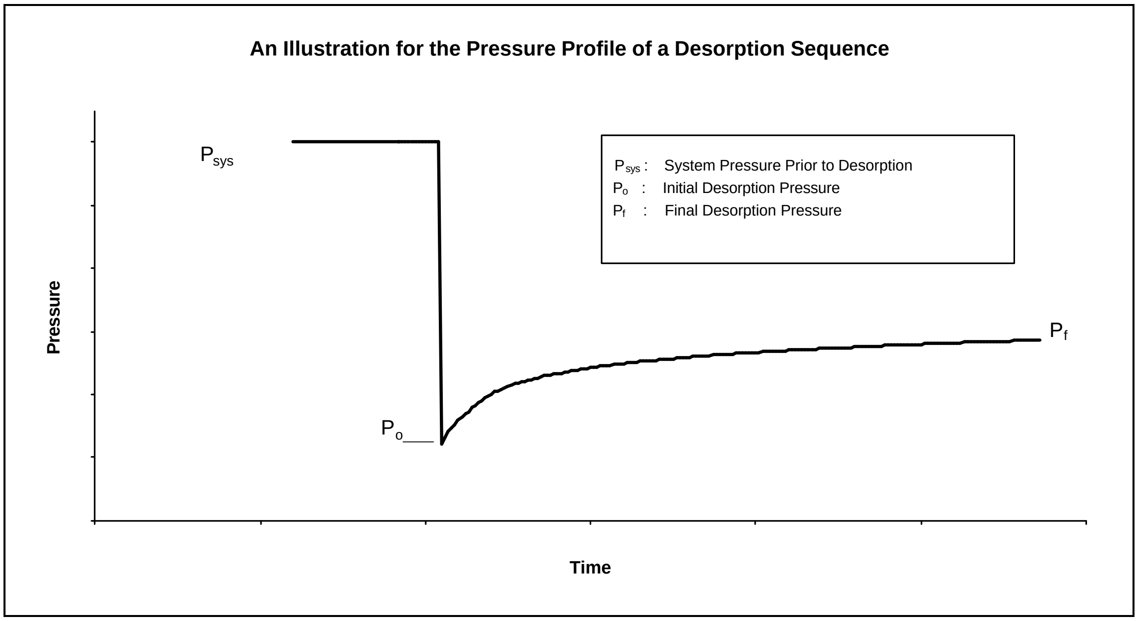
To facilitate sorption-time measurements, an analog acquisition card was installed in our pressure console. Thus, a graphic representation of how pressure varies with time can be displayed *in real time* using conventional Excel tools. Temperature was also measured by a thermocouple and sent to an analog converter and then to the analog computer acquisition board.

A desorption step is initiated by reducing the equilibrium pressure of the adsorbed gas. This adsorption pressure reduction is accomplished by opening a valve connecting the equilibrium cell (where the coal sample is in contact with the adsorbate) to the injection pump, which is set at lower pressure. The valve between the cell and injection pump is opened as quickly as possible to simulate a step change in pressure. The coal sample then desorbs its gas, and the pressure rises from the initial desorption pressure (P_0) to a new equilibrium pressure (P_f). The pressure at any given time (P_t) is monitored and recorded along with time (t) by the data acquisition module. Thus, the sorption-time estimates are generated from the desorption-time increment involving P_0 and P_f, as depicted by the illustration below.

The pressure fractional uptake, Λ, is defined as:

$$\Lambda = (P_t - P_0)/(P_f - P_0) \quad (19)$$

Here P_0 is the initial desorption pressure, P_f is the final desorption pressure, and P_t is the pressure at time t. Typically, a scaled-time plot produces a generalizeable desorption profile for different equilibrium pressures.



An alternative representation for the adsorption kinetics may be expressed in terms of sorption fractional uptake, defined as:

$$\Theta = (\omega_t - \omega_0)/(\omega_f - \omega_0) = (V_{SCF\,t} - V_{SCF\,0})/(V_{SCF\,f} - V_{SCF\,0}) \quad (20)$$

where ω is the amount of gas adsorbed, and V_{SCF} is the corresponding volume at the standard conditions. If a Langmuir-type model is used to correlate the equilibrium sorption data, then Equation 20 can be rewritten as:

$$\Theta = \Lambda\left(\frac{1 + BP_f}{1 + BP_t}\right) \quad (21)$$

where B is the Langmuir constant regressed from sorption experimental data.

D. Data Correlation

The newly acquired adsorption data on the Tiffany coal samples were correlated using (a) the extended Langmuir model, (b) the loading ratio correlation, and (c) the Zhou-Gasem-Robinson (ZGR) two-dimensional equation of state. Following is a brief description of the models used. An assessment for the quality of their representation and prediction of the present pure and mixture Tiffany coal data is presented in Section E.

(a) Langmuir/Loading Ratio Correlation

Historically, simple models have been used to represent the behavior of pure and mixed gas adsorption on coal. The extended Langmuir model is used almost exclusively in literature studies [e.g., 6], although the Ideal Adsorbed Solution (IAS) model has also been employed [7, 8]. Both of these models work well for essentially ideal adsorbed solutions, but neither is capable of handling nonidealities in the adsorbed phase with any accuracy. The extended Langmuir model is shown below as an illustration of the simple modeling approach used in most previous studies. For mixtures, it takes the form

$$\theta_i = \frac{\omega_i}{L_i} = \frac{B_i P y_i}{1 + \sum_j B_j P y_j} \quad (22)$$

where ω_i is the amount of component "i" adsorbed (SCF of "i" adsorbed per ton of coal), L_i and B_i are Langmuir constants for "i", P is pressure, and y_i is the mole fraction of "i" in the gas phase. This relation allows mixture adsorption to be predicted from pure-component data, since values of L_i and B_i may be determined from the pure-component form of Equation 22. For pure-fluid adsorption, Equation 22 reduces to the Langmuir model:

$$\theta = \frac{\omega}{L} = \frac{BP}{1 + BP} \quad (23)$$

The combined Langmuir-Freundlick adsorption isotherm, expressed in terms of ω_i, yields the loading ratio correlation (LRC) for mixtures:

$$\theta_i = \frac{\omega_i}{L_i} = \frac{(B_i P y_i)^{\eta_i}}{1 + \sum_j (B_j P y_j)^{\eta_j}} \quad (24)$$

The additional parameter (η_i) in the LRC lends the Langmuir model more flexibility. Although the simplicity of Langmuir models is attractive, our data show that they are inadequate to represent the behavior of mixtures of the gases CO_2, methane, and nitrogen. In fact, previously we found errors greater than 100% when the extended Langmuir model was applied to our data on the adsorption of nitrogen from nitrogen + CO_2 mixtures [2].

(b) ZGR Equation of State

Simulations of coalbed gas recovery and CO_2 sequestering require reliable, yet simple, analytic models beyond Langmuir-type correlations. Equation-of-state (EOS) frameworks offer an attractive potential for such requirements. A general two-dimensional EOS can be written as follows [9]:

$$\left[A\pi + \frac{\alpha\omega^2}{1+U\beta\omega + W(\beta\omega)^2}\right]\left[1-(\beta\omega)^m\right] = \omega RT \quad (25)$$

where A is the specific surface area, π is the spreading pressure, ω is the specific amount adsorbed, and α, β and m are model parameters. The model coefficients, U, W, and m must be specified to obtain a specific form of the 2-D EOS for application. For example, an analog of the van der Waals (VDW) EOS is obtained by setting m = 1 and U = W = 0; similarly for the Soave-Redlich-Kwong (SRK) (m = U = 1 and W = 0); the Peng-Robinson (PR) (m = 1, U = 2, and W = -1); and the Eyring (m = 1/2 and U = W = 0) EOS.

This general 2-D EOS can be used to investigate EOS behaviors by specifying various combinations of model coefficients. Selection of the model coefficient m is the most important among the EOS model coefficients, because it has a significant effect on the shape of the pure adsorption isotherm. If U and W are equal to zero, then by setting m to values of ∞, 1, and 1/2, we obtain the 2-D ideal gas law, the VDW EOS, and the Eyring EOS, respectively. Actually, the pure gas isotherms vary considerably in shape and we have found that it is sometimes desirable to select an m value even smaller than 1/2 to describe pure isotherms. We have determined that an equation with m = 1/3 and U = W = 0 (the ZGR EOS) is promising [9]. The 2-D EOS can be applied to adsorbed phases containing mixtures by utilizing the traditional mixing rules (where x is the mole fraction in the adsorbed phase):

$$\alpha = \sum_i \sum_j x_i x_j \alpha_{ij} \quad (26)$$

$$\beta = \sum_i \sum_j x_i x_j \beta_{ij} \quad (27)$$

along with the non-traditional combination rules [9],

$$\begin{aligned} \alpha_{ij} &= (1-C_{ij})(\alpha_i + \alpha_j)/2 \\ \beta_{ij} &= (1+D_{ij})\sqrt{\beta_i\beta_j} \end{aligned} \quad (28)$$

where C_{ij} and D_{ij} are the EOS binary interaction parameters.

E. Results and Discussion

1. Experimental Data

(a) Comparison of Tiffany Coal Samples

Coal characterization measurements are presented in Tables 1-3 and Figures 2-4. Table 1 presents the compositional analyses for coal samples from Wells #1 and #10. Table 2 and Figures 2-4 present the coal particle size distribution for the two samples. The analyses indicate that the two coal samples are similar in composition and particle size distribution.

The density of the compact solid coal is called the coal helium density, in reference to the helium displacement measurements used to determine the adsorbent density [10]. We have measured the coal helium densities for Well #1, Well #10, and the mixed sample. They are 1.73, 1.57, and 1.67±0.07 g/cc, respectively. The equilibrium moisture content of Well #1 coal sample is 3.8±0.2% and the equilibrium moisture content of Well #10 coal sample is 3.7±0.2%.

Vitrinite reflectance analyses conducted by National Petrographic Services indicate that the present Tiffany coal samples are medium volatility bituminous coal. As summarized in Table 3, Wells #1 and 10 have average oil-based vitrinite reflectance values of 1.31 and 1.35, respectively.

Initial methane adsorption isotherms were measured separately for Wells #1 and #10. Results are presented in Tables 4 and 5 (on moisture-free and ash-free bases) and Figure 5. They indicate that the adsorption capacities of samples from the two wells are comparable with a maximum variation of 5% in the amount adsorbed at 2000 psia.

Because of the similarity in the methane adsorption behavior for Tiffany Well #1 and Well #10 coal samples, and upon agreement with BP Amoco personnel, coal samples from the two wells were mixed on an equal-mass basis. Large chunks of coal (dime-size) were broken up and the coal mixture was gently shaken to ensure a final homogenous mixture. The coal samples were placed into a tightly-capped jar. Helium was injected into the jar to prevent oxidation of the coal.

(b) Adsorption Isotherms

Pure Gas Adsorption

Gas adsorption measurements for pure methane, nitrogen and CO_2 were conducted on wet Tiffany coal samples at $130^{o}F$ and pressures to 2000 psia. Our error analysis indicates that the average uncertainties for the methane, nitrogen, and CO_2 adsorption measurements are approximately 3% (9 SCF/ton), 6% (8 SCF/ton) and 7% (62 SCF/ton), respectively. These estimates, which are depicted as error bars in some of the figures, were generated by error propagation of uncertainties in all measured quantities. The repeated isotherms confirm the estimated precision of the measurements.

The adsorption data are presented in Tables 4-8 and Figures 5-10. Figure 6 presents the Gibbs adsorption isotherms for methane, nitrogen, and CO_2, respectively. The absolute adsorption data for these gases are presented in Figures 7-10. In this study, unless otherwise noted, we use the adsorbed-phase density approximation suggested by Yee [6]. For nitrogen, methane, and CO_2, densities of 0.808, 0.421, and 1.18 g/cm^3, respectively, were used to convert the Gibbs to absolute adsorption.

Tables 4 and 5 present isotherms for methane on Well #1 and Well #10 coal samples, respectively. Replicate runs were conducted to confirm our measurements. These measurements show good agreement between the replicate runs, which yield an expected uncertainty of about 5%. A four-point adsorption isotherm was measured on the Tiffany mixed coal sample, as presented in Table 6. As expected, the mixed coal sample produced an intermediate adsorption capacity; i.e., it shows less adsorption than the Well #1 coal sample and more than the Well #10 sample.

The replicate runs for methane (Figure 5 and Tables 4-6) show good agreement. The average expected uncertainty for these measurements is approximately 3% (9 SCF/ton), as depicted by the error bars in Figure 5. (Notice that error bars are included only for one run).

The adsorption isotherm for pure nitrogen on the mixed Tiffany coal sample is presented in Table 7 and Figure 8. As indicated by Figure 8, no significant differences exist between the replicate runs. The average expected uncertainty for these measurements is approximately 6% (8 SCF/ton). Similarly, adsorption isotherm measurements for pure CO_2 on wet Tiffany mixed coal sample are given in Table 8 and Figure 9. The replicate runs show reasonable agreement with an average expected uncertainty of about 7% (62 SCF/ton).

Both methane and nitrogen adsorption measurements on Tiffany coal indicate lower adsorption capacity than the adsorption on the Fruitland coal reported previously [1]. The measurements on Tiffany coal are about one half that on Fruitland coal at the same conditions. This difference might be due to variations in coal composition. Ash content in Tiffany coal is about twice that of the Fruitland coal. In contrast, the carbon content in Tiffany coal is about two thirds that in Fruitland coal. Nevertheless, the new measurements agree with the previous ones in the *relative* amounts of nitrogen, methane and CO_2 adsorbed, which are in the approximate ratio of 1 : 2.7 : 5 at 1000 psia.

As previously reported [1], a slightly different moisture content in each measurement set indicates that water content values beyond the equilibrium water content have no significant effect the adsorption behavior. In contrast, the adsorbed-phase density estimates may affect the calculated absolute adsorption isotherm. Figure 10 illustrates the effect of variation in the adsorbed-phase density on the CO_2 absolute adsorption. Here, three estimates are used: (1) the triple point liquid density (1.18 g/cm^3), (2) the ZGR model estimate (1.25 g/cm^3), and (3) a graphical estimate based on the Gibbs adsorption isotherm (1.40 g/cm^3). Differences in the calculated adsorption increase with pressure, rising to as much as 15% at 2000 psia.

Binary Mixture Adsorption

Adsorptions isotherms were measured for methane/nitrogen, methane/CO_2 and nitrogen/CO_2 on wet, mixed Tiffany coal at 130 ^oF and pressures to 2000 psia. The measurements were conducted at one feed composition for each mixture. The expected uncertainties in the amount adsorbed for these binary mixtures vary with pressure and composition. In general, percent average uncertainties are below 5% (19 SCF/ton) for total adsorption; however, the expected uncertainties in the amount of individual-component adsorption are significantly higher for the less-adsorbed gas at lower molar feed concentrations (e.g., nitrogen in the 20/80 nitrogen/CO_2 system).

Mixture absolute adsorption estimates were calculated assuming ideal-solution additive volumes in the condensed phase (i.e., the mixture volume is the mole-fraction-weighted average of the pure component volumes). The traditional values of 0.808 g/cm^3, 0.421 g/cm^3, and 1.18 g/cm^3, were used to estimate the adsorbed-phase density of methane, nitrogen, and CO_2, respectively.

Table 9 and Figure 11 present the experimental data for methane/nitrogen adsorption at the nominal molar feed composition of 50% methane. In general, the average expected uncertainties in the amount of individual-component adsorption are 7% (13 SCF/ton) for methane, and 17% (8 SCF/ton) for nitrogen. The total adsorption has estimated uncertainties of 7% (15 SCF/ton). Figure 12 presents the absolute adsorption for this binary system, including predictions from the LRC and ZGR models. As shown in Figures 11 and 12, methane is more strongly adsorbed than nitrogen.

Table 10 and Figure 13 present the experimental data of methane/CO_2 adsorption at a nominal molar feed composition of 40% methane. The average expected uncertainties in the amount of individual-component adsorption are 7% (10 SCF/ton) for methane, and 6% (17 SCF/ton) for CO_2. The total adsorption has estimated uncertainties of 4% (20 SCF/ton). Figure 14 presents the absolute adsorption of this system, which indicates that the amount of CO_2 adsorbed is almost three times that observed for methane.

Table 11 and Figure 15 present the experimental data of nitrogen/CO_2 adsorption at the nominal molar feed composition of 20% nitrogen. A small amount of nitrogen is adsorbed at this feed composition. This results in higher uncertainties for the nitrogen component adsorption, which could be around 29% (8 SCF/ton).

In comparison, the CO_2 component adsorption has estimated uncertainties 6% (23 SCF/ton), and the total adsorption has estimated uncertainties of 5% (22 SCF/ton). Figure 16 presents the absolute adsorption of this binary system, which indicates that the amount of CO_2 adsorbed is almost 20 times that observed for nitrogen.

Ternary Mixture Adsorption

The ternary adsorption of methane/nitrogen/CO_2 on wet, mixed Tiffany coal at 130 ^{o}F and pressures to 2000 psia was conducted at 10/40/50 mole % feed composition. Table 12 and Figure 17 present the excess Gibbs adsorption data for this mixture, and Figure 18 depicts the absolute adsorption isotherms. The average expected uncertainty for the total adsorption and CO_2 adsorption is about 5% (17 SCF/ton). However, the low adsorption of nitrogen and methane in this ternary yielded experimental uncertainties of 14% (9 SCF/ton) and 27% (9 SCF/ton), respectively. The absolute adsorption data for this ternary were generated using the same procedure used for the binary mixtures.

(c) Sorption-Time Estimates for Pure Gases

Tables 13-16 present the desorption data for pure methane, nitrogen and CO_2, respectively. The tables provide a record for a number of desorption runs for each gas off the Tiffany coal samples, where values for the initial desorption pressure, final desorption pressure and the time of desorption are given. In addition, information is shown for the 90% pressure fractional uptake, Λ; and the 63% sorption fractional uptake, Θ.

Figure 19 presents three methane desorption runs for the Well #1 coal sample. Similarly, Figure 20 presents two methane desorption runs for Well #10 coal sample. The results for three nitrogen runs and six CO_2 desorption runs off the Tiffany mixed coal sample are given in Figures 21 and 22, respectively. Other runs for the various gases, which are not included, show the same trend.

For the Well #1 coal sample, the sorption time at 90% pressure uptake for methane varies from 8 minutes to 140 minutes depending on the pressure. For the Well #10 coal sample, the 90% sorption time for methane varies from 4 minutes to 50 minutes depending on the pressure. Accordingly, methane desorption on Well #10 coal is faster than on Well #1 coal. Moreover, desorption at higher pressures is faster than desorption at lower pressures. Similar trends for the effect of pressure on sorption time are observed for nitrogen and CO_2 on the Tiffany mixed coal sample.

2. Data Correlation and Model Evaluation

(a) Adsorption Isotherms

The data correlation and model evaluation effort undertaken here addresses two important issues: (a) the ability of the LRC and ZGR EOS to correlate or represent the acquired adsorption data, and (b) the ability of the two models to predict the binary and ternary mixture adsorptions. Thus, beyond establishing the model precision in summarizing existing data, we are also interested in evaluating the efficacy of such models in using pure and/or binary measurements to provide accurate predictions for ternary and other multicomponent mixtures.

Accordingly, in the following discussion two case studies are considered. First, we evaluate model **representations** of the Tiffany adsorption data, where the model parameters (L, B, and η for the LRC; α, β, C_{ij}, D_{ij} for ZGR EOS) are regressed to correlate the data considered and to establish the quality of precision attainable for the present models. Next, we examine binary model **predictions** based on pure-fluid parameters, and ternary predictions based on pure or a combination of pure and binary parameters.

The following weighted-error objective function was used to regress model parameters:

$$SS = \sum_i \sum_j \left(\frac{\omega_{ij}^{calc} - \omega_{ij}^{exp\,t}}{\sigma_{ij}^{exp\,t}} \right)^2 \qquad \text{i=1, NPTS; j=1, NC (29)}$$

Here, j and i are component and data point indices, respectively, NC the total number of components in the mixture, NPTS the total number of data points, and $\sigma_{ij}^{exp\,t}$ is the expected experimental uncertainty for the individual data point. The root-mean-square error (RMSE) and the %AAD for the individual isotherms, calculated as

$$RMSE = \sqrt{\frac{\sum_i^{NPTS} (\omega_i^{calc} - \omega_i^{exp\,t})^2}{NPTS}}$$

$$\%AAD = 100 \sum_i^{NPTS} \left| \frac{\omega_i^{calc} - \omega_i^{exp\,t}}{\omega_i^{exp\,t}} \right|$$

were used to express the quality of fit in our model evaluations. Similar expressions were used for the overall fit.

Pure Adsorption

Tables 17-20 present a summary of our model evaluation results for the three models used to correlate the present adsorption data for methane, nitrogen, and CO_2. The model parameters, shown in Tables 17-20, were determined by minimizing the sum of squares of weighted errors in the calculated adsorption, ω, for the pure gas of interest (Equation 29).

Table 17 presents the results for the Langmuir model. AADs of 2 to 4% (4-17 SCF/ton) were obtained for the systems considered. Table 18 presents the results for the LRC using system-specific pressure exponents (η_i). The results indicate that the LRC produces better quality fit than the Langmuir correlation for the three gases studied. This in part reflects the added flexibility gained by the additional parameter η_i in the regressions. AADs of 1 to 2% (2-12 SCF/ton) were observed for the systems considered. When a common pressure exponent (η_i) was forced on the model, a value of 0.90 was obtained. Table 19 presents the results of this LRC using the common exponent, which yielded an AAD of 1-2% (2-12 SCF/ton).

Table 20 presents a summary of our model evaluation results for ZGR EOS. These results reveal the ability of the ZGR EOS to represent the adsorption of CO_2, methane and nitrogen on Tiffany coals within their expected experimental uncertainties. Similar to the LRC results, fits with 2 to 3% AAD (3-15 SCF/ton) were obtained.

Figures 7-10 illustrate the abilities of the LRC and ZGR models to describe the present pure-fluid adsorption data.

Binary Mixture Adsorptions

Figures 12, 14, and 16 present the LRC **representations** of the binary absolute adsorption data. The LRC parameters generated for these mixtures and the model statistics are given in Table 21. In general, AADs of 1-10% (1-19 SCF/ton) are observed for the individual-component adsorption. However, an AAD of 32% (11 SCF/ton) was obtained for the nitrogen adsorption in the nitrogen/CO_2 mixture adsorption.

Table 22 summarizes the results for the **LRC predictions** based on pure-gas adsorption data. As shown in this table, the LRC model predicts the methane/nitrogen and methane/CO_2 binary adsorptions within the experimental uncertainties (2-21%, 5-42 SCF/ton) using pure-fluid adsorption parameters; however, the model predictions for the nitrogen/CO_2 binary are less accurate (AAD of 39% or 14 SCF/ton for the nitrogen adsorption). Moreover, variation of the pressure exponent η does not significantly change the results. Figures 23-25 illustrate the quality of the LRC predictions for the binary mixtures.

Table 25 presents a summary of the evaluation results for ZGR EOS, where various binary parameter regressions have been considered. The results indicate that using two interaction parameters (C_{ij} and D_{ij}) leads to the best overall fit for the Tiffany coal adsorption data. **Representations** within the expected experimental uncertainty (AAD of 3-15%, 3-33 SCF/ton) are obtained for the three binaries. Figures 12, 14, and 16 illustrate the abilities of the ZGR EOS to describe the present binary mixture adsorption data. In most cases, the ZGR and LRC give comparable results, with slightly better statistics for the LRC.

In addition, Table 25 summarizes the results for the **ZGR predictions** based on pure-gas adsorption data. As shown in this table and Figures 23-25, the ZGR EOS predicts the binary adsorption isotherms of methane/nitrogen and methane/CO_2 within twice the experimental uncertainty (about 1-27%, 5-35 SCF/ton). Significantly higher deviations, however, are observed for the less-adsorbed nitrogen (up to 49% AAD, 13 SCF/ton) in the nitrogen/CO_2 binary.

Ternary Mixture Adsorption

Figure 18 presents the LRC **representations** of the ternary adsorption data. The LRC parameters generated for this mixture and the model statistics are given in Table 23. AAD of 3-12% (4-17 SCF/ton) are observed for the individual adsorption, and 3% (16 SCF/ton) for the total adsorption. The results suggest that the quality of fit is directly related to the amount adsorbed.

The **predictive capability** of the LRC is examined in Figure 26 and Table 24. In this case, the LRC model parameters obtained from the pure adsorption were used to predict the ternary mixture adsorption on wet Tiffany coal. Poor model predictions were obtained for this ternary when only pure-adsorption data are utilized in model optimization. AAD of 5-45% (2-55 SCF/ton) were observed for the individual-component isotherms. This translates roughly to prediction errors within one to four times the expected experimental uncertainty. Variation in the pressure exponent ? did not alter the results significantly.

Table 25 presents a summary the evaluation results for ZGR EOS, which indicate the ability of the ZGR EOS to predict the methane/nitrogen/CO_2 ternary adsorption isotherms within three times their expected experimental uncertainties (4-56% AAD, 5-52 SCF/ton). The ZGR **representations** using binary interaction parameters (C_{ij}, D_{ij}) are comparable to those obtained by the LRC using the same amount of input data. The ZGR binary interaction parameters generated for this mixture are also given in Table 25.

The **predictive capability** of the ZGR EOS is examined in Figure 26 and Table 25. The ZGR predictions based on pure (α_i, β_i, $\ln k_i$) and binary (C_{ij}, D_{ij}) parameters are within three times the experimental uncertainty (10-32% AAD, 5-49 SCF/ton). However, the results indicate that for the present mixtures little improvement is realized by predicting the individual-component ternary isotherms based on parameters generated from both pure and binary adsorption data. Further, the quality of the model predictions indicate that although the LRC and ZGR EOS are capable of predicting total adsorption isotherms adequately, they predict the individual-component isotherms poorly, especially when dealing with the less-adsorbed component of the mixture. In fact, diminishing the influence of the less-adsorbed components on the parameter regressions, by using a least-squares (un-weighted) objective function, improves the ternary model predictions based on pure and binary data.

These results suggest significant model improvements are required to realize the expected benefit of improving multicomponent predictions using binary adsorption measurements.

(b) Sorption-Time Estimates for Pure Gases

An empirical correlation was used to represent the sorption fractional uptake, Θ:

$$\Theta = \frac{\beta t^{\alpha}}{1+\beta t^{\alpha}} \quad (30)$$

where

$$\alpha = (aP^2 + bP + 0.5)c$$

The coefficients β, a, b and c are regressed from sorption time data [8]. For the systems considered in this study, Equation 30 represents the sorption-time estimates on average within 8%. Table 26 lists the regressed parameters for the gases considered, and Figures 27-30 present the correlated sorption curves for methane, nitrogen and CO_2, respectively.

Table 27 and Figure 31 present time estimates for liberated gas off the Tiffany coal samples. The plot indicates that CO_2 has the fastest sorption time followed by nitrogen and methane. Moreover, the sorption time for the three gases is within 12 minutes for 63% adsorbed-gas liberation.

F. Conclusions

- Characterizations of BP Amoco Tiffany coal samples from Injection Wells #1 and #10 were done. Results for (a) particle size distribution, (b) composition, (c) equilibrium moisture content, and (d) vitrinite reflectance indicate similarity of the two samples.
- The vitrinite reflectance analysis indicates that the samples represent medium volatility bituminous coals.
- Adsorption isotherms for pure methane on the two wet Tiffany coal samples (Wells #1 and #10) at 130°F and pressures to 2000 psia confirmed the similarity of the two samples.
- Adsorption isotherms were then measured for **pure** methane, nitrogen and CO_2 on a mixed Tiffany coal sample. The coal sample was an equal-mass mixture of coals from Well #1 and Well #10. The adsorption measurements were conducted at 130°F and pressures to 2000 psia. The adsorption capacity of the mixed sample is intermediate to that observed for Well #1 and Well #10 samples. The pure adsorption data have average expected experimental uncertainties of 3% (9 SCF/ton), 6% (8 SCF/ton) and 7% (62 SCF/ton) for methane, nitrogen, and CO_2, respectively.
- Sorption times were measured for pure methane, nitrogen and CO_2. The measurements were correlated using a Langmuir-type equation, which yielded average errors within 8%.
- **Binary** adsorption of methane/nitrogen, methane/CO_2 and nitrogen/CO_2 on a wet Tiffany mixed coal at 130 °F and pressures to 2000 psia were measured at one feed composition for each mixture. The expected uncertainties in the amount adsorbed for these binary mixtures vary with pressure and composition. In general, percent average uncertainties are about 7% (19 SCF/ton) for total adsorption; however, the expected uncertainties in the amount of individual-component adsorption are significantly higher, especially at lower feed gas mole fractions (i.e., nitrogen in the nitrogen/CO_2 system at 20/80 mole % feed composition).
- **Ternary** adsorption was measured for methane/nitrogen/CO_2 on a wet Tiffany mixed coal at 130°F and pressures to 2000 psia for a 10/40/50 mole % feed composition. The average expected uncertainty for the total adsorption and CO_2 adsorption is about 5% (17 SCF/ton). However, the low adsorption of nitrogen and methane in this ternary yielded experimental uncertainties of 14% (9 SCF/ton) and 27% (9 SCF/ton), respectively.
- Our newly acquired compressibility factor measurements for mixtures of methane/nitrogen/CO_2 allowed us to optimize the BWR EOS to predict accurately the Z factors required for use in reduction of our mixture adsorption data.

- The total adsorption data can be **correlated** within their experimental uncertainties by the loading ratio correlation (LRC) and the 2D Zhou-Gasem-Robinson (ZGR) equation of state (EOS).

- The present results suggest that both the LRC and ZGR EOS are capable of **predicting** binary adsorption isotherms based on pure-fluid adsorption parameters within twice their experimental uncertainties. In comparison, the ternary predictions based on pure-fluid parameters yield three times the experimental uncertainties. Further, for the present system, little improvement is realized by predicting the individual-component ternary isotherms based on parameters generated from both pure and binary adsorption data.

- The quality of the model predictions indicate that although the LRC and ZGR EOS are capable of predicting the total adsorption adequately, they predict the individual-component adsorption poorly, especially when dealing with the less-adsorbed component of the mixture. This suggests significant model improvements are required to realize the full benefit of improving multicomponent predictions using input from binary adsorption measurements.

G. References

1. Hall, F. E., Zhou, Chunhe, Gasem, K. A. M., and Robinson, Jr., R. L., *Adsorption of Pure Methane, Nitrogen, and Carbon Dioxide and their Binary Mixtures on Wet Fruitland Coal*, SPE Paper 29194, presented at the 1994 Eastern Regional Conference & Exhibition, Charleston, West Virginia, November 8-10, 1994.

2. Hall, F. E., *Adsorption of Pure and Multicomponent Gases on Wet Fruitland Coal*, M. S. Thesis, Oklahoma State University, December 1993.

3. Span, R. and Wagner, W., *A New Equation of State for Carbon Dioxide Covering the Fluid Region from the Triple Point Temperature to 1100 K at Pressures up to 800 MPa*, J. Phys. Chem. Ref. Data, 25, 1509-1590 (1996).

4. *International Thermodynamic Tables of the Fluid State-5 Methane,* Angus, S., Armstrong, B., de Reuck, K.M., IUPAC Chemical Data Series No.16, (1976).

5. *International Thermodynamic Tables of the Fluid State-6 Nitrogen,* Angus, S., Armstrong, B., de Reuck, K.M., IUPAC Chemical Data Series No.20, (1977).

6. Arri, L. E., and Yee, D., *Modeling Coalbed Methane Production with Binary Gas Sorption*, SPE Paper 24363, presented at the SPE Rocky Mountain Regional Meeting, Casper, Wyoming, May 18-21, 1992.

7. Myers, A. L., and Prausnitz, J. M., *Thermodynamics of Mixed-Gas Adsorption*, AIChE J. 11 121-129 (1965).

8. Stevenson, M. D., Pinczewski, W. V., Somers, M. L., and Bagio, S. E., *Adsorption/Desorption of Multicomponent Gas Mixtures on Coal at In-Seam Conditions*, SPE Paper 23026, presented at the SPE Asia-Pacific Conference, Perth, Western Australia, November 4-7, 1991.

9. Zhou, C., Gasem, K. A. M., and Robinson, Jr., R. L., *Predicting Gas Adsorption Using Two-Dimensional Equations of State*, I&EC Research 33 1280-1289 (1994).

10. Malbrunot, P., Vidal, D., and Vermesse, J., *Storage of Gases at Room Temperature by Adsorption at High Pressure*, Applied Thermal Engineering 16 375-382 (1996).

11. Pan, Z., Fitzgerald, J. E., Sudibandriyo, M., Gasem, K. A. M., and Robinson, Jr., R. L., *Measurement and Correlation of Methane/Nitrogen/Carbon Dioxide Compressibility Factors*, Journal of Thermodynamics, to be submitted, 2002.

H. Tables

Table 1. Compositional Analyses of Tiffany Coal Samples*

Analysis	Well #1	Well #10	Well #1 Dried Basis	Well #10 Dried Basis
Dry Loss %	6.85	18.33		
Carbon %	44.51	46.35	47.78	56.75
Hydrogen %	3.20	4.30	2.62	2.77
Oxygen %	11.85	20.51	6.19	5.16
Nitrogen %	0.86	0.83	0.92	1.02
Sulfur %	0.53	0.42	0.57	0.52
Ash %	46.30	38.99	49.71	47.74
Proximate				
Volatile Matter %	14.41	12.54	15.48	15.35
Fixed Carbon %	32.43	30.14	34.82	36.91

*Analysis was conducted on a mass basis by Huffman Laboratories, Inc., 4630 Indiana Street, Golden, CO 80405.

Table 2. Tiffany Coal Particle Size Distribution

Size Range (mm)		Well #1 (% mass)	Well #10 (% mass)
From	To		
0.00	0.25	4.0	5.0
0.25	0.30	4.5	1.4
0.30	0.425	7.5	3.3
0.425	0.60	10.9	8.2
0.60	0.85	13.9	15.0
0.85	1.70	45.7	41.0
1.70	2.00	2.5	5.6
2.00	2.38	6.2	4.3
2.38	5.66	4.7	15.6
5.66	∞	0.0	0.6

Table 3. Vitrinite Reflectance Analysis*

	Well #1	Well #10
Average VRO	1.31	1.35
Range	1.19-1.43	1.21-1.50
Grain Count	50	50
Rank	Medium Volatility Bituminous Coal	Medium Volatility Bituminous Coal

*Analysis was conducted by National Petrographic Service, Inc., 5933 Bellaire Blvd. Suite 108, Houston, TX 77081.

Table 4. Pure Methane Adsorption on Wet Tiffany Well #1 Coal at 130 °F: 5.6% Moisture Content

Run 1 (Moisture Free Basis)			Run 2 (Moisture Free Basis)		
Pressure (psia)	Gibbs Adsorption (SCF/ton)[*]	Absolute Adsorption (SCF/ton)	Pressure (psia)	Gibbs Adsorption (SCF/ton)	Absolute Adsorption (SCF/ton)
62.0	43.2	43.5	322.5	141.7	146.4
139.3	79.7	80.8	657.3	199.7	214.0
298.3	138.6	142.8	1129.1	245.7	278.7
485.0	176.9	186.0	1840.3	260.8	325.9
655.5	205.9	220.6			
898.3	234.1	258.0			
1057.1	246.1	276.6			
1235.1	254.7	292.9			
1446.4	260.5	308.1			
1728.1	264.2	324.9			
1960.3	267.8	340.5			

Run 1 (Moisture and Ash Free Basis)			Run 2 (Moisture and Ash Free Basis)		
Pressure (psia)	Gibbs Adsorption (SCF/ton)	Absolute Adsorption (SCF/ton)	Pressure (psia)	Gibbs Adsorption (SCF/ton)	Absolute Adsorption (SCF/ton)
62.0	85.9	86.5	322.5	281.8	291.1
139.3	158.4	160.7	657.3	397.1	425.5
298.3	275.6	284.0	1129.1	488.5	554.2
485.0	351.8	369.8	1840.3	518.6	648.1
655.5	409.4	438.6			
898.3	465.5	513.0			
1057.1	489.3	550.1			
1235.1	506.4	582.4			
1446.4	518.0	612.7			
1728.1	525.3	646.0			
1960.3	532.5	677.0			

---

[*] 1 mmol/g = 758.98 SCF/ton

Table 5. Pure Methane Adsorption on Wet Tiffany Well #10 Coal at 130 °F: 16.5% Moisture Content

Run 1 (Moisture Free Basis)			Run 2 (Moisture Free Basis)		
Pressure (psia)	**Gibbs Adsorption (SCF/ton)**	**Absolute Adsorption (SCF/ton)**	**Pressure (psia)**	**Gibbs Adsorption (SCF/ton)**	**Absolute Adsorption (SCF/ton)**
81.2	48.8	49.1	251.1	108.3	111.0
191.1	94.1	95.9	681.6	199.0	213.8
375.5	145.5	151.1	1137.8	232.8	264.4
591.6	189.8	201.9	1665.4	238.0	290.4
809.1	219.3	239.2			
1018.2	230.2	257.6			
1194.5	238.6	273.0			
1393.2	241.9	284.1			
1599.8	243.5	294.1			
1807.4	246.9	307.1			
1975.9	250.6	319.4			

Run 1 (Moisture and Ash Free Basis)			Run 2 (Moisture and Ash Free Basis)		
Pressure (psia)	**Gibbs Adsorption (SCF/ton)**	**Absolute Adsorption (SCF/ton)**	**Pressure (psia)**	**Gibbs Adsorption (SCF/ton)**	**Absolute Adsorption (SCF/ton)**
81.2	93.4	94.1	251.1	207.2	212.6
191.1	180.0	183.6	681.6	380.8	409.2
375.5	278.4	289.2	1137.8	445.4	506.1
591.6	363.2	386.3	1665.4	455.5	555.7
809.1	419.6	457.6			
1018.2	440.5	492.8			
1194.5	456.6	522.3			
1393.2	462.9	543.6			
1599.8	465.9	562.8			
1807.4	472.5	587.6			
1975.9	479.5	611.1			

Table 6. Pure Methane Adsorption on Wet Tiffany Mixed Coal Sample at 130 °F: 11.7% Moisture Content

(Moisture Free Basis)		
Pressure (psia)	Gibbs Adsorption (SCF/ton)	Absolute Adsorption (SCF/ton)
255.9	114.0	117.0
824.9	223.1	243.9
1210.2	247.4	283.6
1796.9	254.8	316.6

Table 7. Pure Nitrogen Adsorption on Wet Tiffany Mixed Coal Sample at 130 °F: 11.7% Moisture Content

Run 1 (Moisture Free Basis)			Run 2 (Moisture Free Basis)		
Pressure (psia)	Gibbs Adsorption (SCF/ton)	Absolute Adsorption (SCF/ton)	Pressure (psia)	Gibbs Adsorption (SCF/ton)	Absolute Adsorption (SCF/ton)
126.8	23.5	23.7	106.6	18.0	18.1
222.7	35.2	35.9	202.9	29.4	29.9
418.3	54.3	56.4	406.0	51.0	52.9
615.7	67.8	71.7	602.7	66.0	69.7
808.7	81.7	88.0	795.6	82.0	88.1
1008.9	91.9	100.8	1000.2	93.4	102.3
1211.4	99.8	111.6	1202.5	102.1	113.9
1404.6	108.4	123.4	1410.9	111.2	126.6
1615.8	118.9	138.1	1604.9	119.0	138.0
1817.6	125.8	148.9	1806.2	124.5	147.2
1994.8	132.5	159.5			

Table 8. Pure CO_2 Adsorption on Wet Tiffany Mixed Coal Sample at 130 °F: 11.7% Moisture Content

Run 1 (Moisture Free Basis)			Run 2 (Moisture Free Basis)		
Pressure (psia)	Gibbs Adsorption (SCF/ton)	Absolute Adsorption (SCF/ton)	Pressure (psia)	Gibbs Adsorption (SCF/ton)	Absolute Adsorption (SCF/ton)
69.5	149.6	150.6	97.3	175.1	176.7
204.5	273.1	278.8	526.8	383.0	406.6
400.7	362.8	378.8	1028.3	417.2	486.1
624.3	408.0	439.4	1504.0	357.1	515.4
813.3	422.3	469.5	1956.1	281.5	575.6
1010.0	423.0	490.6			
1209.1	403.6	496.8			
1402.1	372.3	501.2			
1590.5	335.2	520.2			
1784.6	303.4	555.7			
1976.5	271.0	560.1			

Table 9. Methane/Nitrogen Adsorption on a Wet Tiffany Mixed Coal Sample at 130 ^{o}F: 10.5% Moisture Content

Pressure (psia)	Adsorption (SCF/ton dry coal)						Phase Compositions (Mole Fraction Methane)	
	Total		Methane		Nitrogen			
	Gibbs	Absolute	Gibbs	Absolute	Gibbs	Absolute	Gas	Adsorbed*
	Methane Feed Composition: 50.0%							
118.5	45.9	46.4	36.9	37.1	9.0	9.3	0.432	0.799
220.1	79.2	80.8	63.8	64.5	15.3	16.3	0.436	0.798
400.0	120.0	124.7	98.4	100.6	21.6	24.1	0.444	0.806
611.6	155.5	165.1	126.6	130.9	28.9	34.1	0.454	0.793
813.8	180.4	195.7	152.1	159.1	28.3	36.6	0.456	0.813
1005.9	199.1	220.4	167.3	177.1	31.8	43.3	0.461	0.804
1208.5	212.7	240.7	183.2	196.2	29.4	44.5	0.464	0.815
1409.7	223.8	258.7	193.4	209.5	30.4	49.3	0.467	0.810
1609.6	233.7	276.6	203.6	223.8	30.1	52.8	0.469	0.809
1812.8	241.5	292.5	207.8	231.9	33.7	60.6	0.473	0.793
2010.8	251.5	311.6	216.4	244.9	35.1	66.7	0.474	0.786

***** - Based on absolute adsorption

Table 10. Methane/CO_2 Adsorption on a Wet Tiffany Mixed Coal Sample at 130 ^{o}F: 11.4% Moisture Content

Pressure (psia)	Adsorption (SCF/ton dry coal)						Phase Compositions (Mole Fraction Methane)	
	Total		Methane		Carbon Dioxide			
	Gibbs	Absolute	Gibbs	Absolute	Gibbs	Absolute	Gas	Adsorbed*
	Methane Feed Composition: 41.4%							
105.3	136.1	137.5	35.9	36.7	100.2	100.9	0.541	0.267
210.0	209.7	214.1	49.6	52.0	160.1	162.1	0.530	0.243
402.4	288.6	301.1	67.7	73.8	220.9	227.2	0.500	0.245
601.4	334.6	357.0	70.7	81.7	263.9	275.4	0.488	0.229
820.7	361.7	397.0	76.0	92.7	285.8	304.4	0.473	0.234
1010.0	374.4	422.2	75.4	97.6	299.0	324.6	0.465	0.231
1214.0	379.1	441.7	79.2	107.7	299.9	334.0	0.455	0.244
1409.3	376.8	454.6	80.6	115.4	296.2	339.1	0.449	0.254
1609.3	370.4	464.6	82.6	124.2	287.8	340.3	0.443	0.268
1806.7	361.5	473.1	85.4	134.2	276.1	338.9	0.438	0.284
2034.8	344.0	474.7	90.2	146.7	253.7	328.0	0.432	0.309

***** - Based on absolute adsorption

Table 11. Nitrogen/CO_2 Adsorption on a Wet Tiffany Mixed Coal Sample at 130 ^oF: 10.4% Moisture Content

Pressure (psia)	Adsorption (SCF/ton dry coal)						Phase Compositions (Mole Fraction Nitrogen)	
	Total		Nitrogen		Carbon Dioxide			
	Gibbs	Absolute	Gibbs	Absolute	Gibbs	Absolute	Gas	Adsorbed*
	Nitrogen Feed Composition: 20.1 %							
91.8	143.1	144.4	4.3	4.8	138.7	139.6	0.363	0.033
196.3	230.7	235.1	6.6	8.0	224.1	227.1	0.325	0.034
402.7	324.7	338.4	6.5	10.5	318.2	327.9	0.289	0.031
602.9	371.4	396.3	6.9	13.6	364.5	382.8	0.268	0.034
824.4	398.4	438.1	5.5	15.5	392.9	422.6	0.253	0.035
1011.5	405.4	458.7	9.9	22.7	395.5	436.0	0.241	0.050
1213.7	403.4	472.8	8.5	24.7	394.9	448.2	0.233	0.052
1407.7	395.2	481.5	8.7	28.3	386.5	453.2	0.227	0.059
1604.3	376.1	479.3	6.5	29.5	369.5	449.8	0.223	0.062
1805.2	352.6	473.7	5.4	31.9	347.2	441.8	0.219	0.067
2004.2	336.8	478.6	4.2	34.9	332.6	443.7	0.216	0.073

* - Based on absolute adsorption

Table 12. Adsorption of a 10/40/50 Mole % Methane/Nitrogen/CO_2 Feed Mixture on a Wet Tiffany Mixed Coal Sample at 130 ^oF: 10.5% Moisture Content

Pressure (psia)	**Adsorption (SCF/ton dry coal)**							
	Total		**Methane**		**Nitrogen**		**Carbon Dioxide**	
	Gibbs	**Absolute**	**Gibbs**	**Absolute**	**Gibbs**	**Absolute**	**Gibbs**	**Absolute**
102.3	95.4	96.2	9.1	9.2	14.6	15.1	71.7	71.9
199.3	158.9	161.7	13.3	13.6	19.4	21.0	126.2	127.0
393.1	239.4	248.1	18.1	19.1	23.4	28.2	197.9	200.8
612.6	291.6	308.8	20.8	22.7	26.9	36.0	243.8	250.1
807.2	319.5	345.4	21.9	24.8	30.1	43.2	267.6	277.4
1008.8	337.1	372.7	21.7	25.7	30.6	48.2	284.8	298.8
1206.4	345.1	390.5	22.0	27.1	31.5	53.4	291.7	310.0
1410.7	349.8	406.1	20.7	27.0	30.9	57.6	298.2	321.5
1607.6	346.9	413.0	21.6	28.9	32.3	63.2	293.0	320.8
1808.6	344.2	420.4	22.8	31.2	34.0	69.4	287.3	319.8
2005.4	342.7	429.4	25.2	34.5	35.6	75.6	281.9	319.2

Table 12. (Continued) Adsorption of a 10/40/50 Mole % Methane/Nitrogen/CO_2 Feed Mixture on a Wet Tiffany Mixed Coal Sample at 130 ^oF: 10.5% Moisture Content

Pressure (psia)	**Phase Compositions (Mole %)**					
	Methane		**Nitrogen**		**Carbon Dioxide**	
	Gas	**Adsorbed***	**Gas**	**Adsorbed***	**Gas**	**Adsorbed***
102.3	0.107	0.095	0.543	0.157	0.350	0.748
199.3	0.112	0.084	0.537	0.130	0.352	0.786
393.1	0.112	0.077	0.514	0.114	0.374	0.810
612.6	0.111	0.074	0.491	0.116	0.398	0.810
807.2	0.111	0.072	0.476	0.125	0.414	0.803
1008.8	0.110	0.069	0.464	0.129	0.426	0.802
1206.4	0.109	0.069	0.455	0.137	0.436	0.794
1410.7	0.109	0.067	0.448	0.142	0.443	0.792
1607.6	0.107	0.070	0.442	0.153	0.451	0.777
1808.6	0.106	0.074	0.436	0.165	0.457	0.761
2005.4	0.105	0.081	0.432	0.176	0.463	0.743

***** - Based on absolute adsorption

Table 13. Desorption Time for Methane on Wet Tiffany Well #1 Coal Sample at 130 ^{o}F

Equilibrium Pressures (psia)			Time at L=0.9 (min)	Time at Q=0.63 (min)
Initial System	Desorption			
	From	To		
1958.2	1697.1	1722.8	7.5	0.6
1722.8	1496.9	1519.4	11.1	0.9
1519.4	1288.7	1310.6	17.4	1.4
1310.6	1098.4	1115.7	21.8	1.7
1115.7	894.4	911.8	28.2	2.2
911.8	682.3	704.6	44.0	3.5
704.6	484.3	505.6	56.3	4.5
283.9	43.1	87.1	169.0	14.6

Table 14. Desorption Time for Methane on Wet Tiffany Well #10 Coal Sample at 130 ^{o}F

Equilibrium Pressures (psia)			Time at L=0.9 (min)	Time at Q=0.63 (min)
Initial System	Desorption			
	From	To		
1976.4	1650.0	1678.2	4.4	0.3
1678.2	1351.0	1377.2	8.0	0.6
1377.2	1071.5	1098.7	8.8	0.7
649.1	430.4	460.1	8.4	0.7
460.1	242.4	324.7	26.1	2.3
324.7	142.4	238.1	40.3	3.7

Table 15. Desorption Time for Nitrogen on Wet Tiffany Mixed Coal Sample at 130 ^{o}F

Equilibrium Pressures (psia)			Time at L=0.9 (min)	Time at Q=0.63 (min)
Initial System	Desorption			
	From	To		
1954.4	1304.4	1310.1	22.0	4.0
1310.1	716.0	728.7	30.0	5.6
728.7	325.0	332.2	60.0	7.2
332.2	40.7	42.3	60.0	12.0

Table 16. Adsorption Time for CO_2 on Wet Tiffany Mixed Coal Sample at 130°F

Equilibrium Pressures (psia)			Time at L=0.9 (min)	Time at Q=0.63 (min)
Initial System	Adsorption			
	From	To		
3.0	159.2	69.5	39.5	2.9
69.5	462.0	400.7	27.6	2.5
400.7	662.0	624.3	22.0	2.2
624.3	834.0	813.3	15.6	2.0
813.3	1031.0	1010.0	10.7	1.8
1010.0	1233.0	1209.1	8.4	1.6

Table 17. Langmuir Model Representation of Adsorption on Wet Tiffany Coals at 130 °F

Pure Gas	L (SCF/ton)	B×1000 $(psia^{-1})$	h	RMSE (SCF/ton)	%AAD
CH_4 (Well #1)	432.0	1.6107	1.0	4.2	1.9
CH_4 (Well #10)	417.5	1.5654	1.0	2.6	1.1
CH_4 (Mixed Coal)	434.9	1.5074	1.0	7.2	2.6
N_2 (Mixed Coal)	266.9	0.6303	1.0	3.9	3.5
CO_2 (Mixed Coal)	590.9	4.5121	1.0	16.6	2.0

Table 18. LRC Model Representation of Adsorption on Wet Tiffany Coals at 130 °F

Pure Gas	L (SCF/ton)	B×1000 $(psia^{-1})$	h	RMSE (SCF/ton)	%AAD
CH_4 (Well #1)	509.0	1.1089	0.89	2.9	0.8
CH_4 (Well #10)	440.7	1.3946	0.96	2.8	0.9
CH_4 (Mixed Coal)	491.8	1.1113	0.91	7.4	2.3
N_2 (Mixed Coal)	416.3	0.2708	0.87	2.2	2.1
CO_2 (Mixed Coal)	631.2	3.9299	0.91	12.4	1.8

Table 19. LRC Model Representation of Adsorption on Wet, Mixed Tiffany Coals at 130 °F (common h)

Pure Gas	L (SCF/ton)	Bx1000 ($psia^{-1}$)	h	RMSE (SCF/ton)	%AAD
CH_4	504.4	1.0854	0.90	7.6	2.3
N_2	364.6	0.3512	0.90	2.4	2.3
CO_2	634.8	3.8024	0.90	12.2	1.8

Table 20. ZGR Equation-of-State Representation of Adsorption on Wet, Mixed Tiffany Coals at 130 °F

Pure Gas	a	b	$-\ln k$	RMSE (SCF/ton)	%AAD
CH_4	144770	1.0140	2.84	8.1	3.0
N_2	193160	1.3926	4.29	1.7	2.3
CO_2	74425	0.6069	1.26	15.4	2.1

Table 21. LRC Model Representation of Binary Adsorption on Wet Tiffany Coals at 130 °F

Mixture	L (SCF/ton)	Bx1000 ($psia^{-1}$)	h	RMSE (SCF/ton)	%AAD
CH_4 - N_2:					
CH_4	435.8	1.522	0.96	16.6	9.7
N_2	366.6	0.337	0.89	5.8	9.0
Total				20.9	8.2
CH_4 - CO_2:					
CH_4	435.8	1.522	0.96	12.0	7.3
CO_2	702.6	2.868	0.80	17.0	4.2
Total				5.5	1.2
N_2 - CO_2:					
N_2	366.6	0.337	0.89	11.3	31.6
CO_2	702.6	2.868	0.80	36.2	6.7
Total				26.2	4.7
Pure:					
CH_4	435.8	1.522	0.96	8.3	3.3
N_2	366.6	0.337	0.89	2.9	2.7
CO_2	702.6	2.868	0.80	12.6	2.1

Table 22. LRC Model Predictions of Binary Adsorption on Wet Tiffany Coals at 130 °F

Mixture	h= 1 (**Langmuir)**		**Regressed** h		h= **0.90**	
	RMSE (SCF/ton)	**%AAD**	**RMSE (SCF/ton)**	**%AAD**	**RMSE (SCF/ton)**	**%AAD**
CH_4 - N_2:						
CH_4	29.5	15.8	15.5	9.0	23.2	12.0
N_2	3.8	6.2	4.0	8.3	3.8	9.3
Total	30.2	12.2	16.2	6.4	21.7	8.2
CH_4- CO_2:						
CH_4	36.5	25.9	31.3	21.1	31.4	21.0
CO_2	39.1	9.0	42.5	10.1	44.1	10.5
Total	4.9	1.2	11.2	1.9	12.8	2.2
N_2 - CO_2:						
N_2	15.2	44.9	14.1	38.9	13.7	37.3
CO_2	27.7	5.2	35.6	5.9	33.1	5.7
Total	15.9	3.5	22.7	3.8	21.1	3.8

Table 23. LRC Model Representation of Ternary Adsorption on Wet Tiffany Coals at 130 °F

Individual Adsorption	**L (SCF/ton)**	**Bx1000 (psia^{-1})**	h	**RMSE (SCF/ton)**	**%AAD**
CH_4	478.2	1.8205	0.97	4.2	9.0
N_2	212.8	2.0495	1.30	8.1	11.7
CO_2	631.2	4.4225	1.05	12.8	3.3
Total				1.7	0.5

Table 24. LRC Model Predictions of Ternary Adsorption on Wet Tiffany Coals at 130 °F

Individual Adsorption	L (SCF/ton)	BX1000 (psia^{-1})	h	RMSE (SCF/ton)	% AAD
Parameters based on pure data					
h= 1 (**Langmuir)**					
CH_4	434.9	1.507	1.0	5.9	20.7
N_2	266.9	0.630	1.0	29.8	47.8
CO_2	590.9	4.512	1.0	49.6	13.2
Total				14.9	2.9
h **Regressed**					
CH_4	491.8	1.111	0.91	2.1	5.3
N_2	416.3	0.271	0.87	29.6	46.1
CO_2	631.2	3.930	0.91	61.4	17.7
Total				30.5	6.7
h= **0.90**					
CH_4	504.4	1.085	0.90	2.2	5.2
N_2	364.6	0.351	0.90	28.2	44.5
CO_2	634.8	3.802	0.90	54.7	15.8
Total				24.9	5.4
Parameters based on pure and binary data					
CH_4	435.8	1.522	0.96	4.6	16.6
N_2	366.6	0.337	0.89	25.1	45.8
CO_2	702.6	2.868	0.80	43.9	12.0
Total				26.1	6.0

Table 25. ZGR EOS Representation of Mixtures on Tiffany Mixed Coal at 130 °F

Mixture			%AAD			RMSE (SCF/ton coal)		
$C_{ij} = D_{ij} = 0$								
	C_{ij}	D_{ij}	ω_1	ω_2	Total	ω_1	ω_2	Total
CH_4 / N_2	0.000	0.000	11.9	10.0	11.5	20.5	6.7	26.3
CH_4 / CO_2	0.000	0.000	27.0	10.4	1.4	30.2	35.0	5.4
N_2 / CO_2	0.000	0.000	48.7	4.9	3.5	13.1	25.4	15.6
Regressed C_{ij} (D_{ij}=0)								
	C_{ij}	D_{ij}	ω_1	ω_2	Total	ω_1	ω_2	Total
CH_4 / N_2	-0.090	0.000	10.6	7.3	7.6	18.8	3.9	17.5
CH_4 / CO_2	-0.125	0.000	8.4	10.6	6.1	11.2	32.9	25.4
N_2 / CO_2	-0.140	0.000	16.0	4.1	3.2	3.9	20.9	17.7
Regressed D_{ij} (C_{ij}=0)								
	C_{ij}	D_{ij}	ω_1	ω_2	Total	ω_1	ω_2	Total
CH_4 / N_2	0.000	-0.068	10.6	7.1	7.5	18.4	3.8	16.9
CH_4 / CO_2	0.000	-0.090	7.7	11.0	6.6	9.6	34.7	28.6
N_2 / CO_2	0.000	-0.108	14.5	4.3	3.5	3.3	21.8	19.0
Regressed C_{ij} and D_{ij}								
	C_{ij}	D_{ij}	ω_1	ω_2	Total	ω_1	ω_2	Total
CH_4 / N_2	-0.060	-0.023	10.6	7.2	7.5	18.7	3.8	17.3
CH_4 / CO_2	-0.098	-0.019	8.2	10.7	6.2	10.9	33.2	26.1
N_2 / CO_2	-0.011	-0.100	14.6	4.3	3.4	3.4	21.7	18.9
Predicted Ternary								
Mixture	%AAD				RMSE (SCF/ton coal)			
From pure data $C_{ij} = D_{ij} = 0$								
	ω_1	ω_2	ω_3	Total	ω_1	ω_2	ω_3	Total
$CH_4 / N_2 / CO_2$	21.6	55.9	17.6	4.3	4.9	29.2	51.5	18.1
C_{ij} from Binary (D_{ij}=0)								
	ω_1	ω_2	ω_3	Total	ω_1	ω_2	ω_3	Total
$CH_4 / N_2 / CO_2$	18.0	32.8	17.4	9.3	4.6	17.1	48.1	35.2
D_{ij} from Binary (C_{ij}=0)								
	ω_1	ω_2	ω_3	Total	ω_1	ω_2	ω_3	Total
$CH_4 / N_2 / CO_2$	18.3	31.6	17.7	9.7	4.8	16.1	49.6	37.9
C_{ij} and D_{ij} from Binary								
	ω_1	ω_2	ω_3	Total	ω_1	ω_2	ω_3	Total
$CH_4 / N_2 / CO_2$	18.6	31.9	17.6	9.6	4.8	16.4	49.1	37.1

Table 26. Sorption Fractional Uptake Correlation

Pure Gas	a = $(aP^2+bP+0.5)c$	b	%AAD
CH_4 (Well #1)	$(-5.530\times10^{-8}\times P^2+2.960\times10^{-4}\times P+0.5)(1.030)$	0.4570	4.1
CH_4 (Well #10)	$(1.251\text{x}10^{-8}\times P^2+7.397\text{x}10^{-4}\times P+0.5)(1.327)$	0.3912	6.4
N_2 (Mixed Coal)	$(0.5)\times1.700$	0.2833	7.2
CO_2 (Mixed Coal)	$1.264\times10^{-7}\times P^2+9.497\text{x}10^{-5}\times P+0.5)(1.066)$	0.6404	2.2

Table 27. Sorption-Time Estimates on Wet Tiffany Coal Samples at 130 °F for 63% Desorption

Starting Desorption Pressure (psia)	Methane on Well #1 (min)	Methane on Well #10 (min)	Nitrogen on Mixed Coal (min)	CO_2 on Mixed Coal (min)
2000	9.3	8.4	8.2	4.7
1800	9.4	8.4	8.2	4.7
1600	9.5	8.5	8.2	4.7
1400	9.6	8.5	8.2	4.7
1200	9.8	8.5	8.2	4.7
1000	9.9	8.6	8.2	4.7
800	10.2	8.6	8.2	4.7
600	10.5	8.7	8.2	4.7
400	10.9	8.8	8.2	4.8
200	11.6	9.0	8.2	4.8

This page intentionally left blank.

Figure 1. Schematic Diagram of Adsorption Apparatus

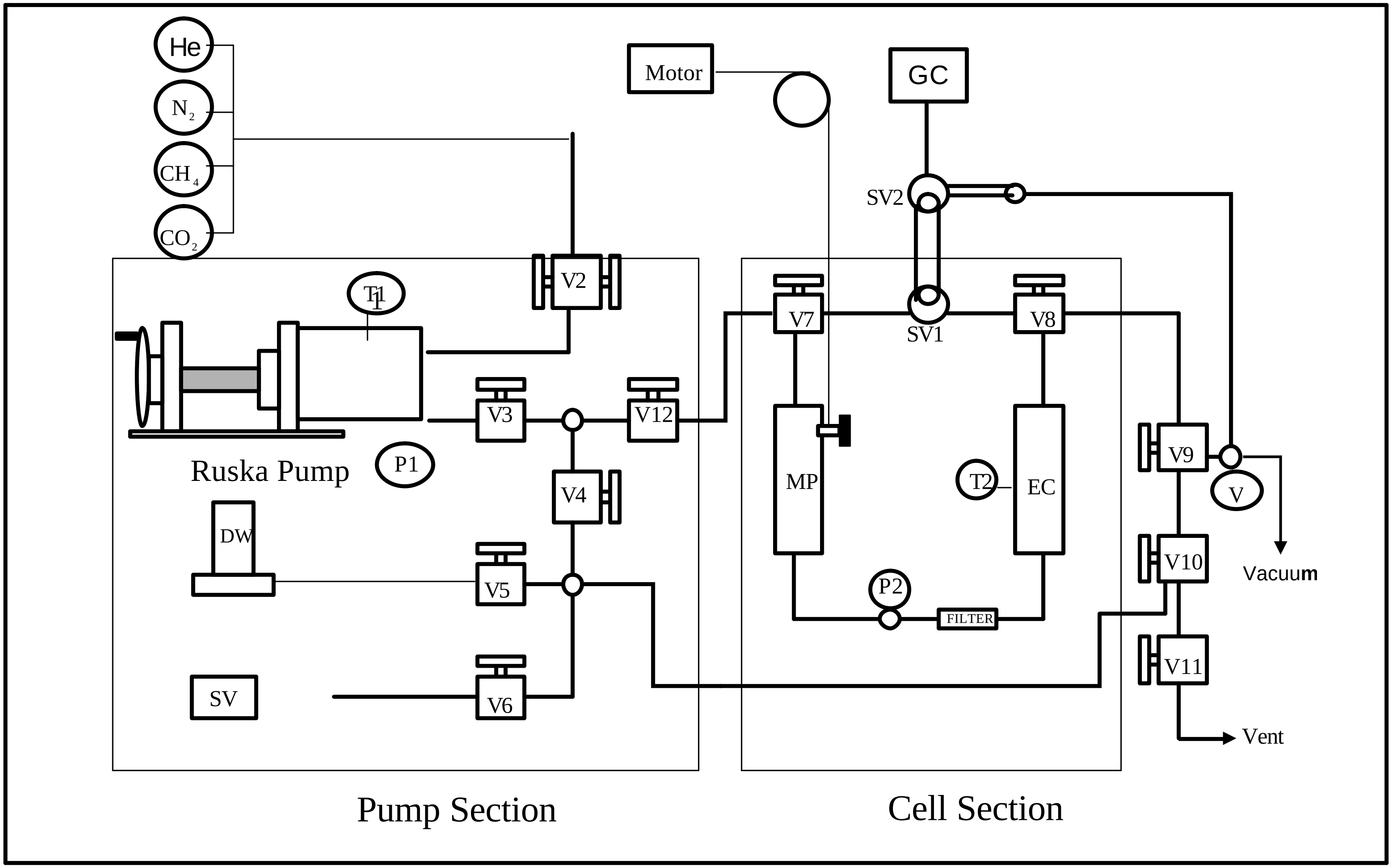


Figure 2. Tiffany Well #1 Coal Particle Size Distribution

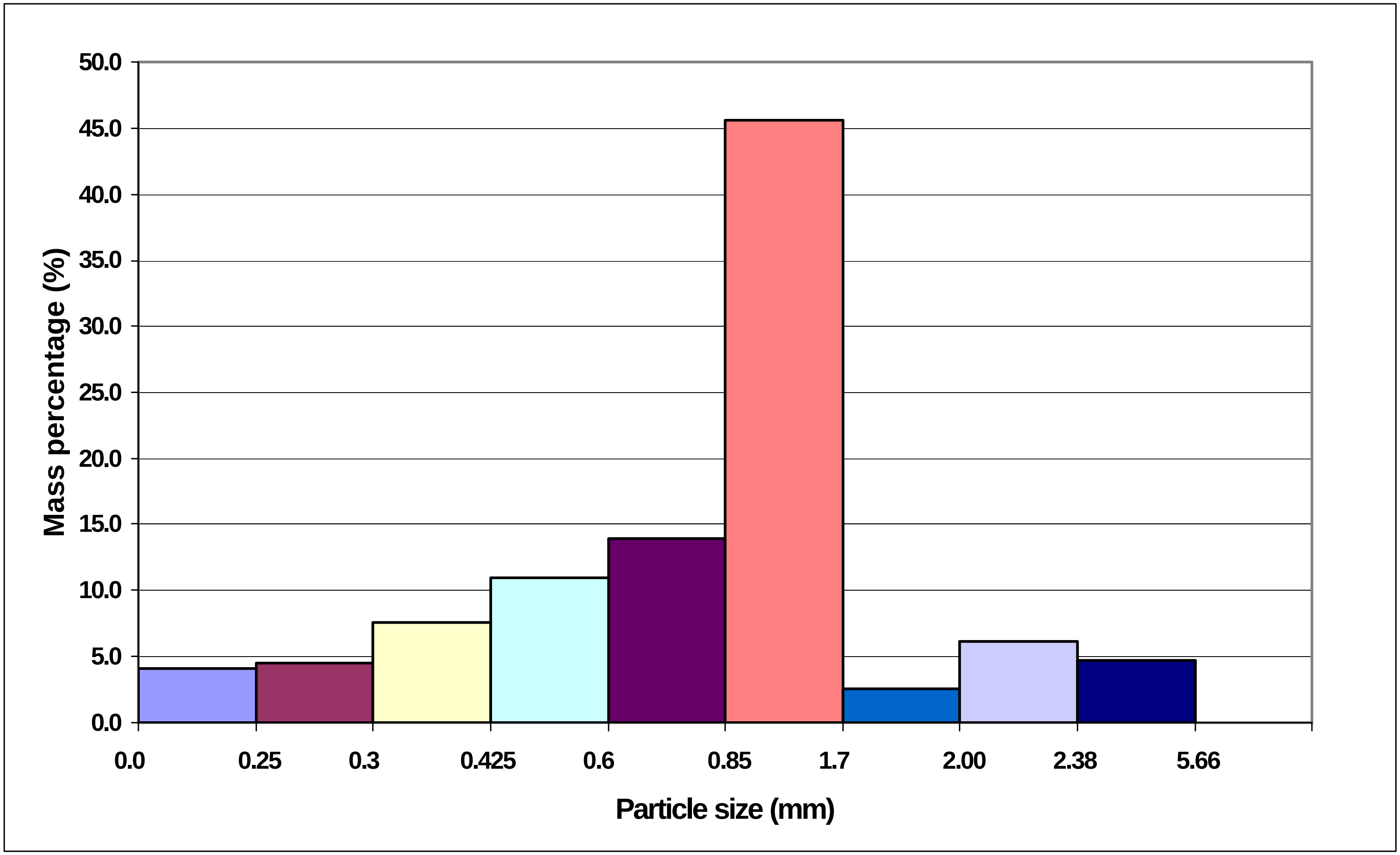


Figure 3. Tiffany Well #10 Coal Particle Size Distribution

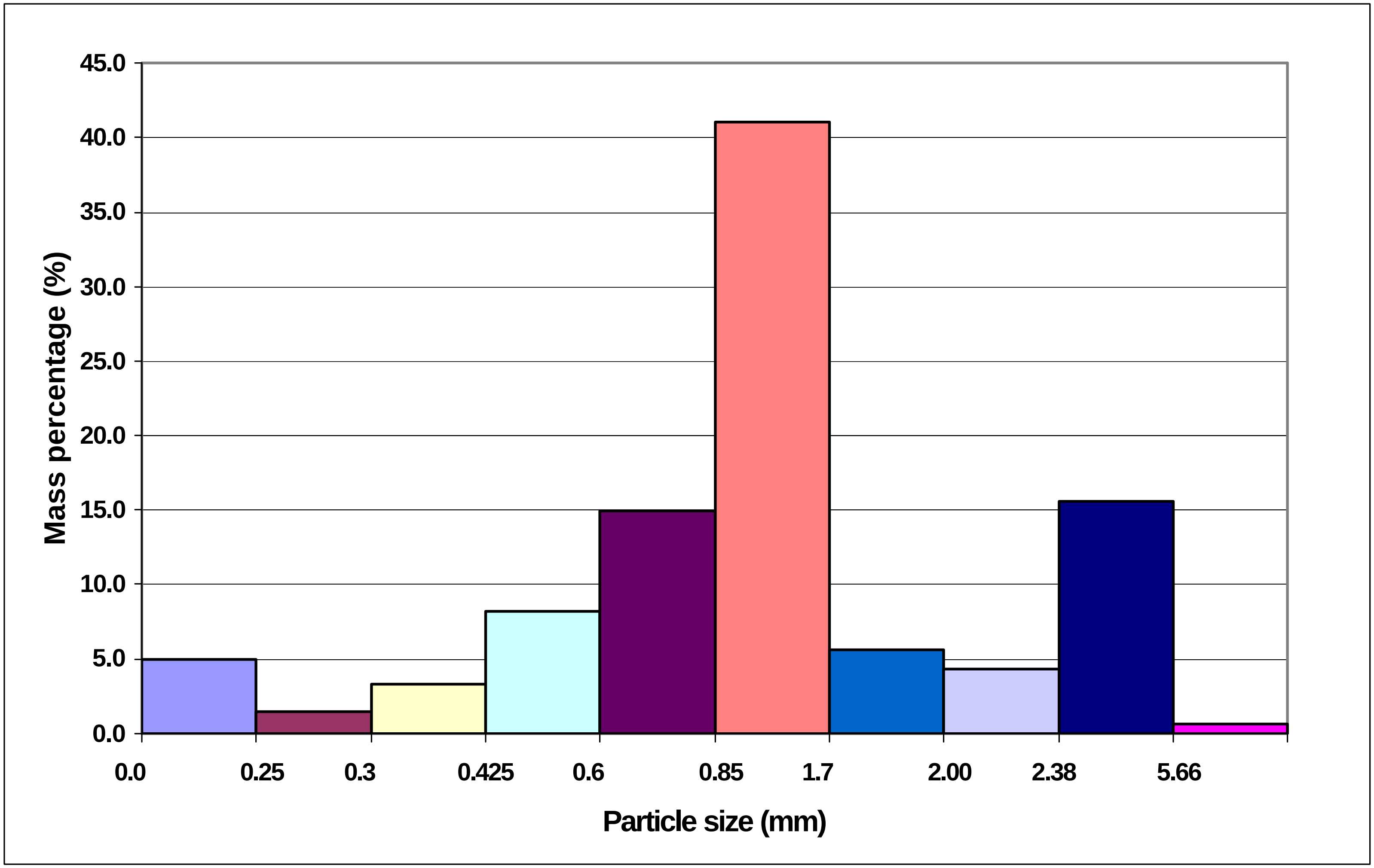


Figure 4. Tiffany Well #1 and Well #10 Coal Particle Size Distributions

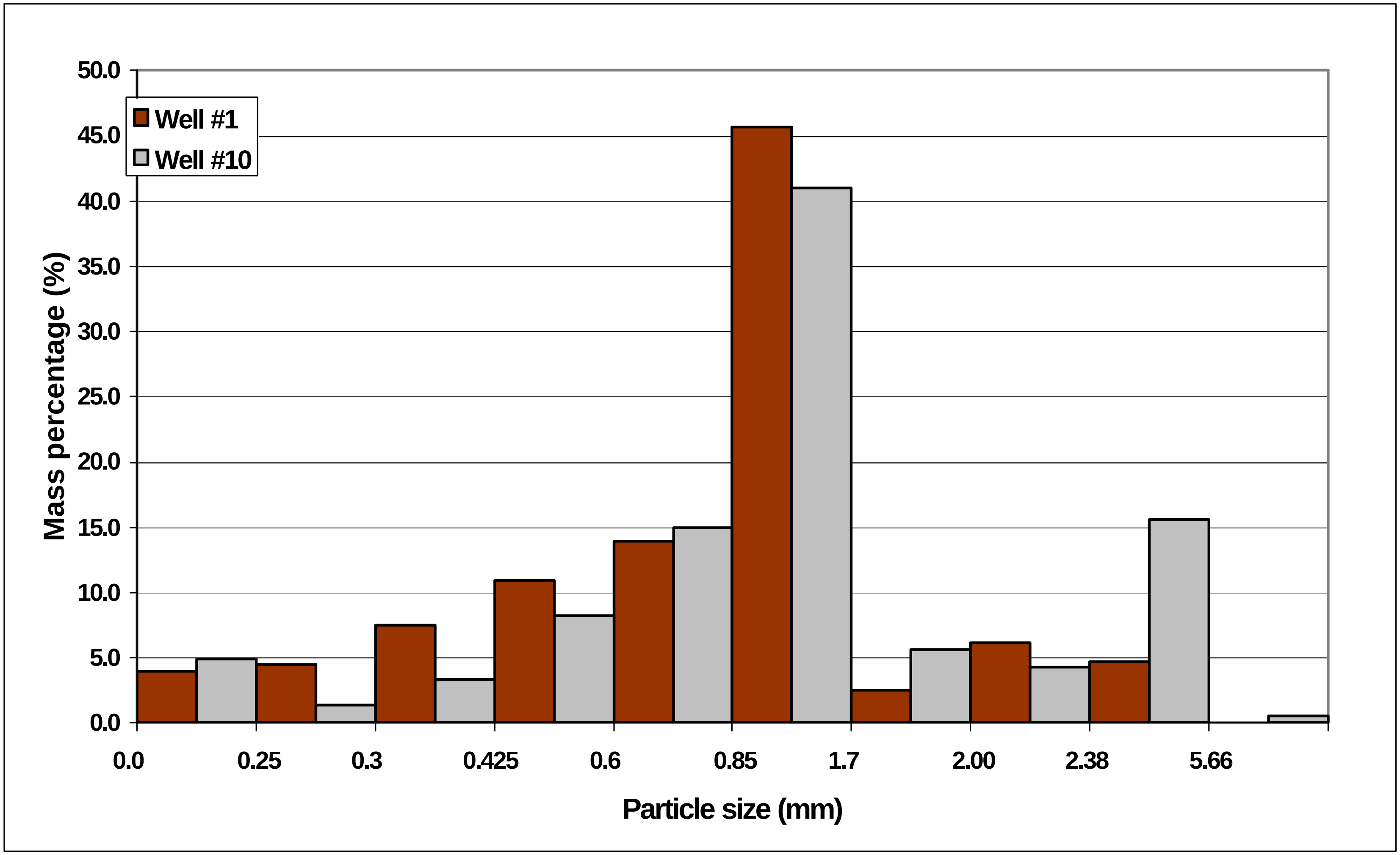


Figure 5. Pure Methane Absolute Adsorption on Tiffany Coal Samples at 130 ºF

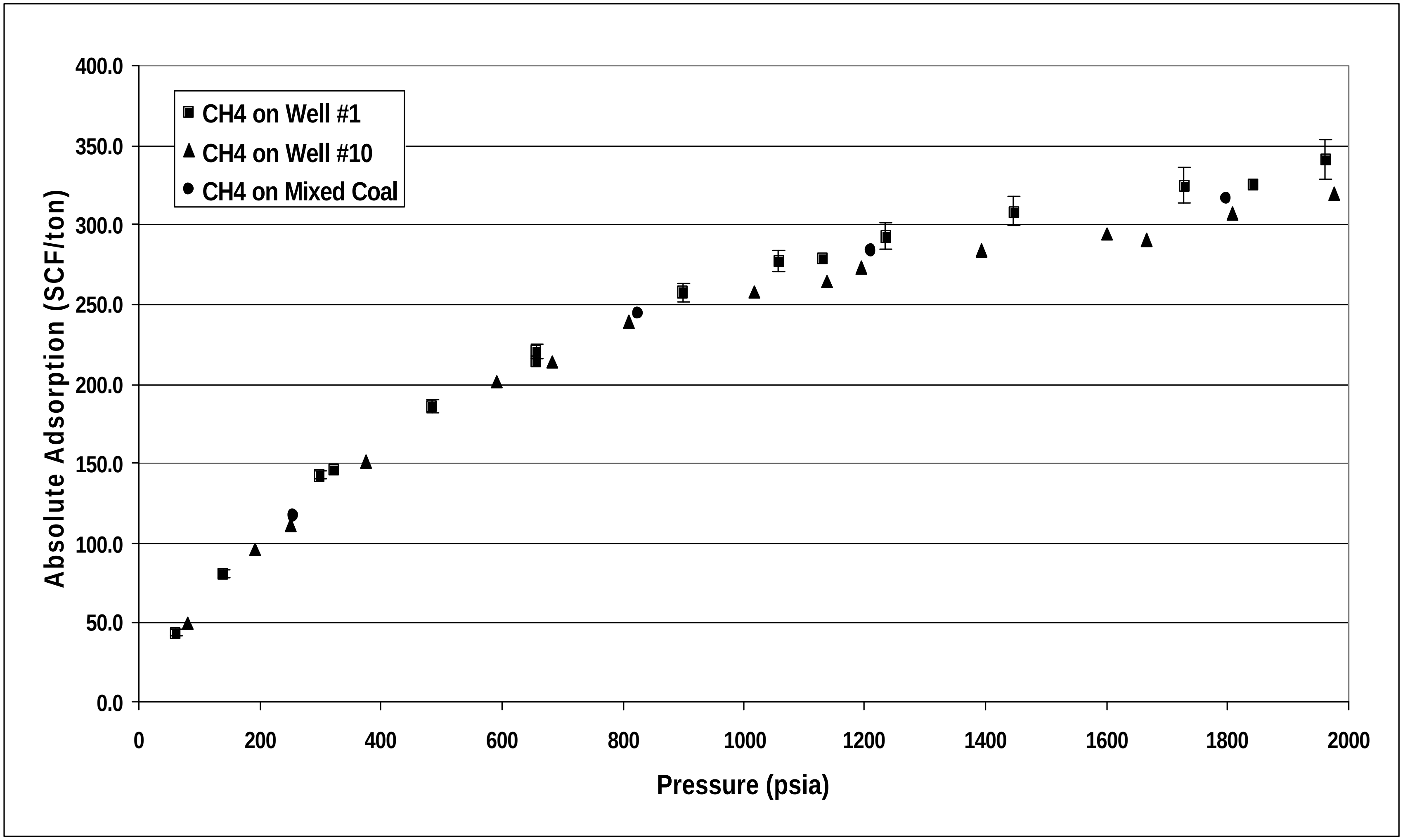


Figure 6. Pure Gas Gibbs Adsorption on Tiffany Coals at 130 °F

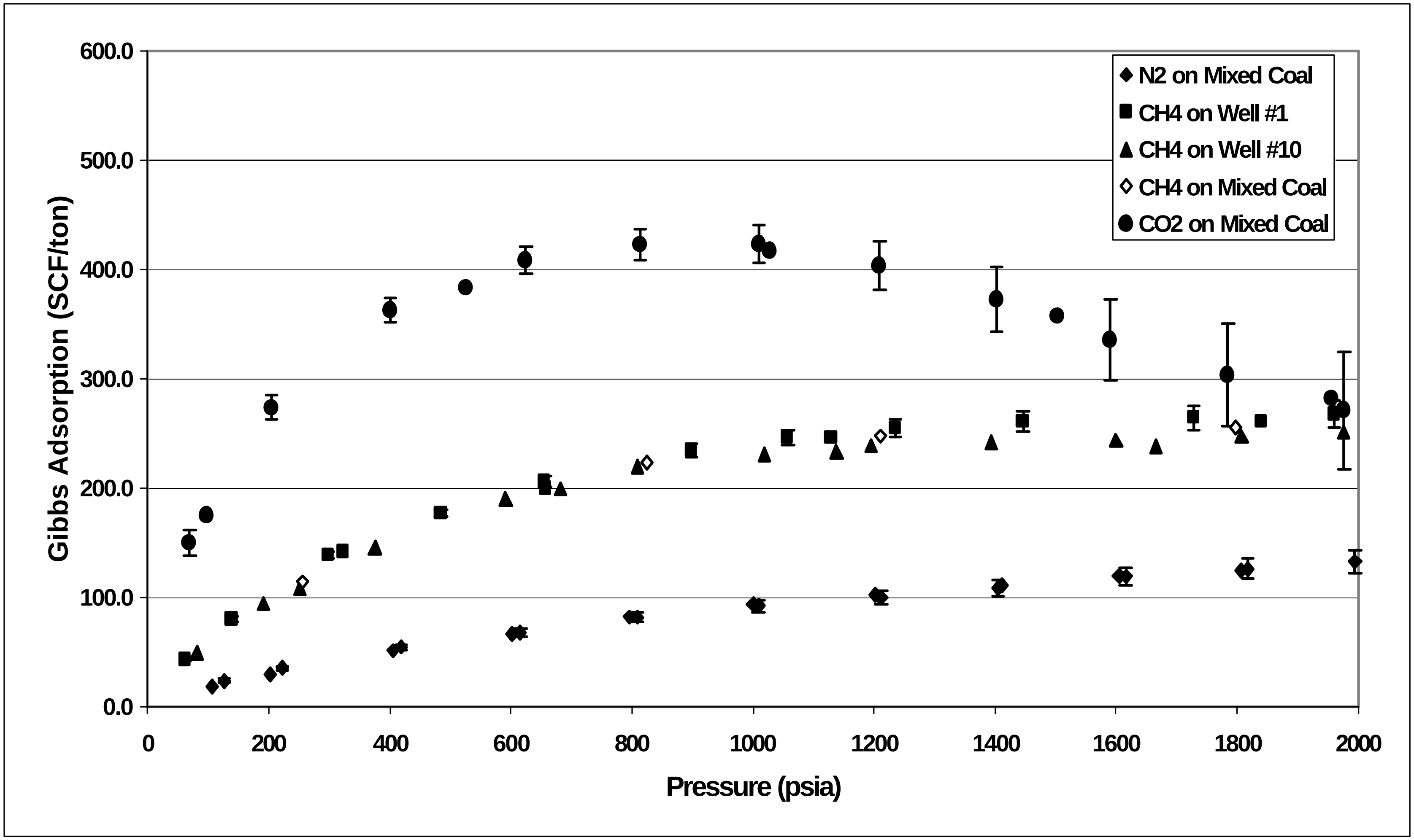


Figure 7. Pure Gas Absolute Adsorption on Tiffany Coals at 130 °F

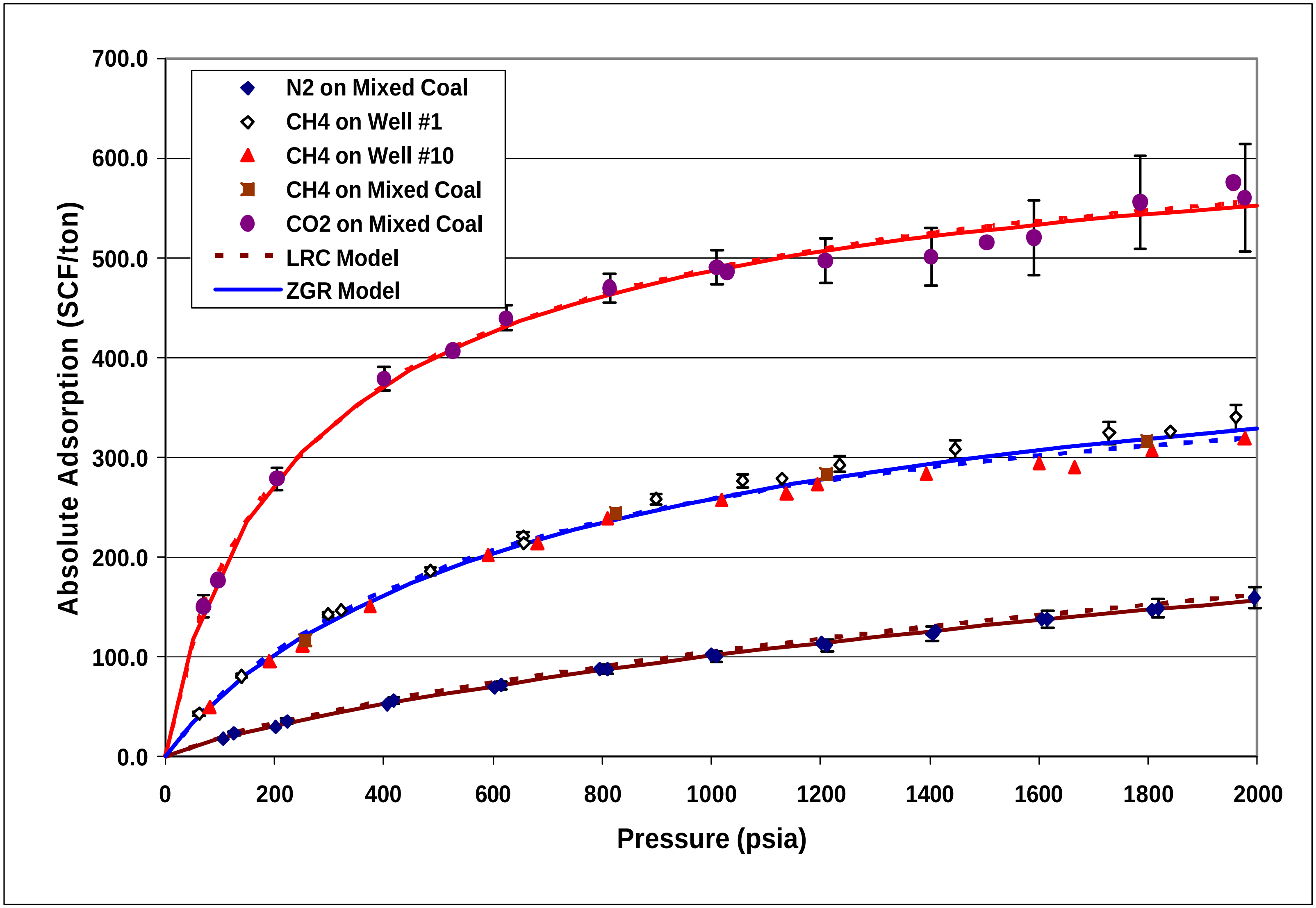


Figure 8. Pure Nitrogen Absolute Adsorption on Tiffany Mixed Coal Sample at 130 °F

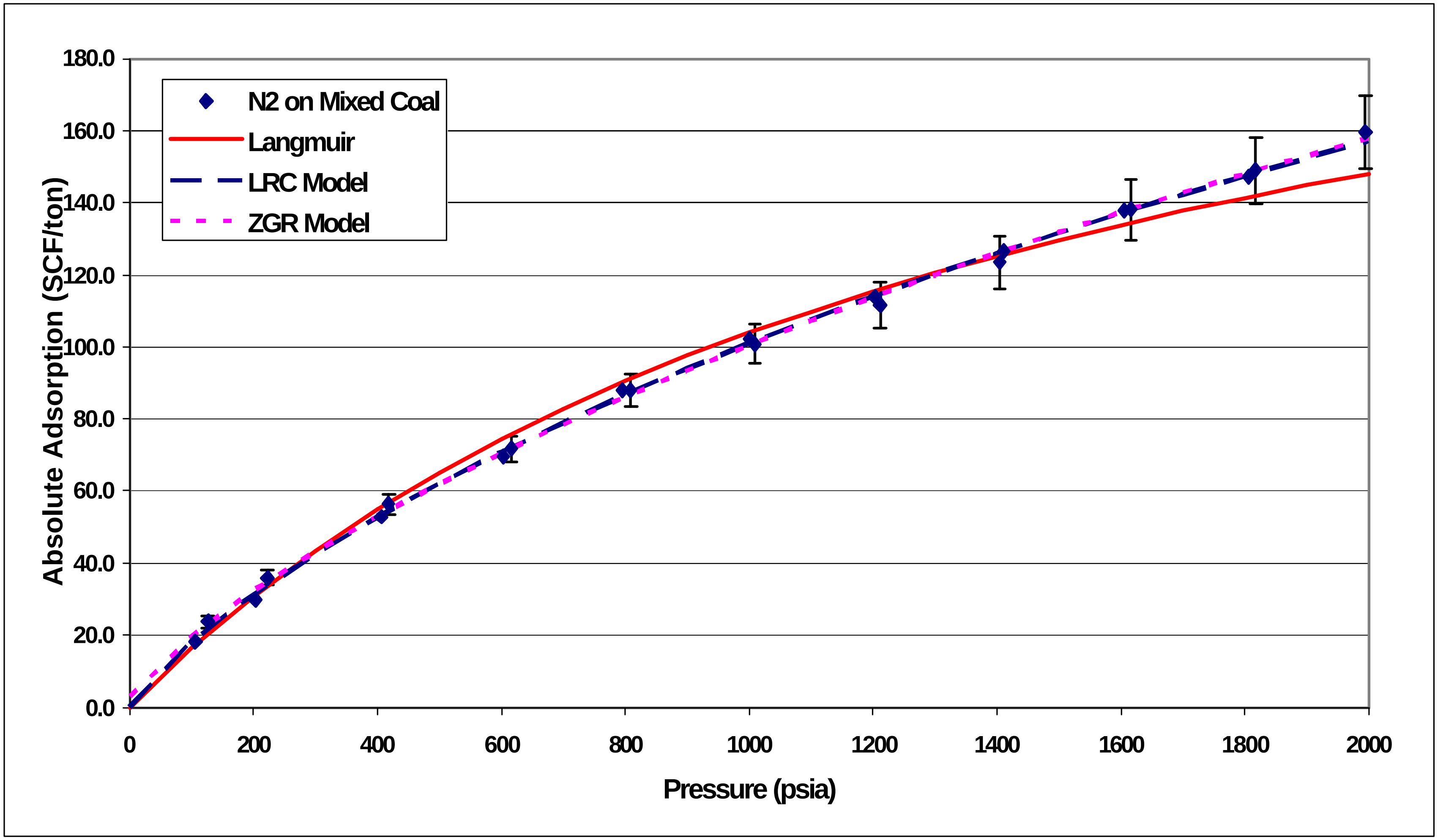


Figure 9. Pure CO_2 Absolute Adsorption on Tiffany Mixed Coal Sample at 130 °F

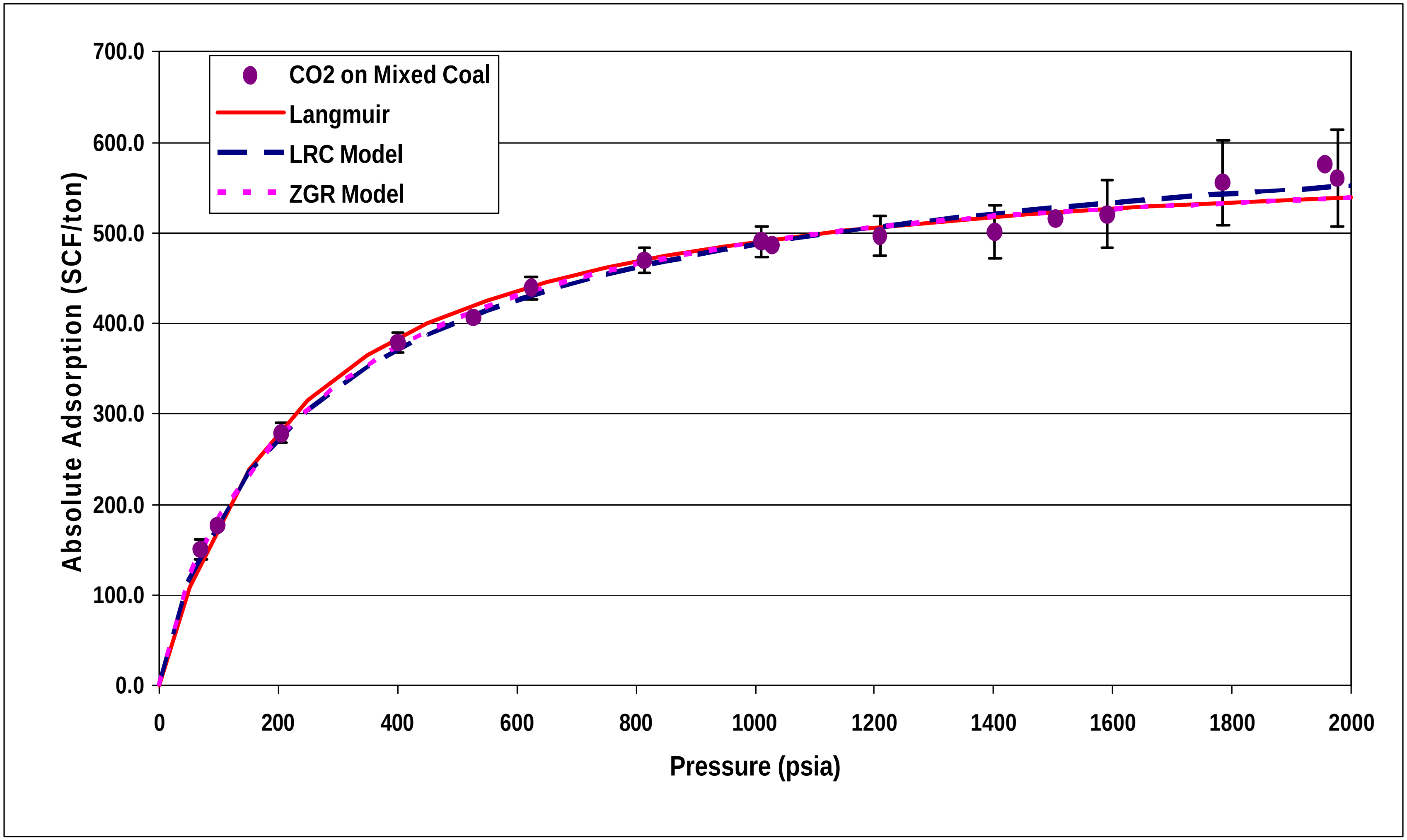


Figure 10. CO_2 Absolute Adsorption on Tiffany Mixed Coal Sample Using Different Adsorbed-Phase Densities

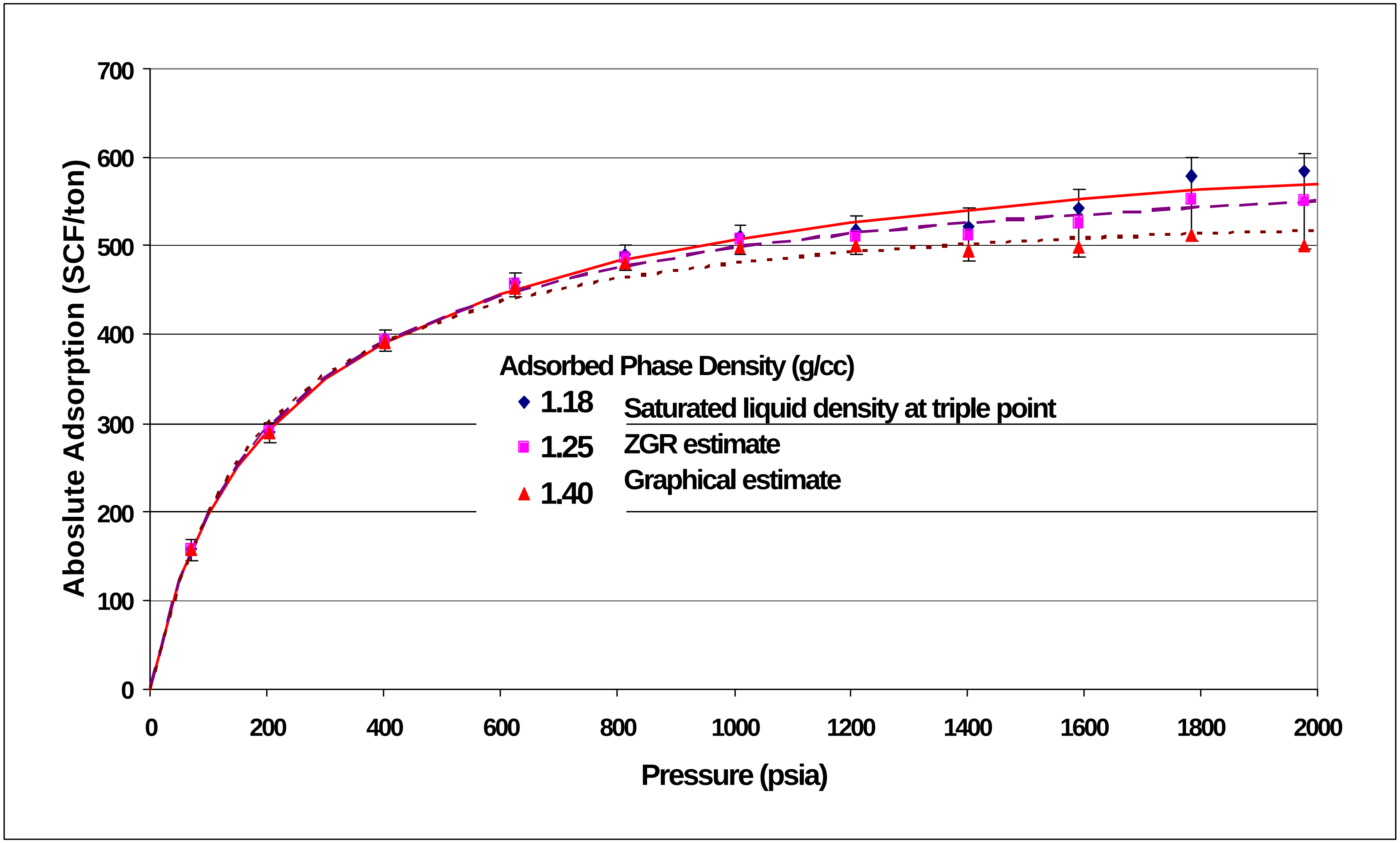


Figure 11. Gibbs Adsorption of a 50/50 Mole % Methane/Nitrogen Feed Mixture on a Wet Tiffany Mixed Coat Sample at 130 ºF

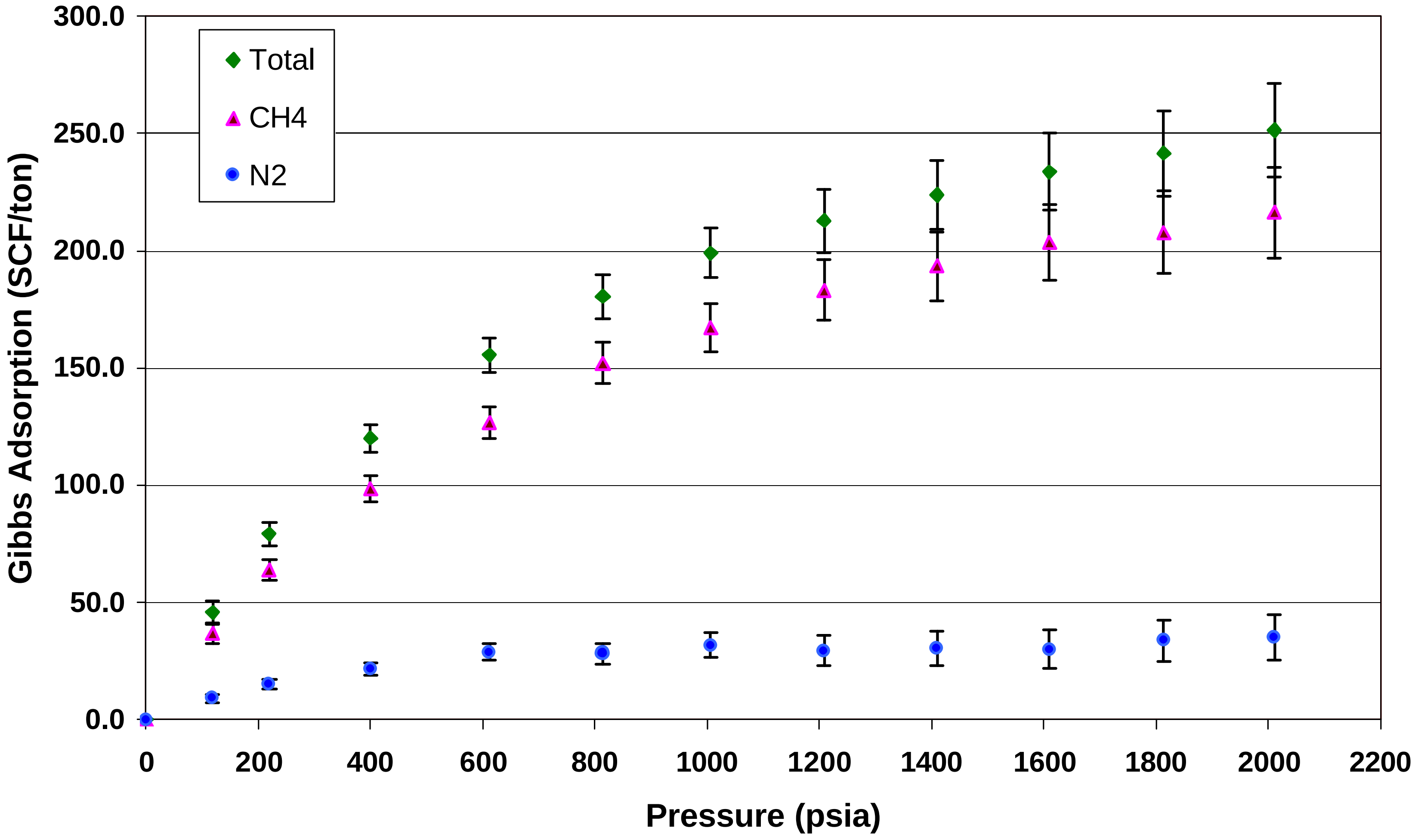


Figure 12. Absolute Adsorption for 50/50 Mole % Methane/Nitrogen Feed Mixture on a Wet Tiffany Mixed Coal Sample at 130 °F

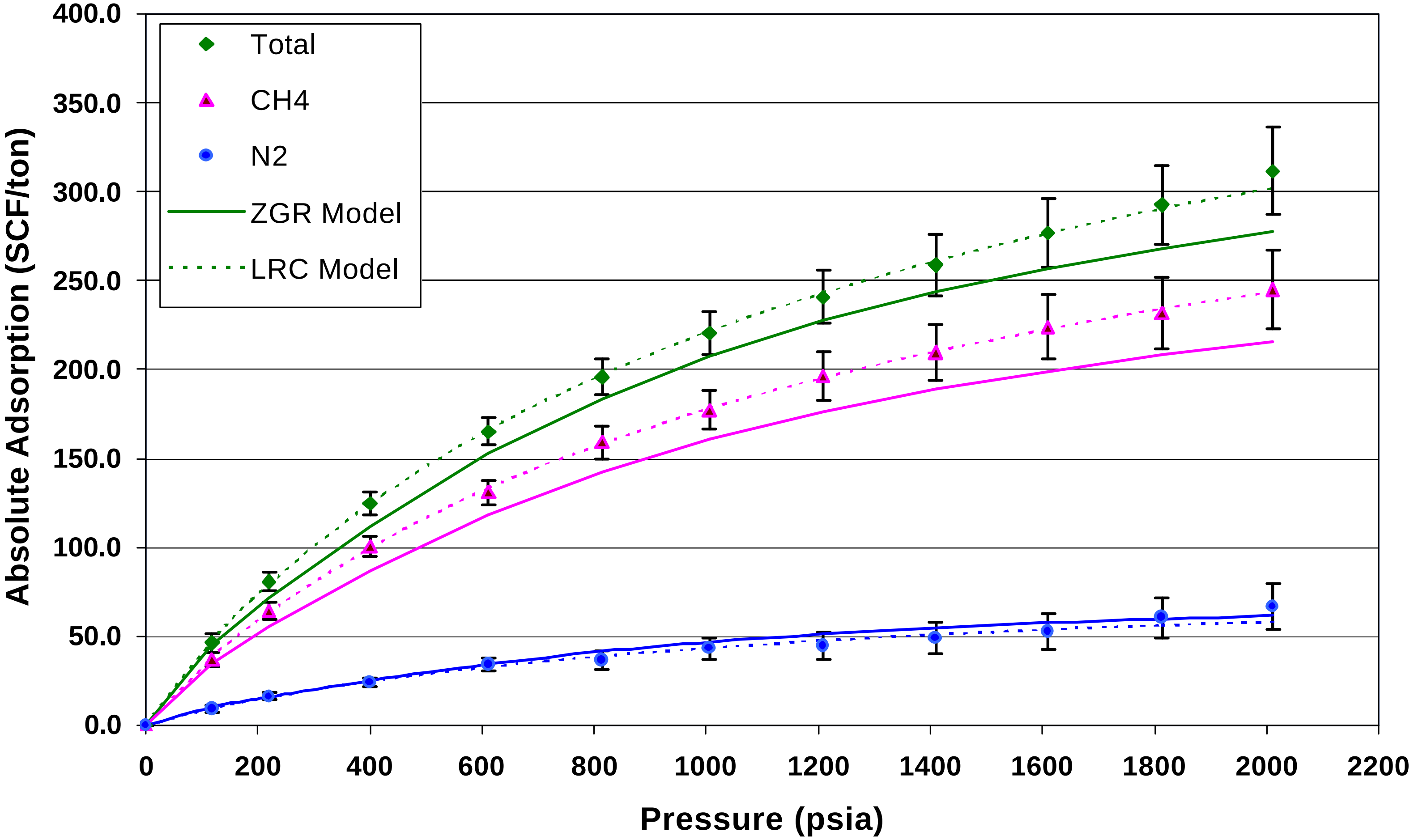


Figure 13. Gibbs Adsorption of a 40/60 Mole % Methane/CO_2 Feed Mixture on a Wet Tiffany Mixed Coal Sample at 130 ^{o}F

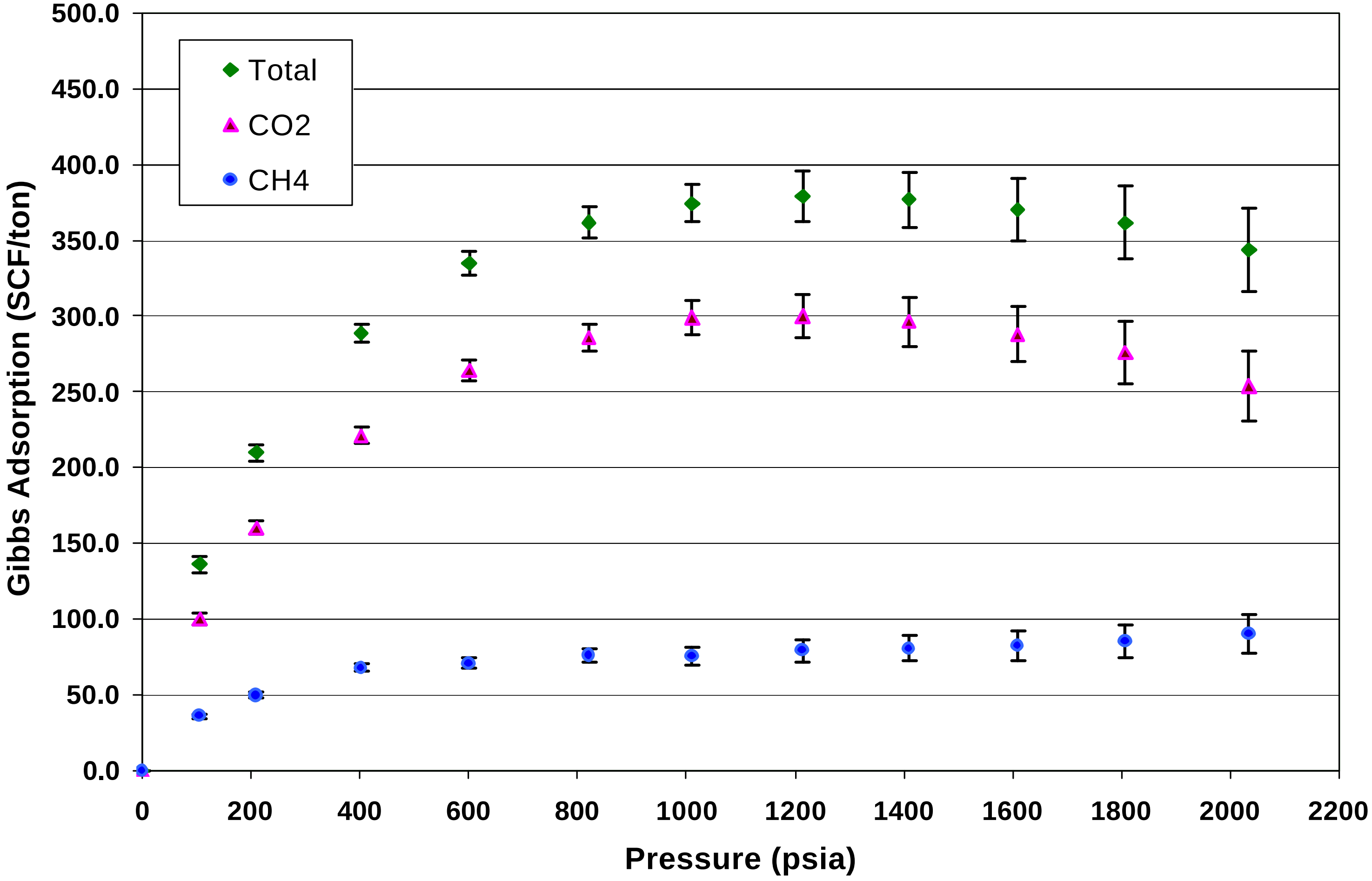


Figure 14. Absolute Adsorption for 40/60 Mole % Methane/CO_2 Feed Mixture on a Wet Tiffany Mixed Coal Sample at 130 °F

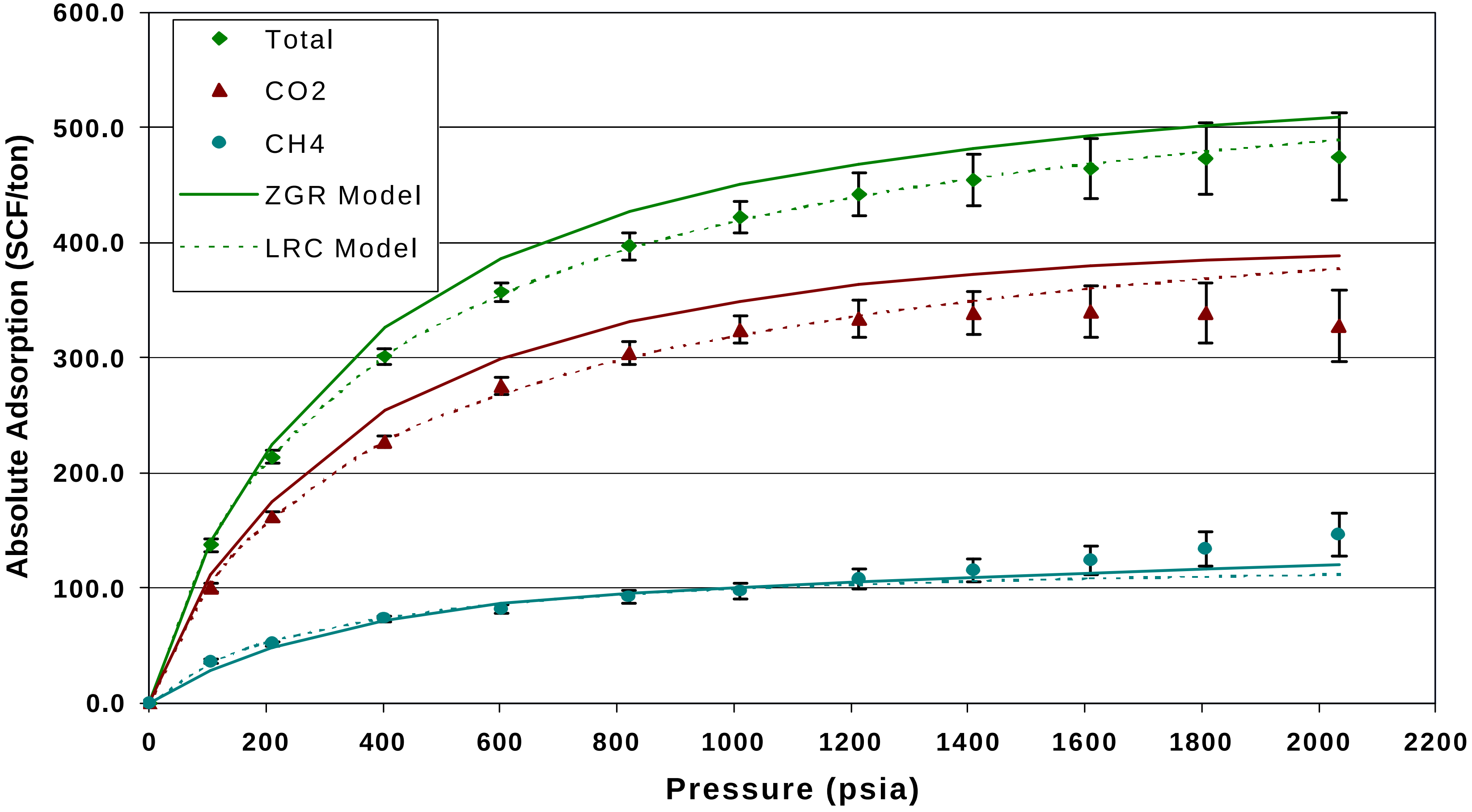


Figure 15. Gibbs Adsorption of a 20/80 Mole % Nitrogen/CO_2 Feed Mixture on a Wet Tiffany Mixed Coal Sample at 130 °F

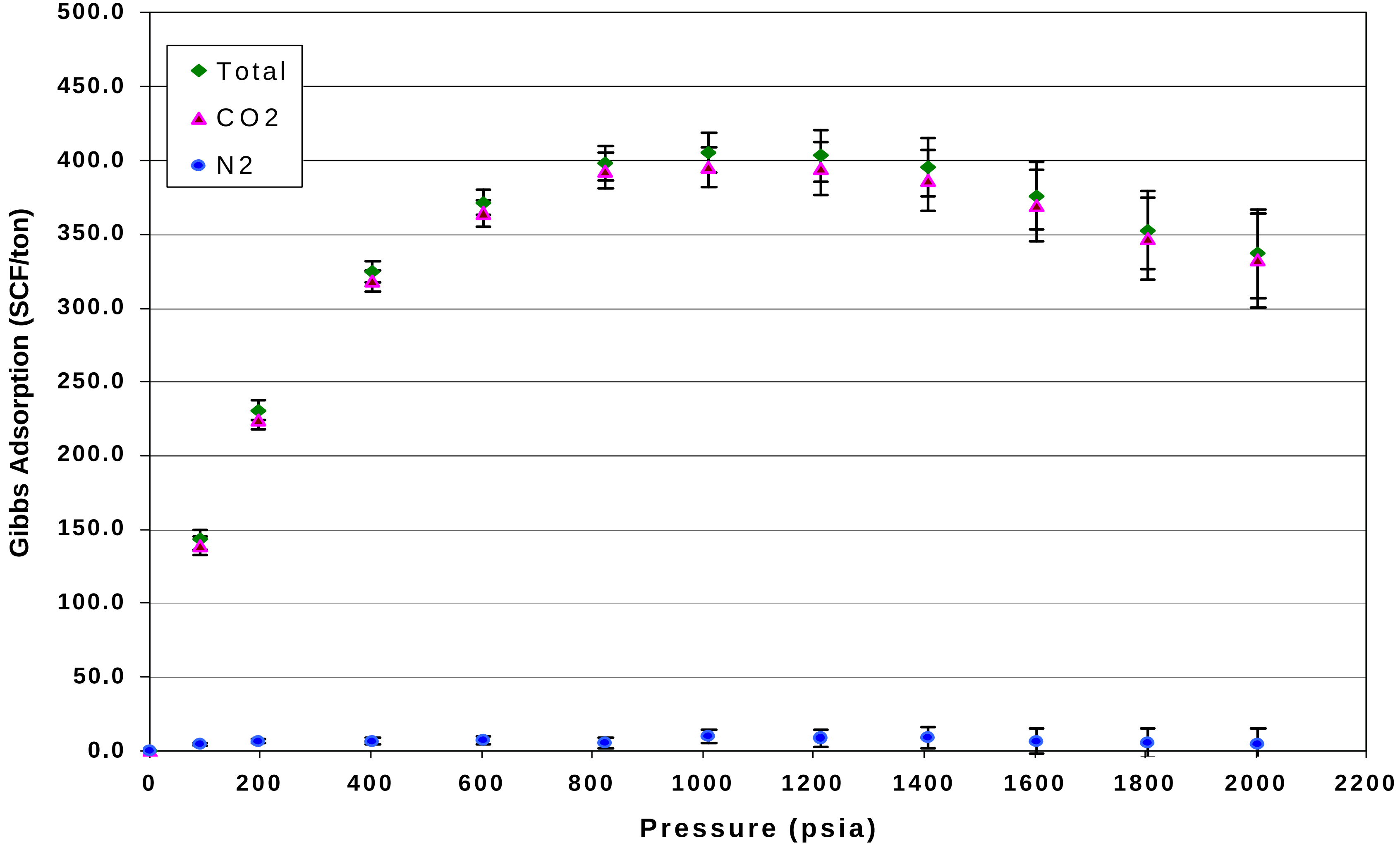


Figure 16. Absolute Adsorption for 20/80 Mole % Nitrogen/CO_2 Feed Mixture on a Wet Tiffany Mixed Coal Sample at 130 °F

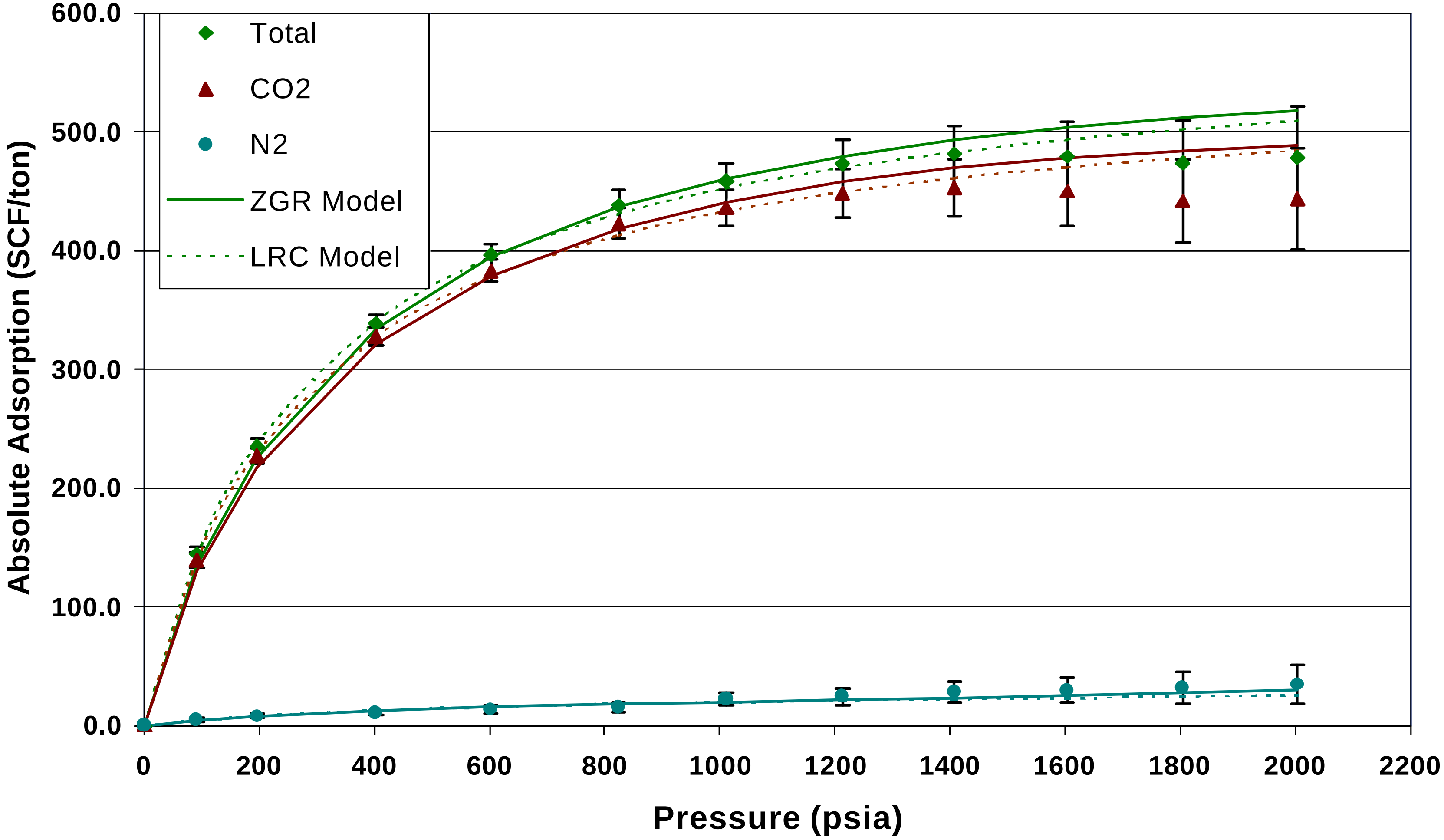


Figure 17. Gibbs Adsorption of a 10/40/50 Mole % Methane/Nitrogen/CO_2 Feed Mixture on a Wet Tiffany Mixed Coal Sample at 130 °F

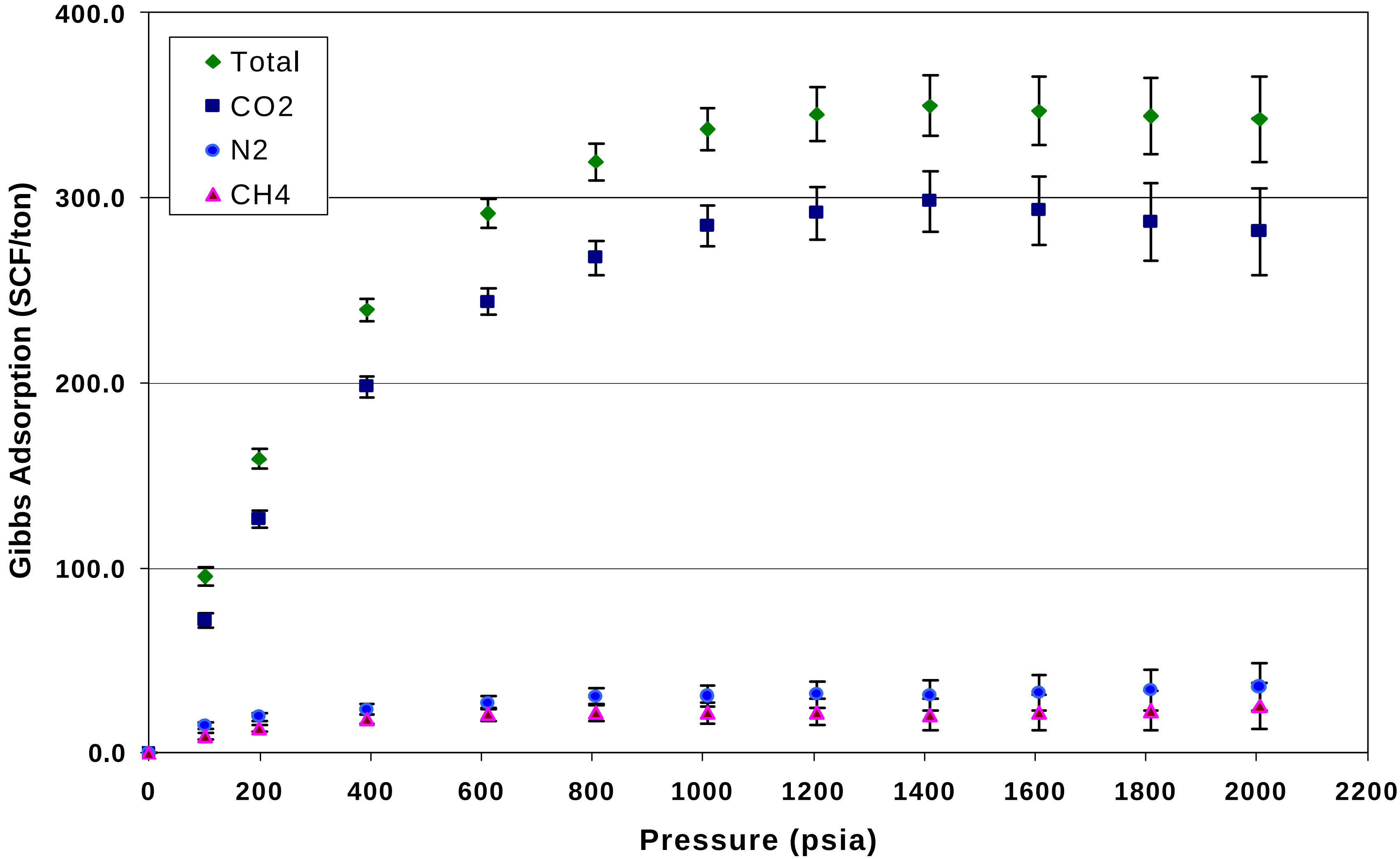


Figure 18. Absolute Adsorption for 10/40/50 Mole % Methane/Nitrogen/CO_2 Feed on Wet Tiffany Mixed Coal Sample at 130 °F

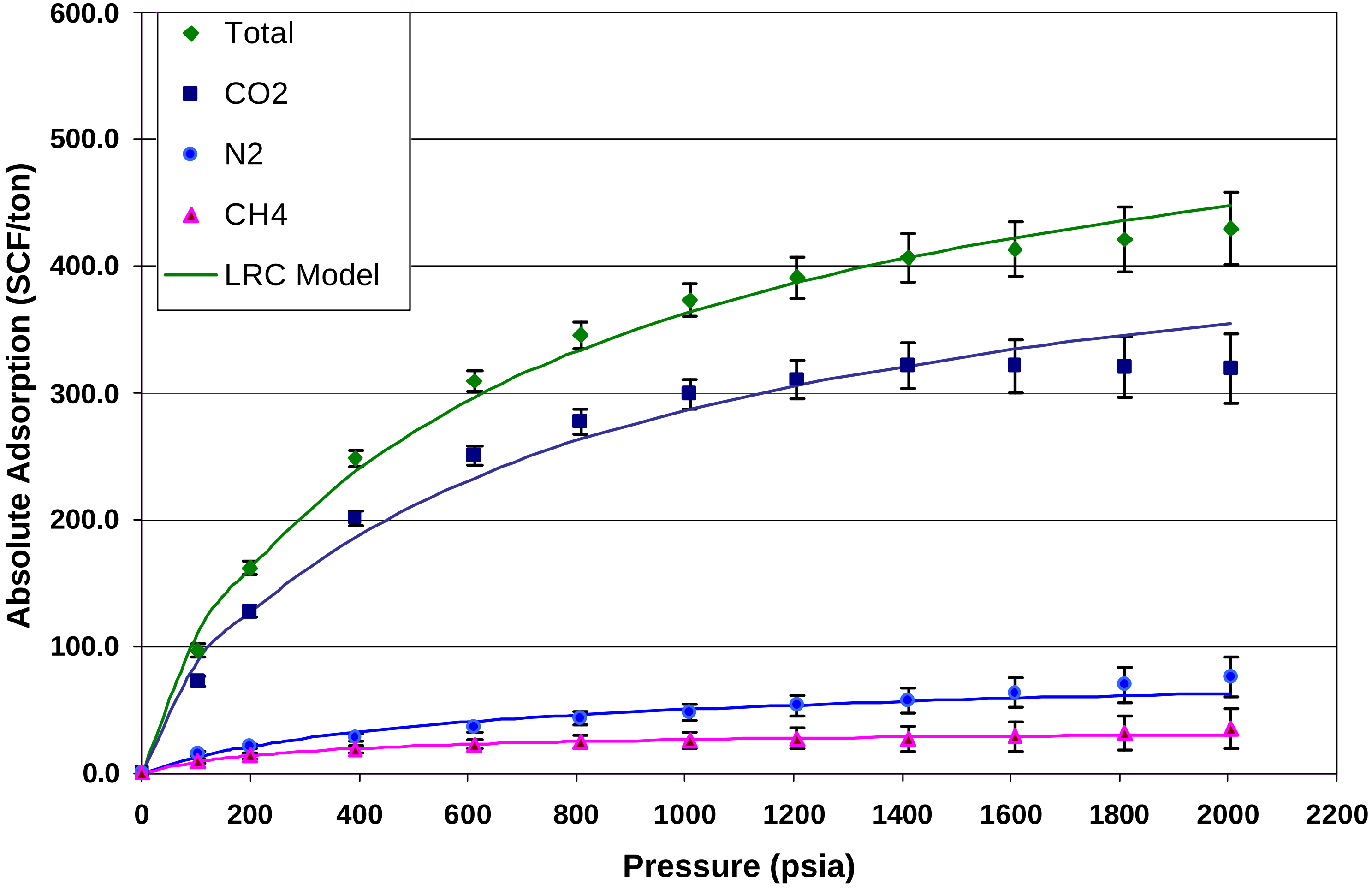


Figure 19. Fractional Uptake of Methane Desorption on Tiffany Well #1 Coal at 130 ^{o}F

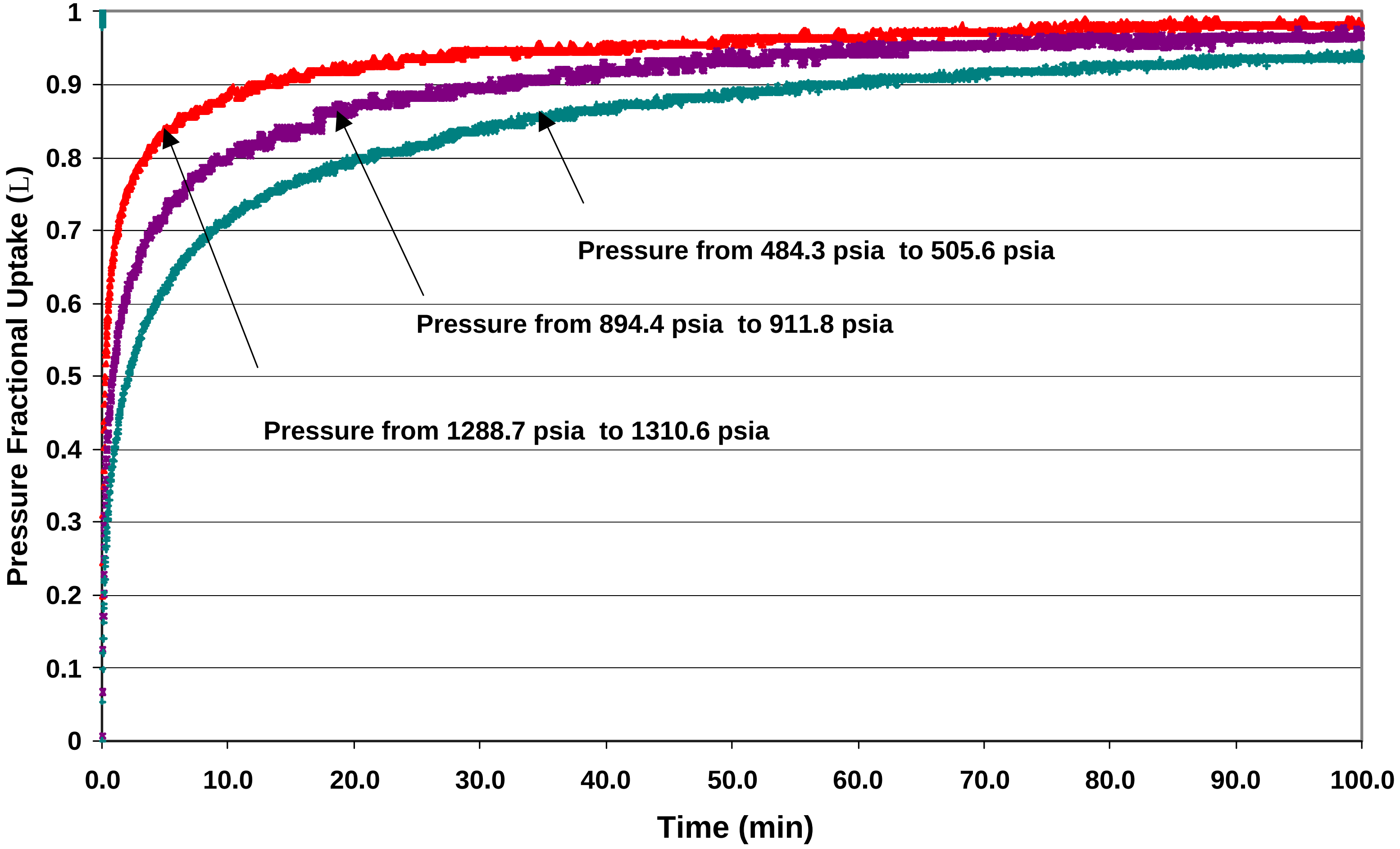


Figure 20. Fractional Uptake of Methane Desorption on Tiffany Well #10 Coal at 130 °F

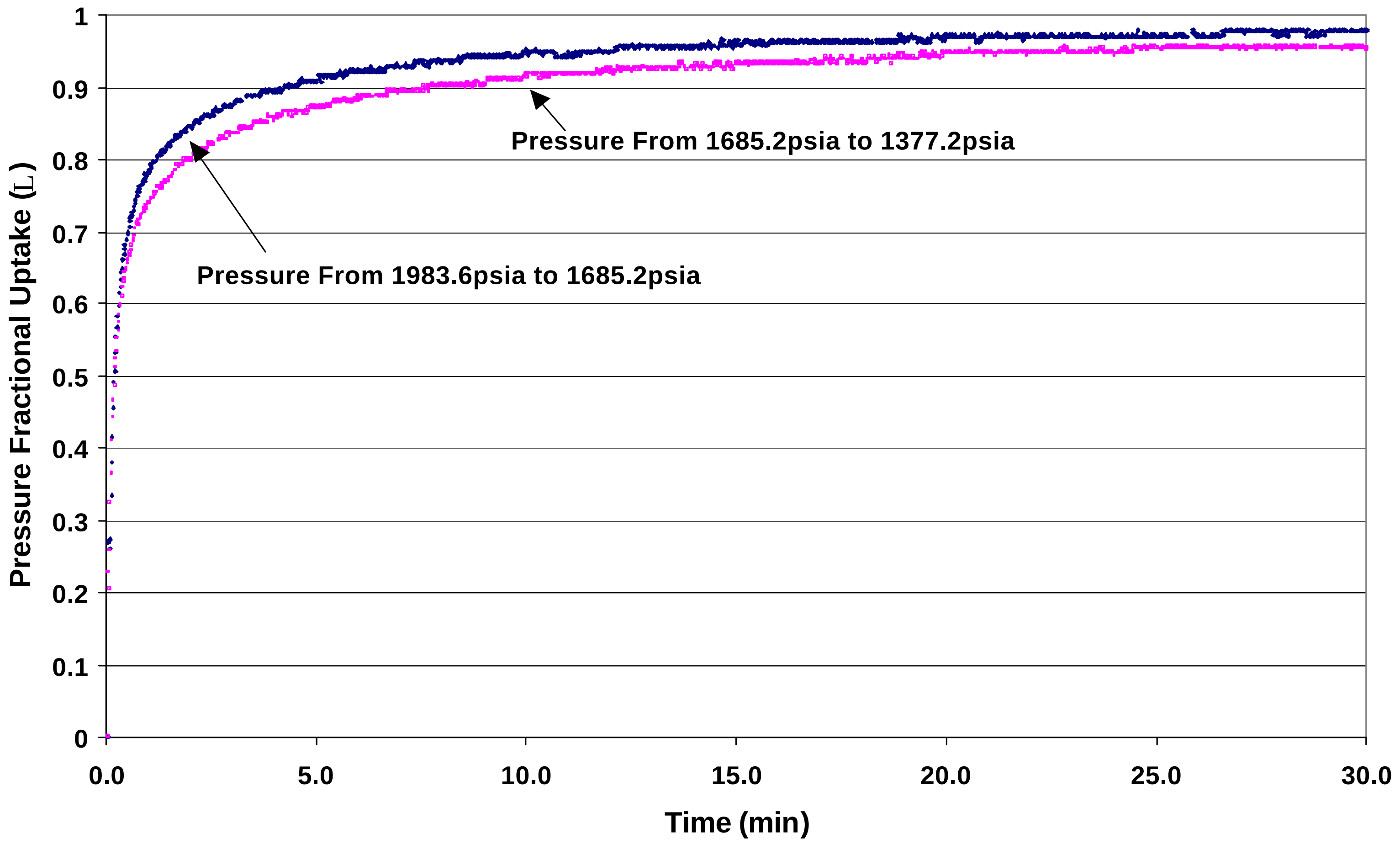


Figure 21. Fractional Uptake of Nitrogen on Tiffany Mixed Coal at 130 °F

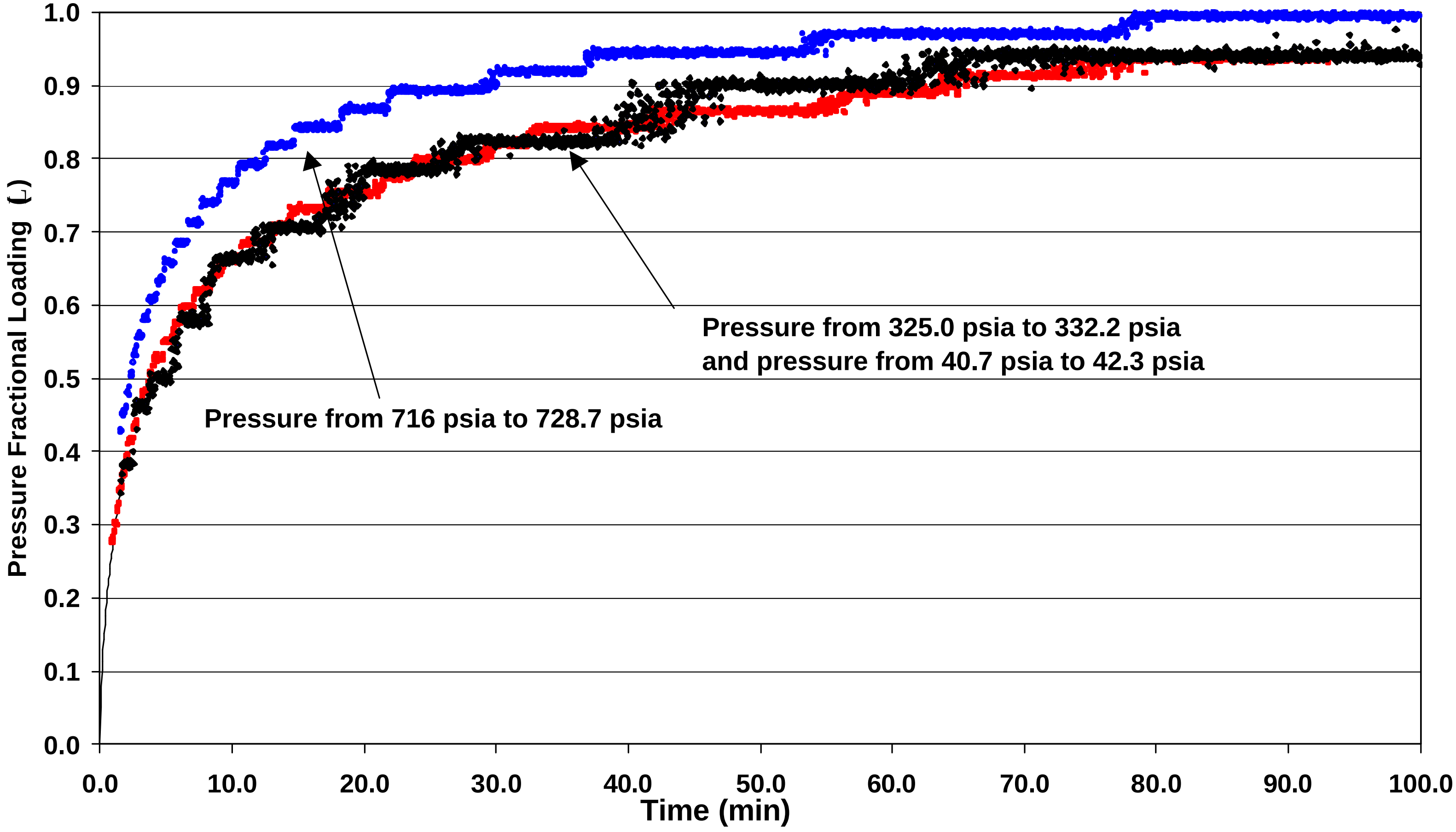


Figure 22. Fractional Uptake of CO_2 Adsorption on Tiffany Mixed Coal at 130°F

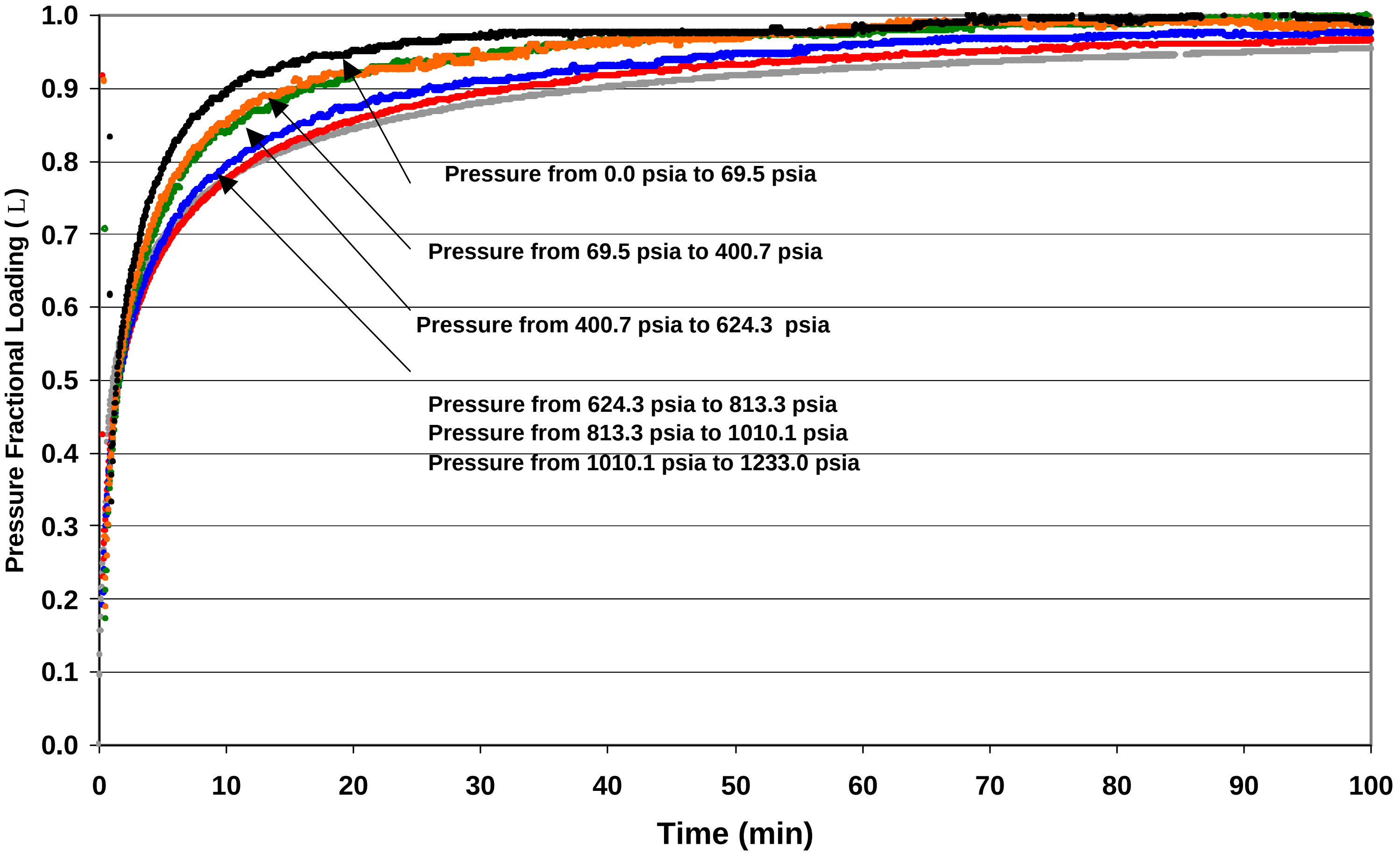


Figure 23. Model Predictions of Absolute Adsorption for 50/50 Mole % Methane/Nitrogen Feed Mixture on a Wet Tiffany Mixed Coal Sample at 130 °F

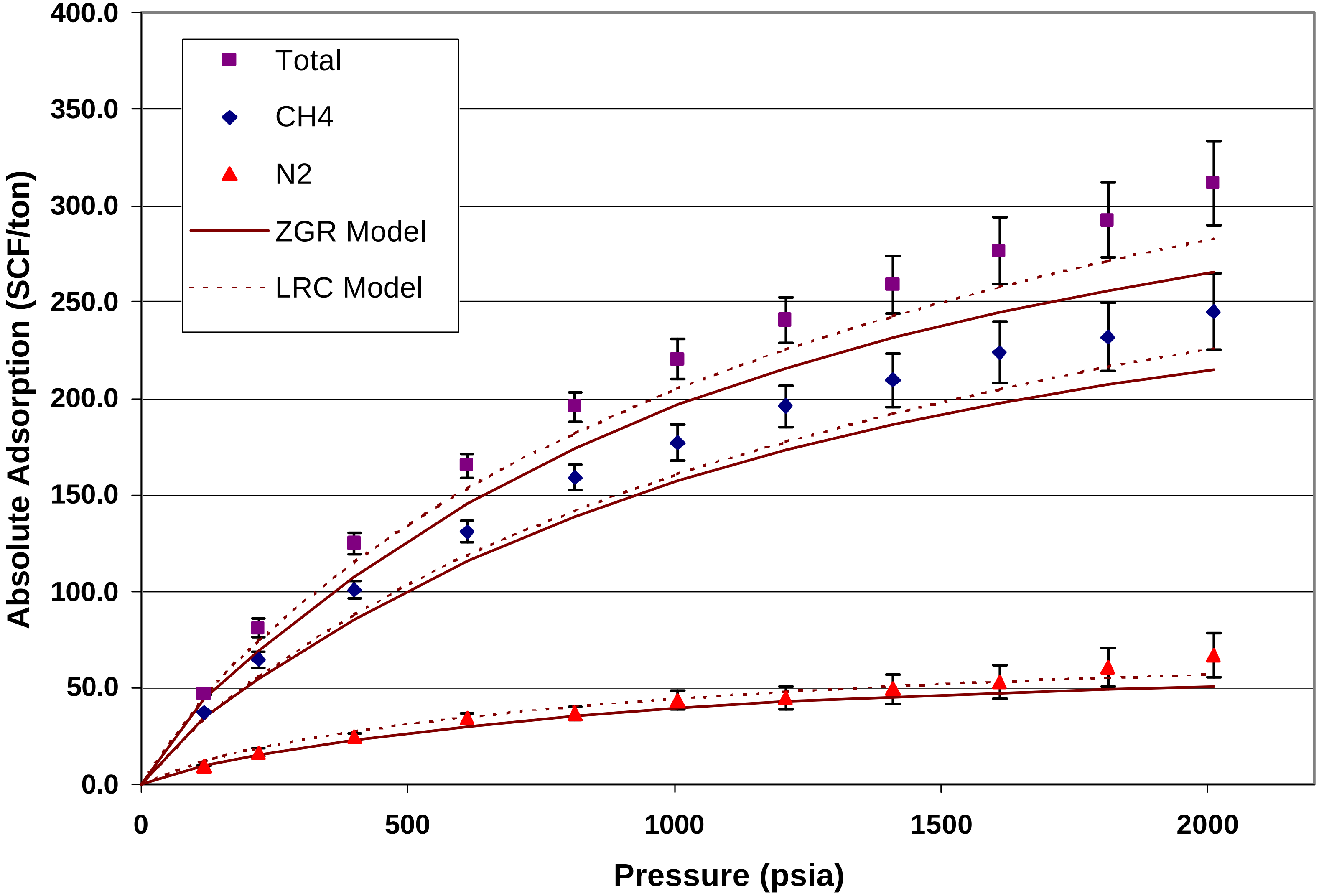


Figure 24. Model Predictions of Absolute Adsorption for 40/60 Mole % Methane/CO_2 Feed Mixture on a Wet Tiffany Mixed Coal Sample at 130 °F

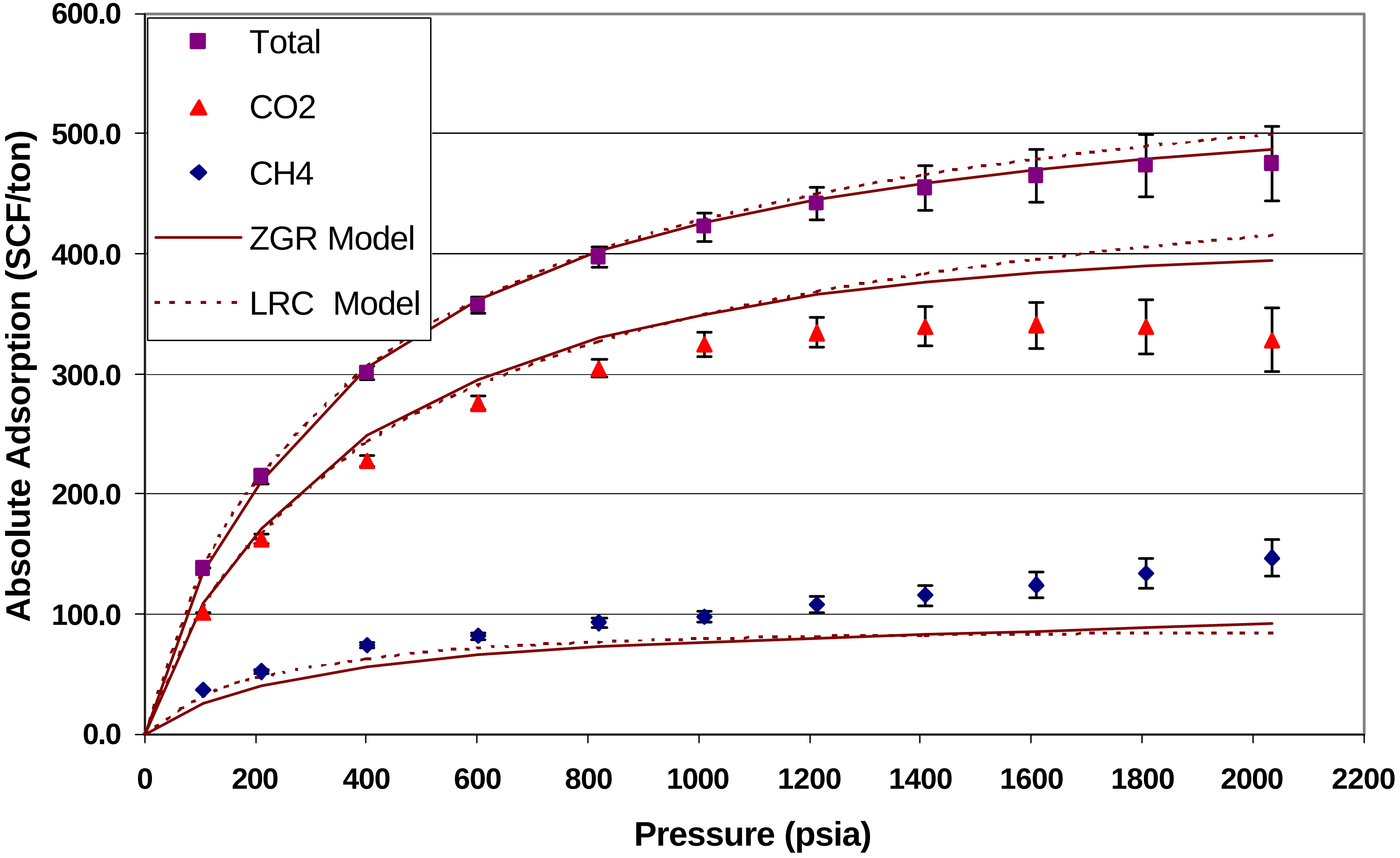


Figure 25. Model Predictions of Absolute Adsorption for 20/80 Mole % Nitrogen/CO_2 Feed Mixture on a Wet Tiffany Mixed Coal Sample at 130 ^oF

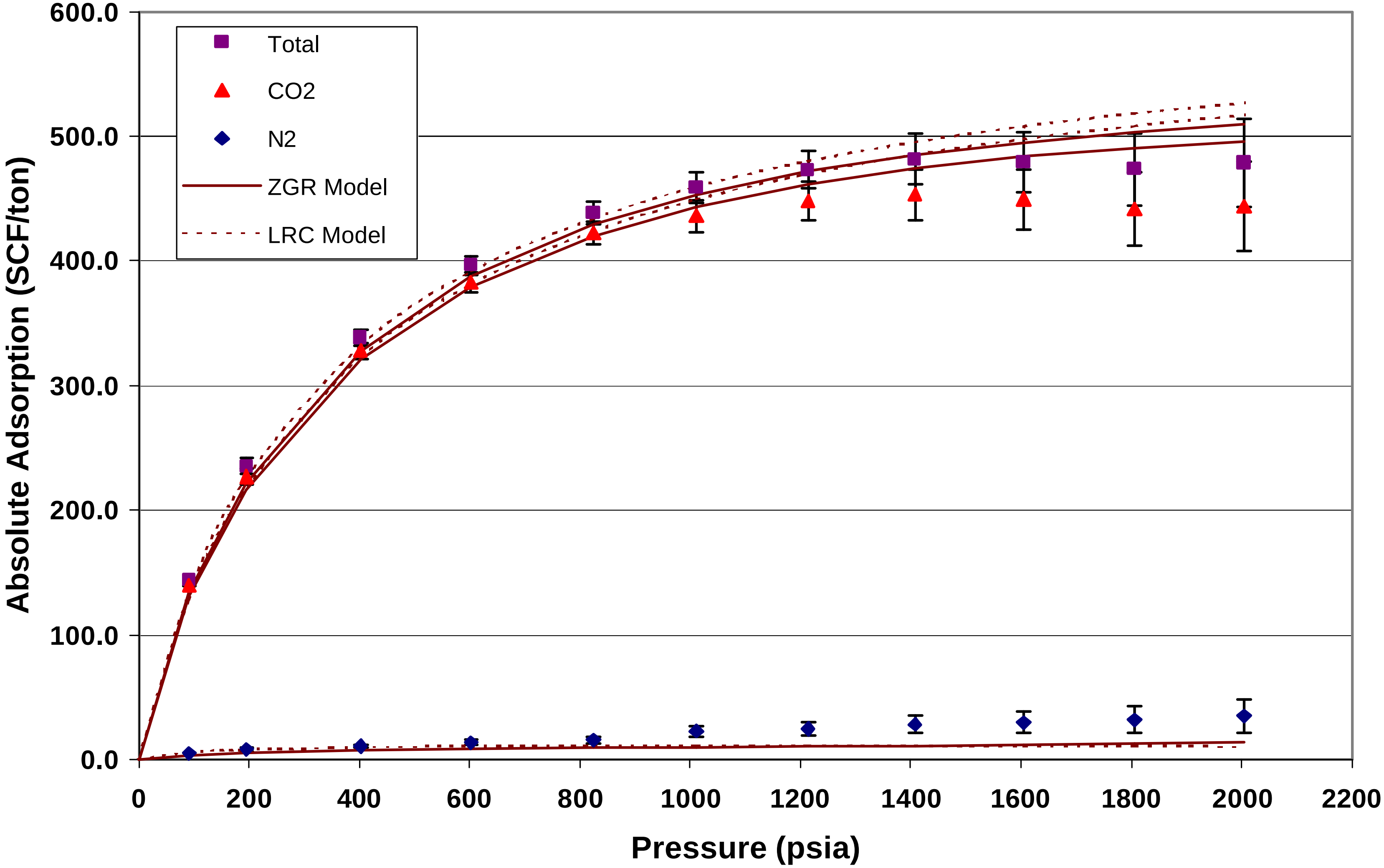
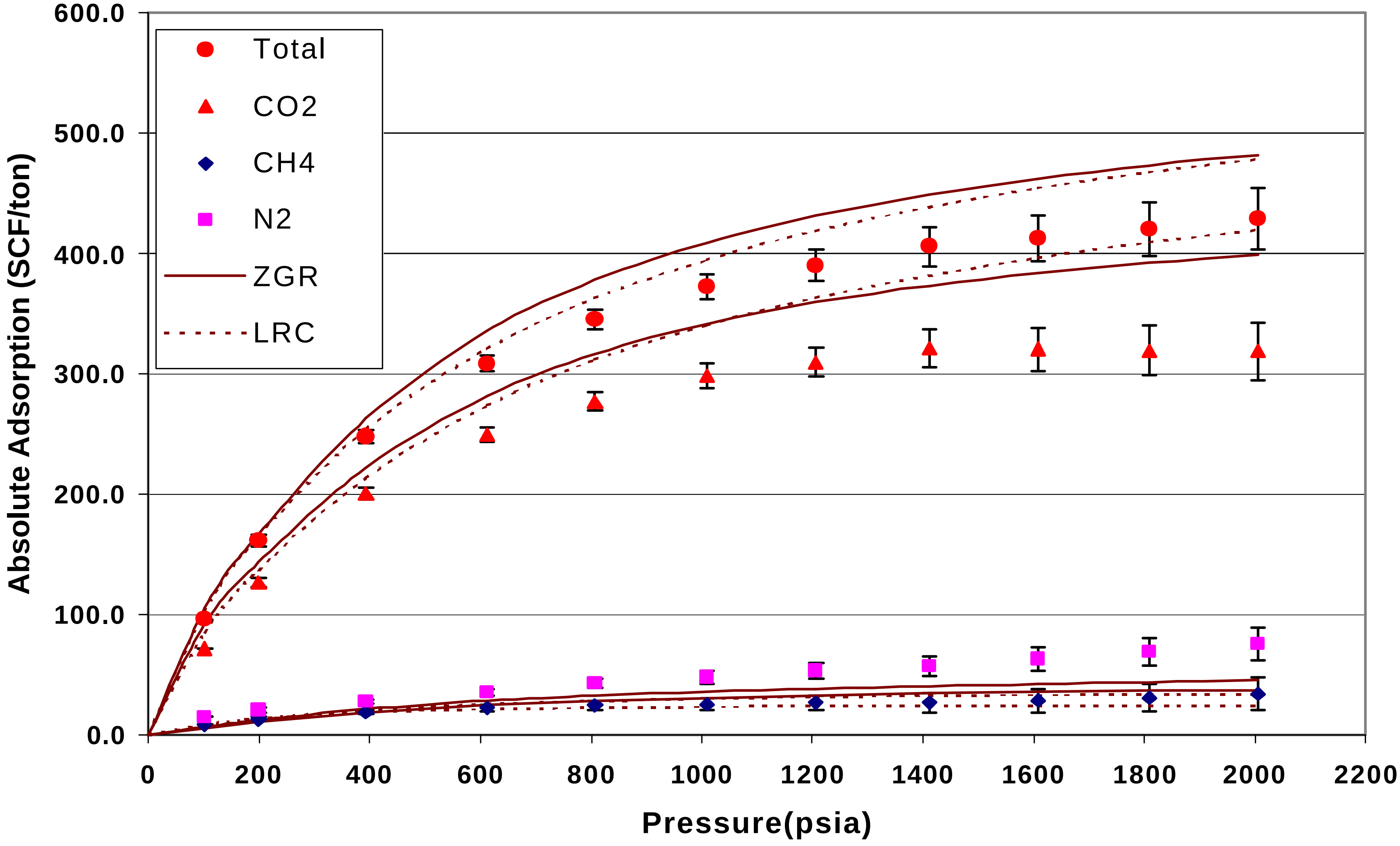


Figure 26 Model Predictions of Absolute Adsorption for 10/40/50 Mole % Methane/Nitrogen/CO_2 Feed on a Wet Tiffany Mixed Coal Sample at 130 °F



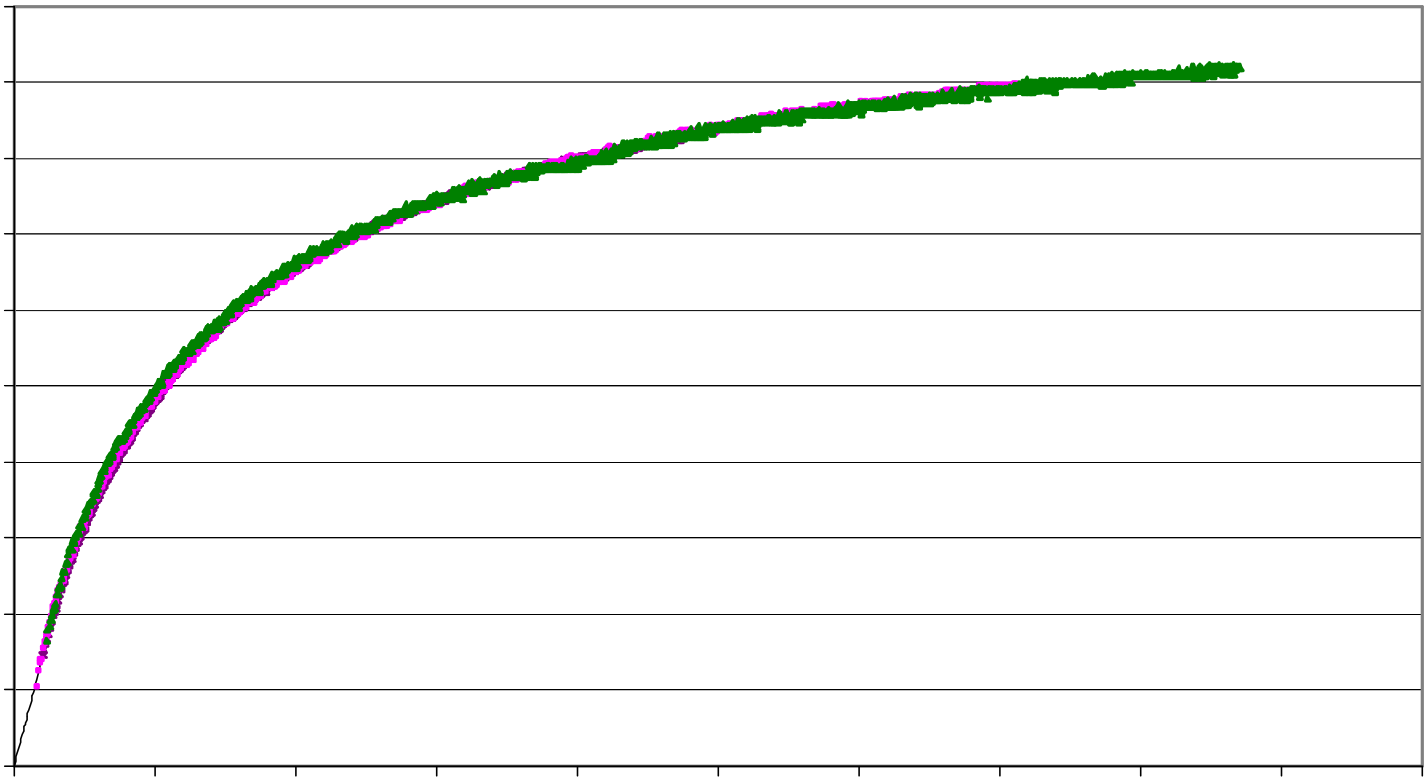


Figure 28. Desorption Curve for Methane on Tiffany Well #10 Coal at 130 °F

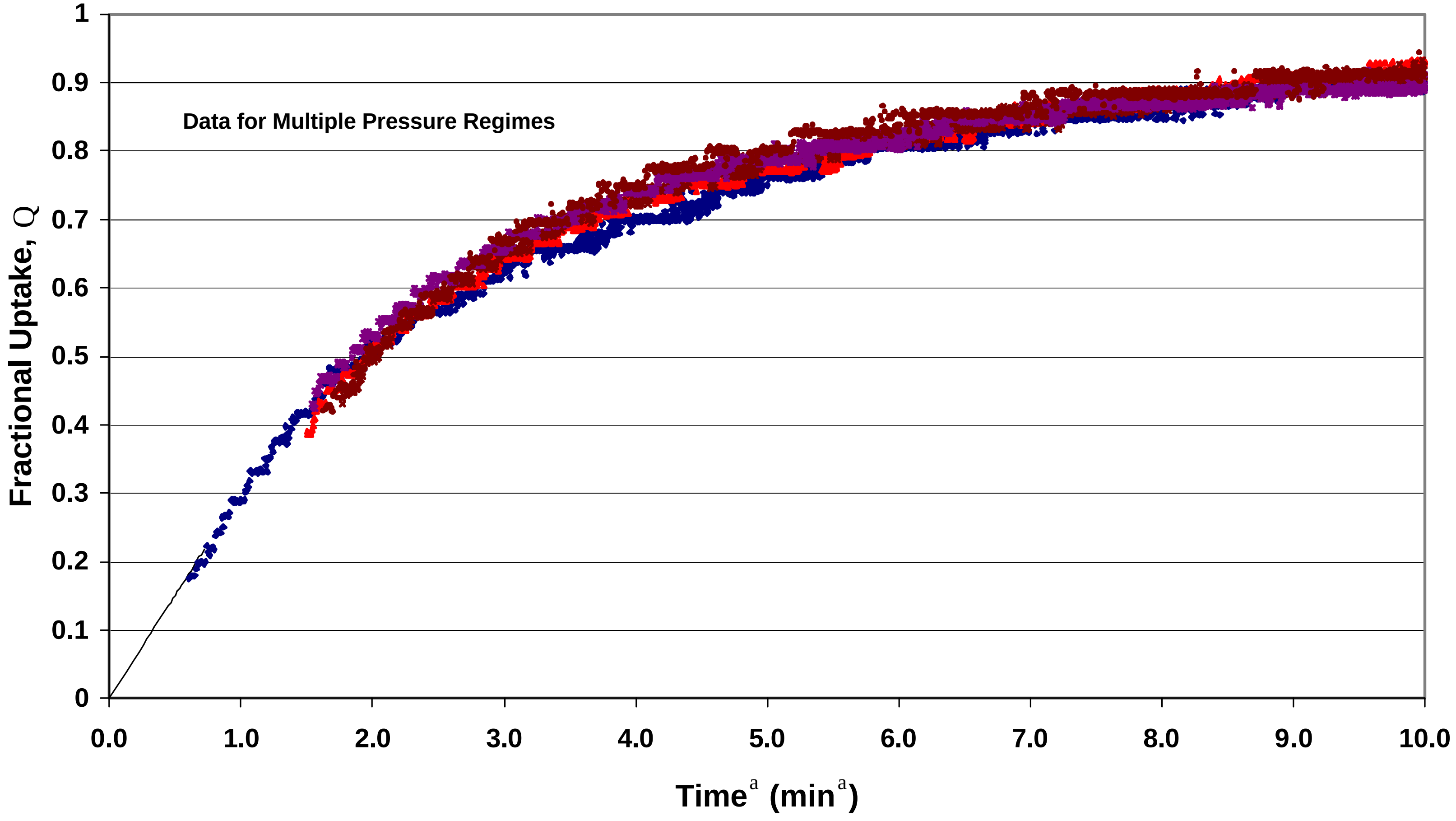


Figure 29. Desorption Curve for Nitrogen on Tiffany Mixed Coal at 130 °F

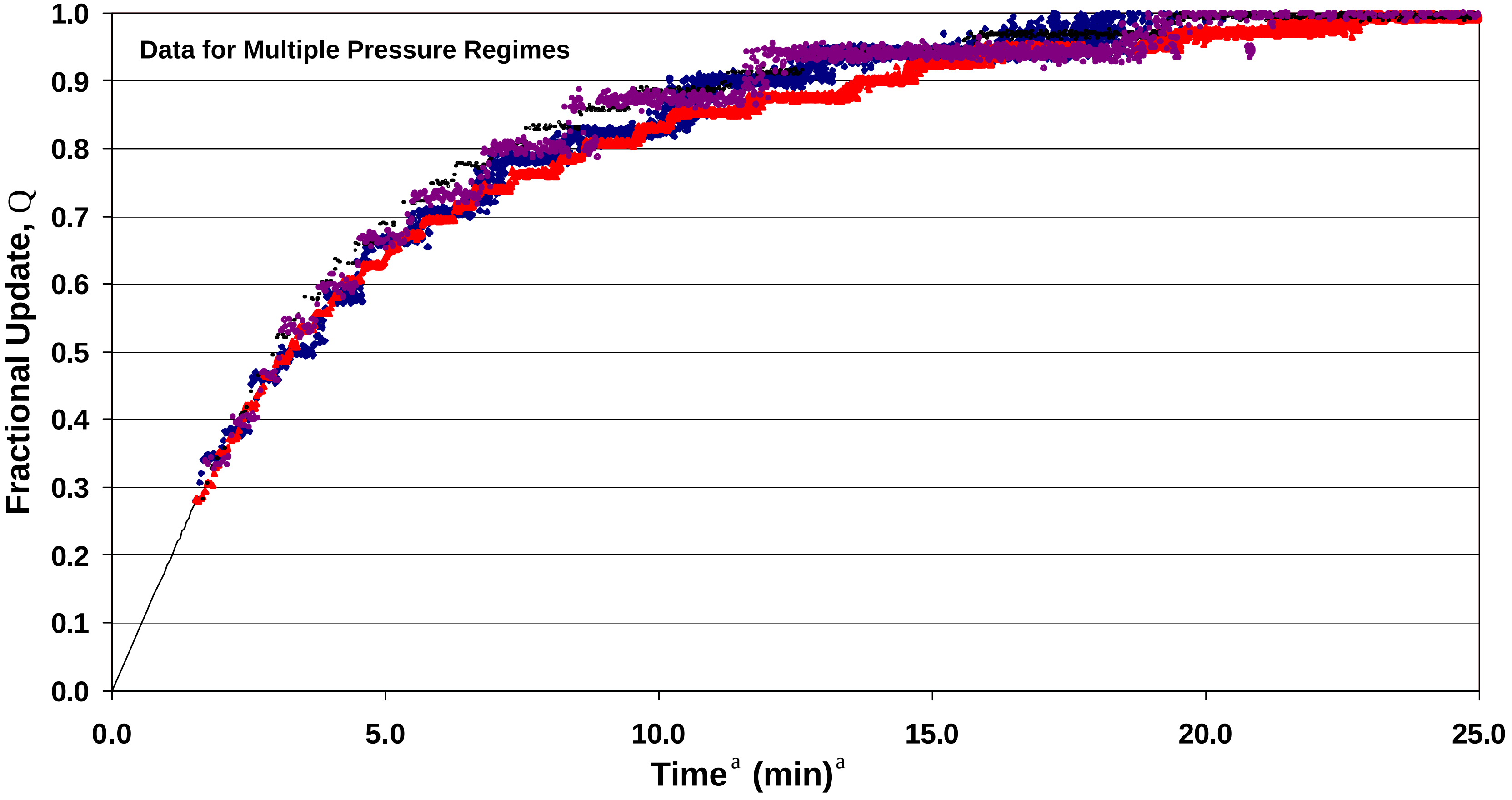


Figure 30. Adsorption Curve for CO_2 on Tiffany Mixed Coal at 130 °F

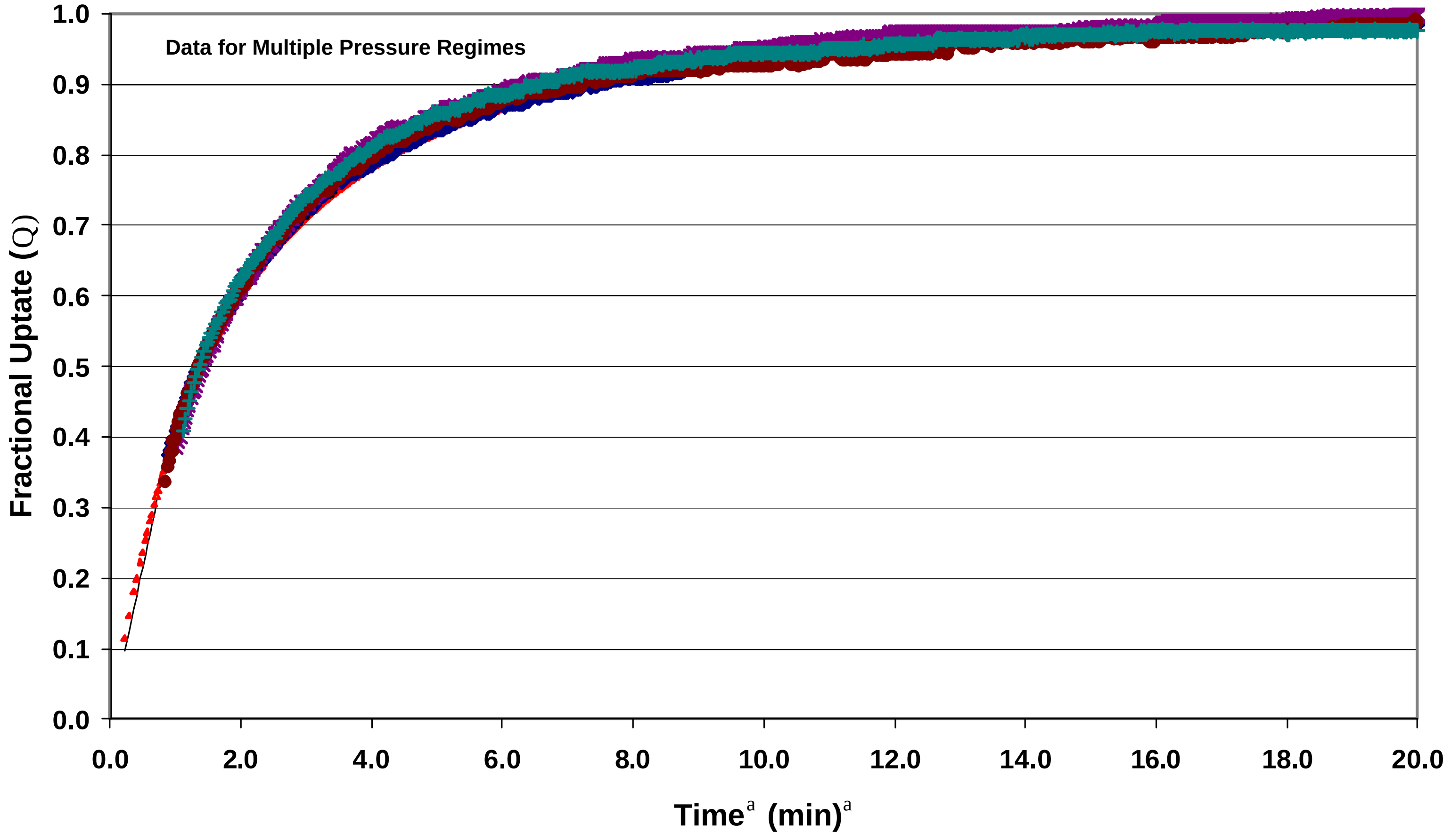


Figure 31. Liberated Gas from Tiffany Coal Samples: 2000 to 14.7 psia