Adsorption Modeling Update

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Sponsored by the
U.S. Department of Energy

Theory / Practice

Theory	Improve our understanding of high-pressure adsorption equilibria through rigorous methodologies.
Practice	Provide reliable models for optimum production of coalbed methane and CO_2 sequestration.
Goal	Develop reliable coal-structure-based generalized equilibrium models using simple, accessible characterizations.
Strategy	Use rigorous methodologies rooted in fundamentals to develop reliable methods of high industrial utility.

Equilibrium Adsorption Modeling

- We seek simple, reliable adsorption equilibrium models that are suitable for generalized predictions and reservoir simulations.

- Such models should:
  - Precisely represent pure and mixture isotherms
  - Facilitate accurate *a priori* predictions

Current Issues in Equilibrium CBM Adsorption Modeling

Fundamental Theory - OSU

▪ Improved mixture modeling	2002
▪ Computational algorithms	2002
▪ Effect of moisture on adsorption behavior	2003
▪ Model parameter generalizations	2003

Matrix Characterization - PSU

▪ Coal characterization	2003/4
▪ Coal-structure-based generalizations	2003/4

Current Issues in Equilibrium CBM Adsorption Modeling - 2

Experimental Work

- Effect of moisture on modeling behavior 2003
- Estimates for adsorbed-phase density
- Matrix swelling
- Near-critical behavior

Reservoir Simulations

- Balancing computational efficiency and reliability
- Reservoir model calibrations

Improved Mixture Adsorption Modeling

Equilibrium Modeling: Four Methods

1. Enhanced forms of Langmuir isotherms

   -- provide simple data correlation

2. Two-dimensional equations of state (2-D EOS)

   -- facilitate generalized simulations

3. Simplified-Local-Density (SLD-EOS) models

   -- account for surface structure and near-critical behavior

4. The Ono-Kondo (OK) lattice model

   -- provides a layering analogue for adsorption

Objectives

The equilibrium models considered have been successful in modeling pure adsorption isotherms. Our objectives are to:

- Amend the one-fluid mixing rules and develop alternative mixing rules to improve **2-D EOS** mixture predictions.
- Extend the **SLD-EOS** and **OK** lattice models to high-pressure mixture adsorption modeling.

Improved 2-D EOS Mixture Modeling

Hypotheses for Improved Mixing

We have investigated two new approaches for improving the 2-D EOS mixing rules, and consequently, the 2-D EOS mixture predictions.

- First, we hypothesized that different molecules have different accessible adsorption surface areas.
- Second, we incorporated excess Gibbs free energy mixing rules in the 2-D EOS.

Accessible Surface Area

- 2-D EOS (OSU, 1992):

$$\left[\pi + \frac{a\sigma^2}{1 + Ub\sigma + W(b\sigma)^2}\right]\left[1 - (b\sigma)^m\right] = \sigma RT$$

- Original mixing and combination rules:

$$a = \sum_i \sum_j x_i x_j a_{ij} \qquad b = \sum_i \sum_j x_i x_j b_{ij}$$

$$a_{ij} = (a_i + a_j)(1 - C_{ij})/2 \qquad b_{ij} = (b_i + b_j)(1 + D_{ij})/2$$

- Relations between the parameters:

$$\alpha = a/A \qquad \beta = b/A$$

Accessible Surface Area Effect

Different adsorbates may have different accessible surface area on the same adsorbent surface.

$$A\alpha = \sum_i \sum_j x_i x_j a_{ij} = x_1^2 A_1 \alpha_1 + x_1 x_2 \left(\alpha_1 A_1 + \alpha_2 A_2\right)\left(1 - C_{ij}\right) + x_2^2 A_2 \alpha_2$$

Where:

$$A = \sum_i \sum_j x_i x_j A_{ij} = x_1^2 A_1 + x_1 x_2 (A_1 + A_2)(1 - L_{ij}) + x_2^2 A_2$$

$$E_{21} = A_2 / A_1 \qquad \tilde{A} = A / A_1$$

$$\alpha = \left(x_1^2 \alpha_1 + x_1 x_2 \left(\alpha_1 + \alpha_2 E_{21}\right)\left(1 - C_{ij}\right) + x_2^2 \alpha_2 E_{21}\right) \Big/ \tilde{A}$$

$$\beta = \left(x_1^2 \beta_1 + x_1 x_2 \left(\beta_1 + \beta_2 E_{21}\right)\left(1 + D_{ij}\right) + x_2^2 \beta_2 E_{21}\right) \Big/ \tilde{A}$$

Wong-Sandler Mixing Rules for 3-D Cubic Equation of State (Sandler, 1992)

$$b-\frac{a}{RT}=\sum_i\sum_j x_i x_j\left(b-\frac{a}{RT}\right)_{ij}$$

$$\frac{A_\gamma^{ex}}{CRT}=-\frac{a}{bRT}+\sum_i x_i\frac{a_i}{b_iRT}$$

where C is a constant and the cross term is:

$$\left(b-\frac{a}{RT}\right)_{ij}=\frac{1}{2}\left[\left(b_i-\frac{a_i}{RT}\right)+\left(b_j-\frac{a_j}{RT}\right)\right]\left(1-K_{ij}\right)$$

Wong-Sandler Mixing Rules for 2-D EOS

The Wong-Sandler mixing rules are extended to 2-D EOS:

$$b = \beta A \qquad a = \alpha A$$

$$\beta - \frac{\alpha}{RT} = \left(\sum_i \sum_j x_i x_j \left(\beta - \frac{\alpha}{RT} \right)_{ij} \right) \Big/ \tilde{A}$$

$$\left(\beta - \frac{\alpha}{RT} \right)_{ij} = \frac{1}{2} \left[\left(\beta_i - \frac{\alpha_i}{RT} \right) E_i + \left(\beta_j - \frac{\alpha_j}{RT} \right) E_j \right] \left(1 - C_{ij} \right)$$

Experimental Data

- In the evaluations presented here, we used our gas adsorption measurements on dry activated carbon, specifically:
  - ➢ Adsorption isotherms for pure methane, nitrogen, CO_2 and their binary mixtures at 318.2 K (113 °F) and pressures to 12.4 MPa (1800 psia)
  - ➢ Nominal gas feed compositions of 20, 40, 60, and 80%

Case Studies

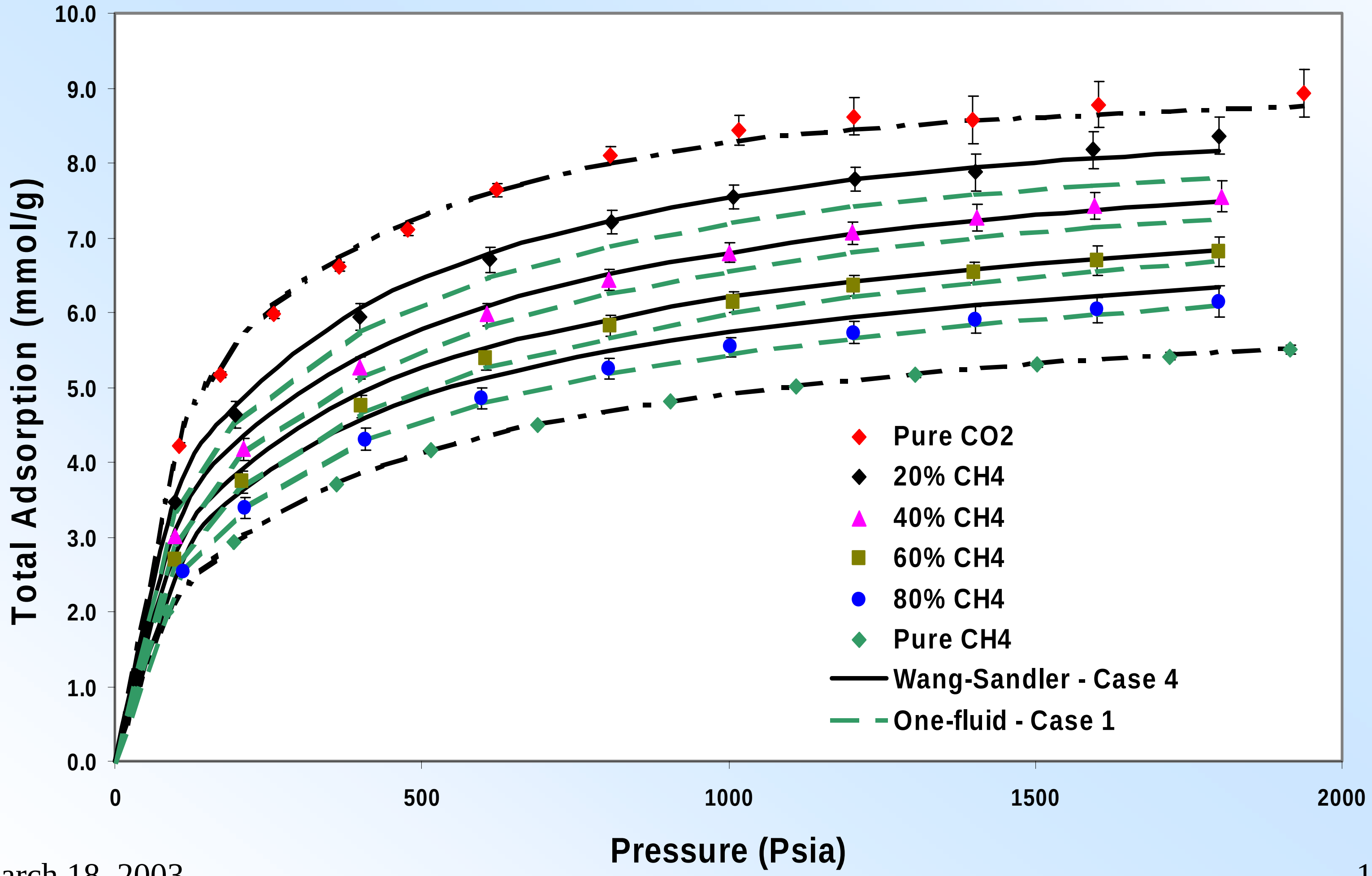
Case 1: One-fluid mixing rules - C_{12} and D_{12} are regressed

Case 2: Accessible area, one-fluid mixing rules - only surface area ratio, E_{21}, is regressed

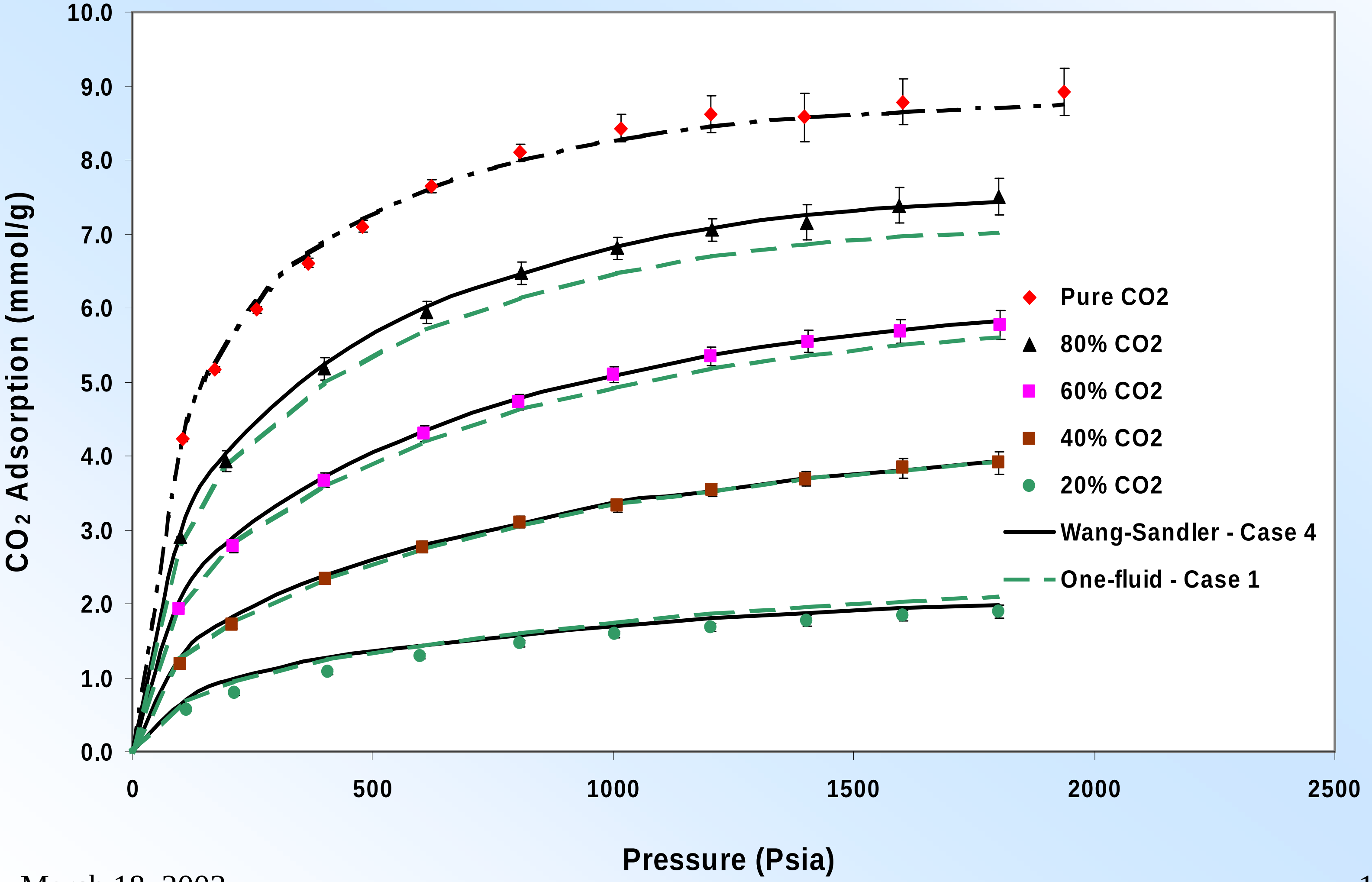
Case 3: Accessible area, one-fluid mixing rules - C_{12}, D_{12}, E_{21}, and surface interaction parameter, L_{12}, are regressed

Case 4: Wong-Sandler mixing rules with NRTL model - C_{ij}, and NTRL parameters, τ_{12}, τ_{21} and α_{12}, are regressed

Total Absolute Adsorption for CH_4 / CO_2 System



CO_2 Absolute Adsorption for CH_4 / CO_2 System



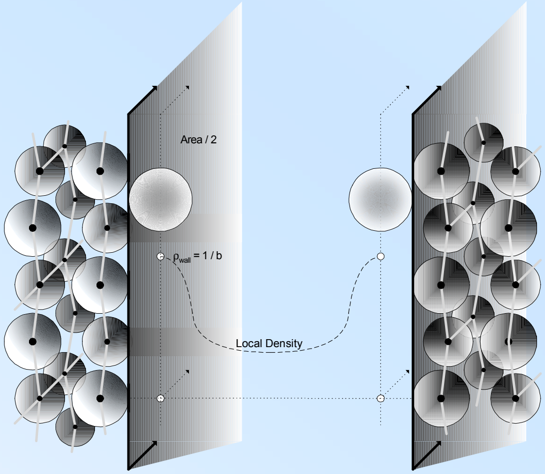
Conclusions: 2-D EOS

- Mixing rules based on accessible-surface and on excess Gibbs free energy are effective in representing the binary mixture data within experimental uncertainties.

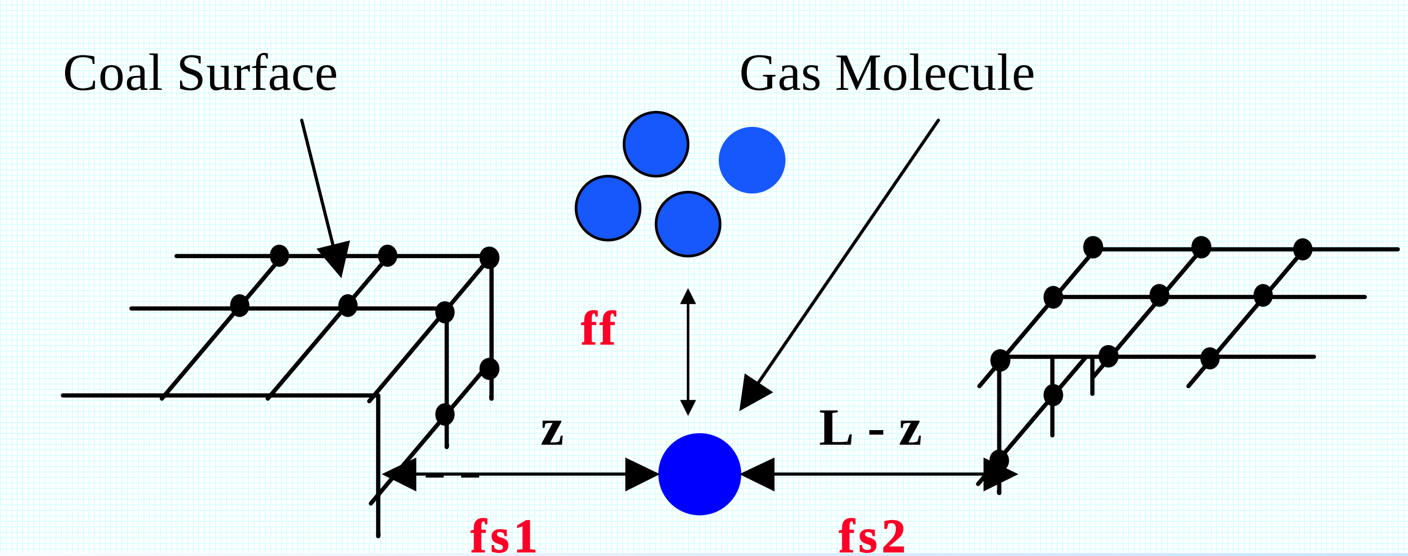
- These results suggest that:
  - Different adsorbates access different surface area on the same adsorbent
  - Mixture adsorption on the surface leads to non-random mixing

SLD-EOS Adsorption Mixture Modeling

The SLD-EOS Model



$$\mu_{fs}(z) = \mu_{fs1}(z) + \mu_{fs2}(L - z)$$



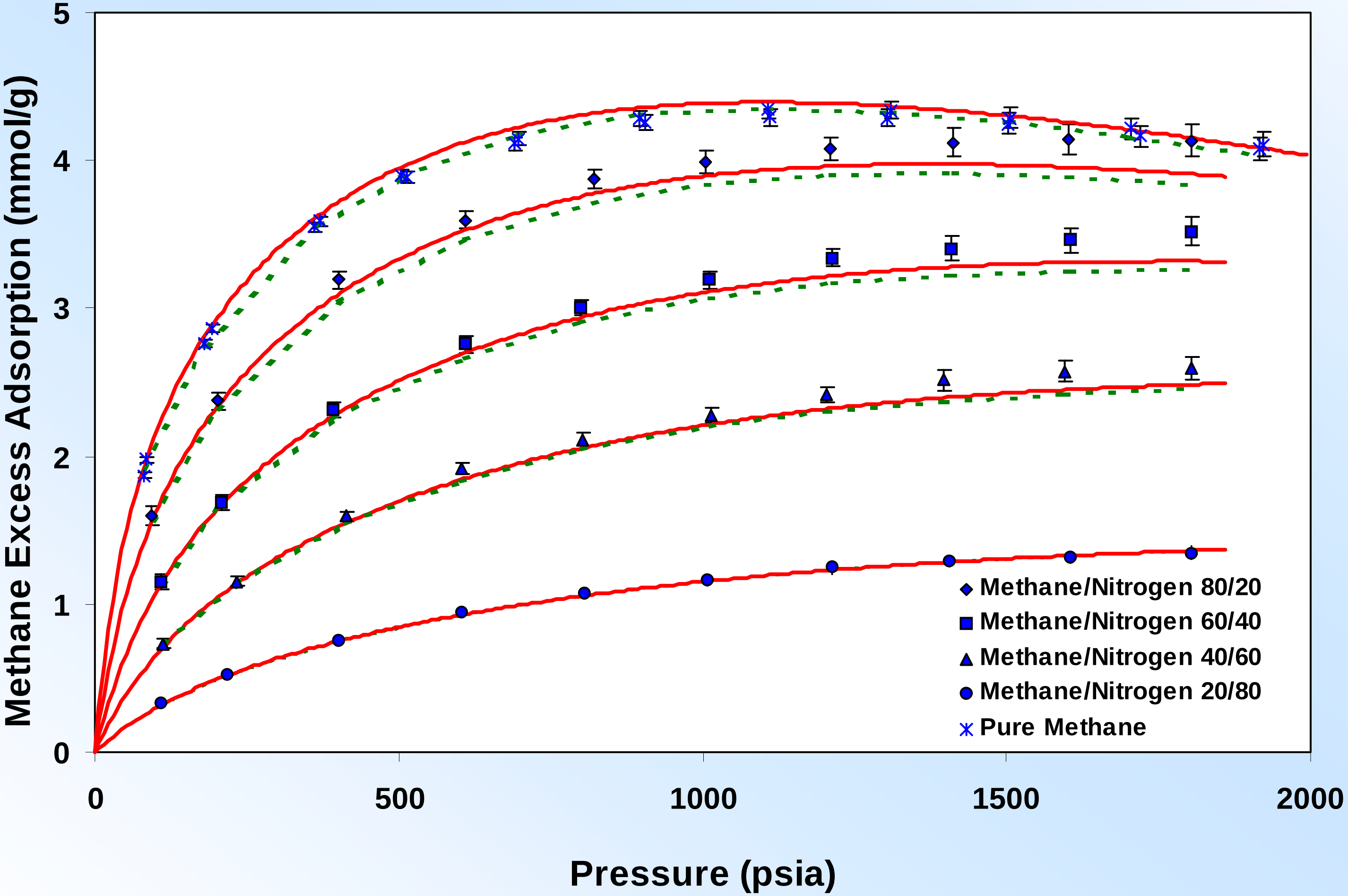
Extending SLD to Mixtures

$$a = \sum_i \sum_j x_i x_j a_{ij} \qquad b = \sum_i \sum_j x_i x_j b_{ij}$$

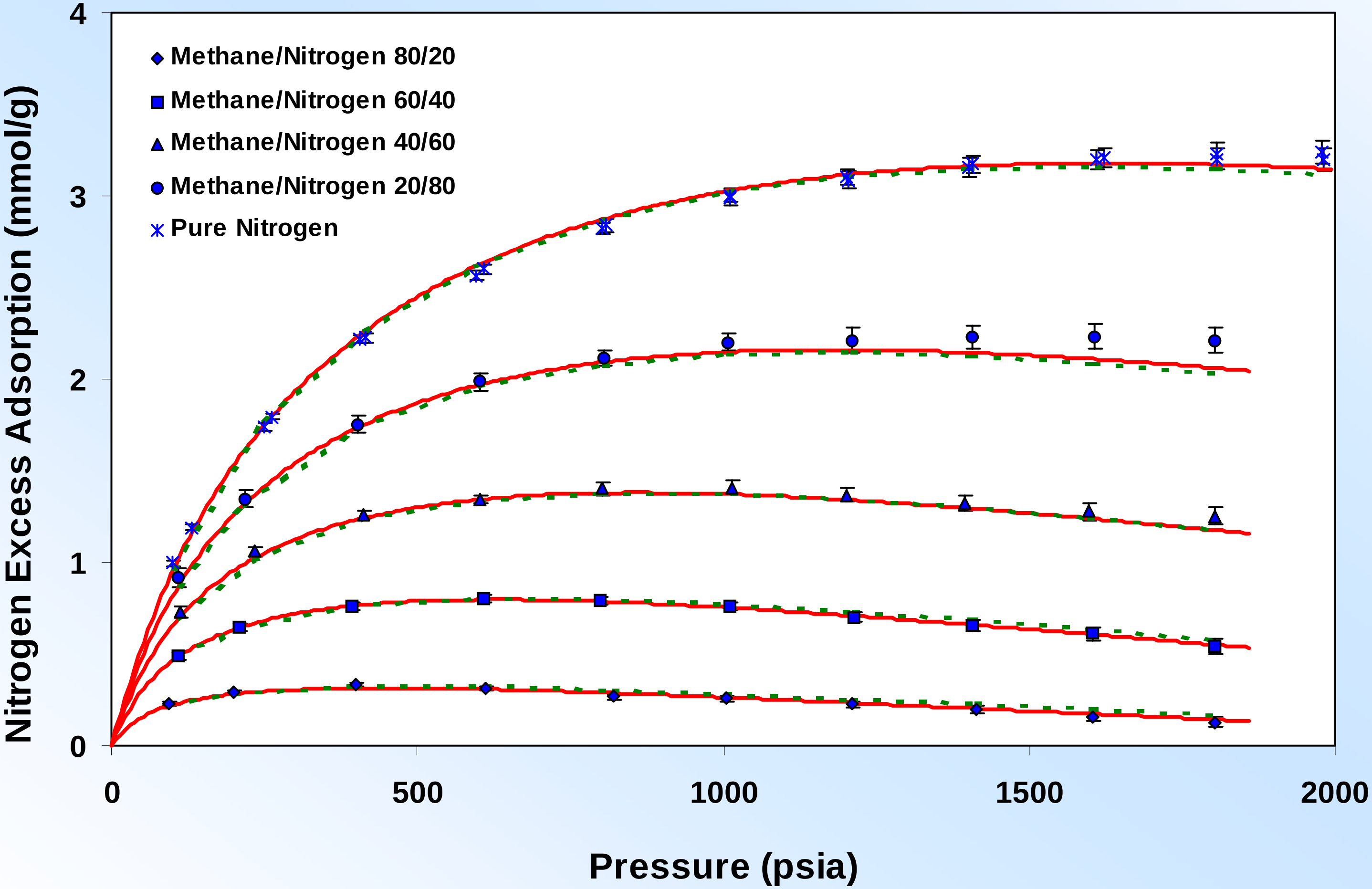
$$a_{ij} = (a_i + a_j)(1 - C_{ij})/2 \qquad b_{ij} = (b_i + b_j)(1 + D_{ij})/2$$

- We set C_{ij} and D_{ij} to zero for all component interactions in the gas phase
- We regress C_{ij} (D_{ij}=0) in the adsorbed phase

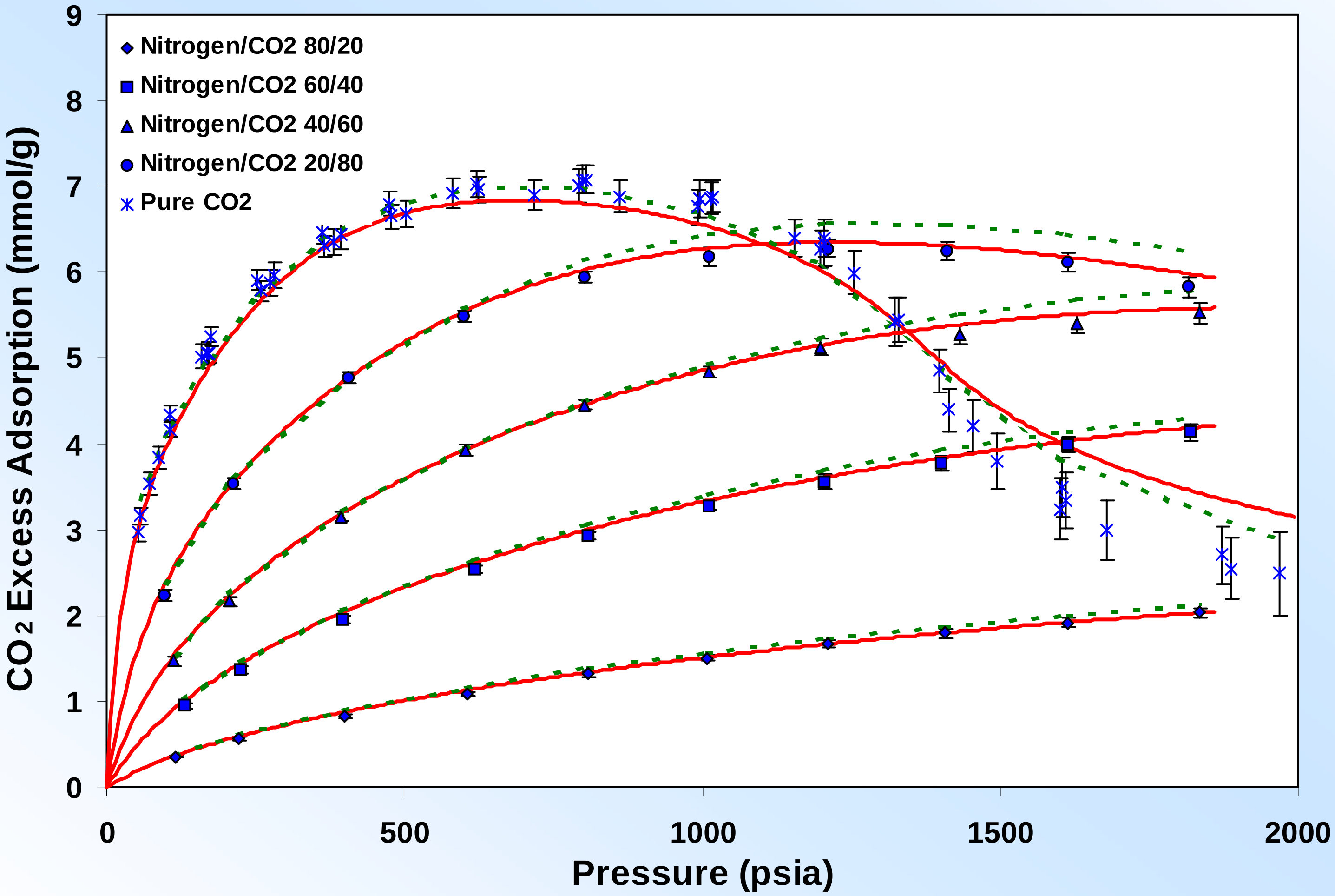
Component Methane Adsorption in Methane/Nitrogen Mixtures



Component Nitrogen Adsorption in Methane/Nitrogen Mixtures



Component CO_2 Adsorption in Nitrogen/CO_2 Mixtures



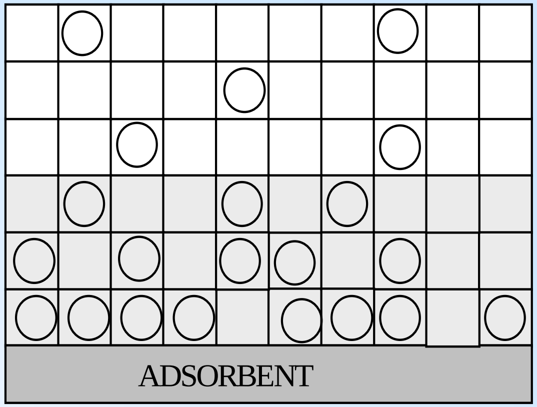
Conclusions: SLD-EOS

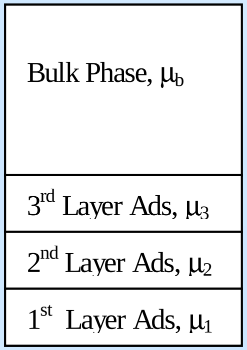
The EOS-SLD models:

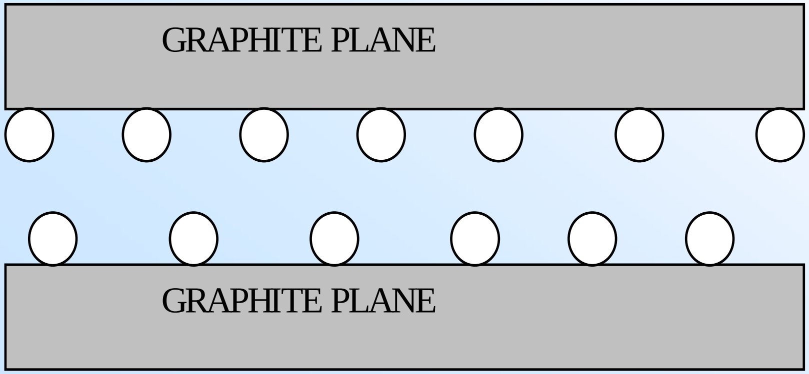
- Correlate binary component adsorption isotherms of methane, nitrogen, and CO_2 mixtures within *expected experimental uncertainties.*
- Predict binary component adsorption isotherms for methane, nitrogen, and CO_2 mixtures, based on pure component isotherms, to within *twice experimental uncertainties on average.*

OK Lattice Adsorption Mixture Modeling

OK Pure-Component Modeling



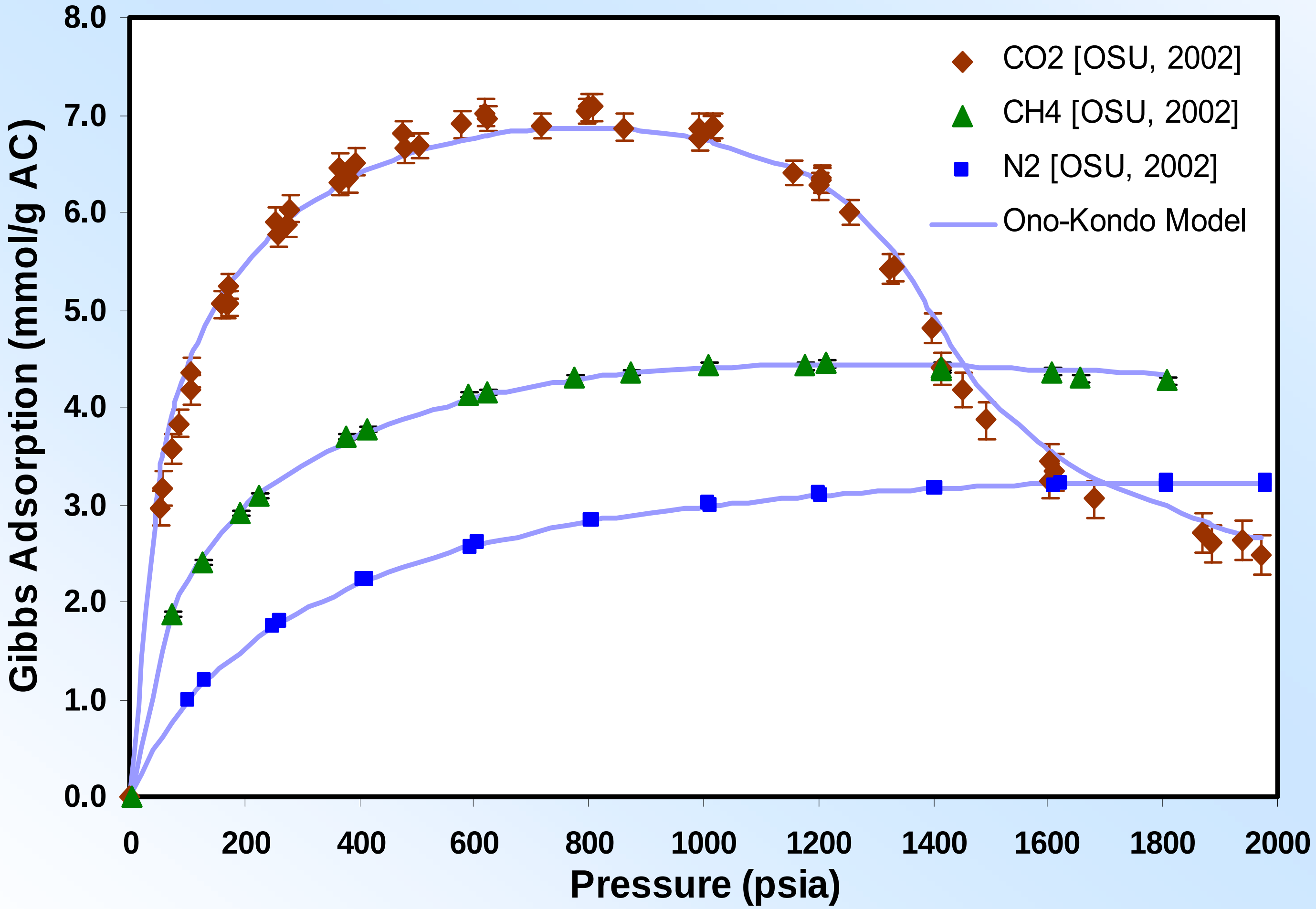




$$\ln\left[x_{ads}(1-x_b)/x_b(1-x_{ads})\right]+(7x_{ads}-8x_b)\varepsilon/kT+\varepsilon_s/kT=0$$

$$\Gamma=2C\,(x_{ads}-x_b)=2C\left(\frac{\rho_{ads}}{\rho_{mc}}-\frac{\rho_b}{\rho_{mc}}\right)$$

OK Regression Results for Pure Gases



OK Lattice Model for Mixtures

Equilibrium Equations:

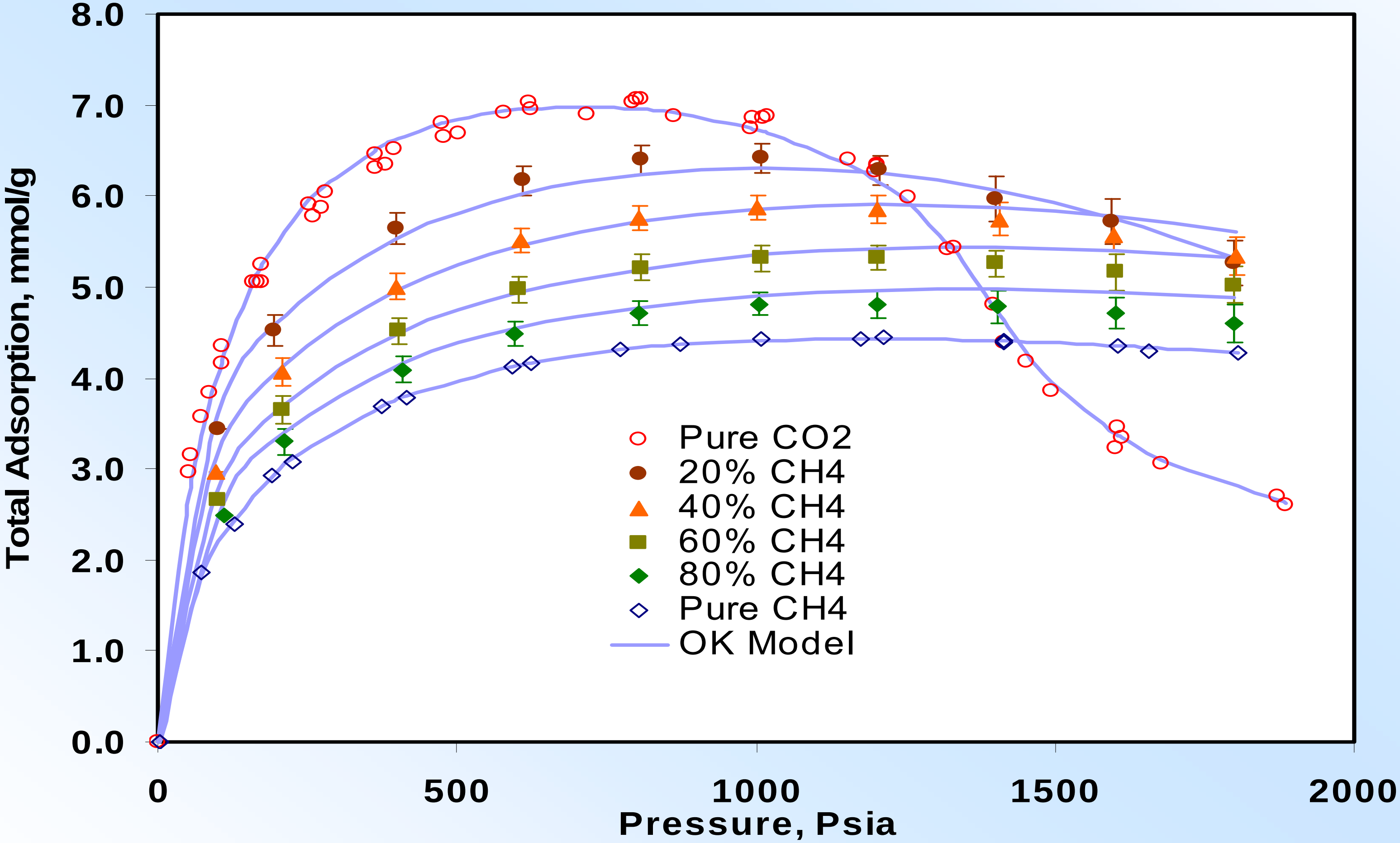
$$\ln\frac{x_A(1-x_{A,b}-x_{B,b})}{x_{A,b}(1-x_A-x_B)}+\frac{\varepsilon_{AA}}{kT}((z_1+1)x_A-z_0x_{A,b})+\frac{\varepsilon_{AB}}{kT}((z_1+1)x_B-z_0x_{B,b})+\frac{\varepsilon_{As}}{kT}=0$$

$$\ln\frac{x_B(1-x_{A,b}-x_{B,b})}{x_{B,b}(1-x_A-x_B)}+\frac{\varepsilon_{BB}}{kT}((z_1+1)x_B-z_0x_{B,b})+\frac{\varepsilon_{AB}}{kT}((z_1+1)x_A-z_0x_{A,b})+\frac{\varepsilon_{Bs}}{kT}=0$$

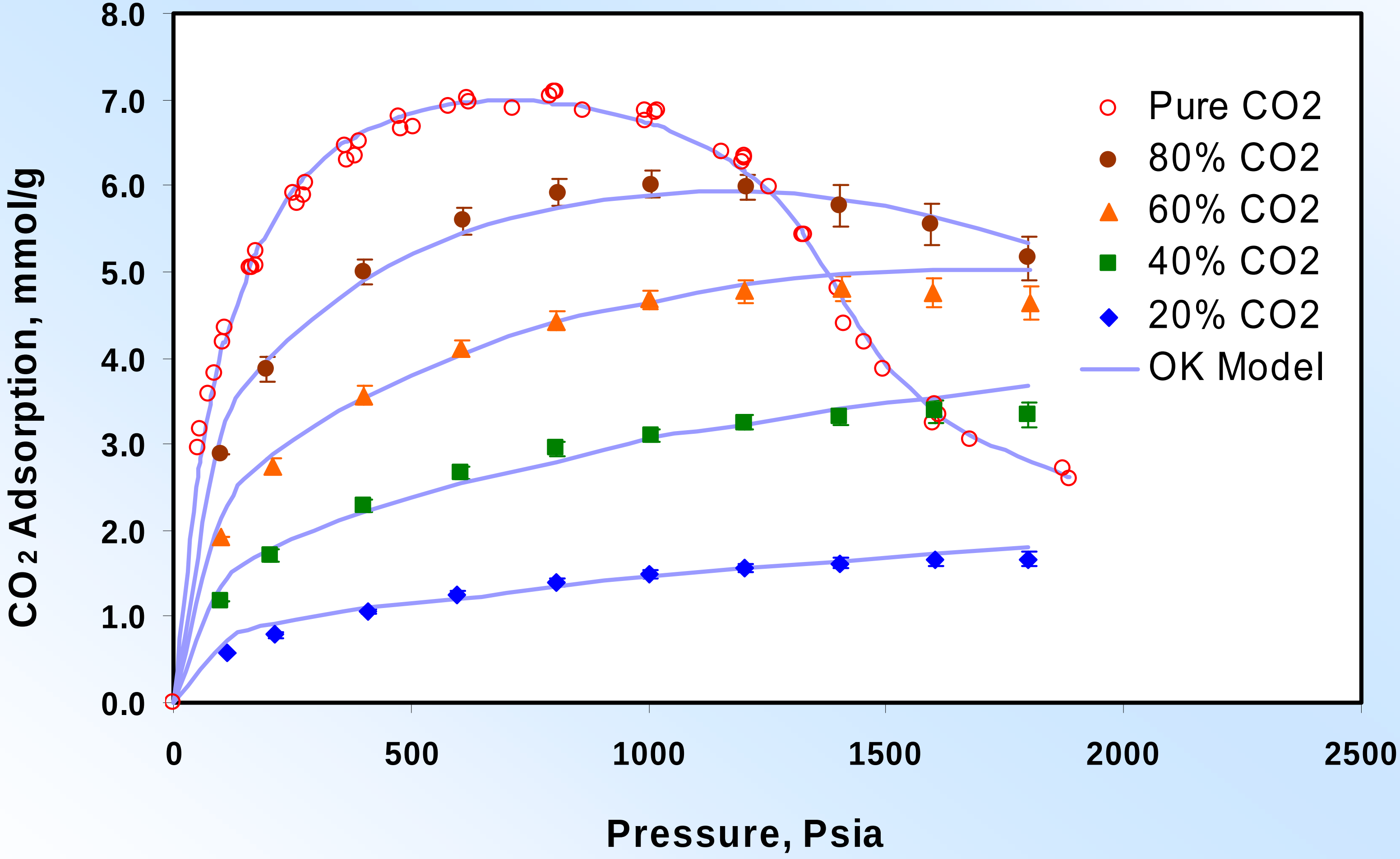
$$\varepsilon_{AB}=(1+C_{ij})(\varepsilon_{AA}+\varepsilon_{BB})/2$$

$$\Gamma_A=2C_A(1+S_{ij})(x_A-x_{A,b}) \quad \text{and} \quad \Gamma_B=2C_B(1-S_{ij})(x_B-x_{B,b})$$

Total Gibbs Adsorption Isotherms



Individual Component Gibbs Adsorption Isotherms



Conclusions: OK Model

The extended OK model:

- Correlates the individual component adsorption in the binary systems within expected experimental uncertainties.

- Predicts total adsorption for the binary systems studied within twice the expected experimental uncertainties.

Current Issues in Equilibrium CBM Adsorption Modeling

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Matrix Characterization - PSU

■ Coal characterization	2003/4
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Computational Algorithms for Equilibrium Adsorption Calculations

Current Method

Solve for ω and x_i by using experimental bulk phase compositions y_i.

At equilibrium, for each component i:

$$Z_a \hat{\phi}_i^a \omega_i = k_i \hat{\phi}_i^g y_i P \;, \quad \sum_i y_i = 1$$

Solve the above equations simultaneously to get ω_i, then:

$$\omega = \sum_i \omega_i \qquad x_i = \frac{\omega_i}{\omega}$$

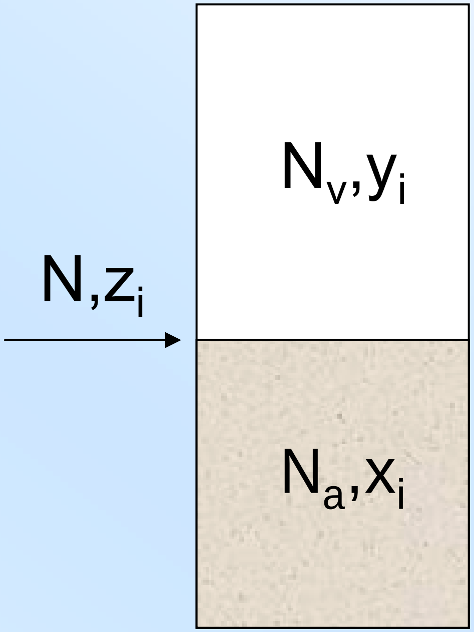
Adsorption Iteration Function Algorithm

Solve for ω, x_i, and y_i by using feed composition z_i

Mass Balance Equations:

$$F\left(\frac{N_a}{N}\right) = \sum_i \frac{(1-K_i)z_i}{\frac{N_a}{N} + \left(1-\frac{N_a}{N}\right)K_i} = 0$$

$$y_i = \frac{K_i z_i}{\frac{N_a}{N} + \left(1-\frac{N_a}{N}\right)K_i} \qquad x_i = \frac{z_i}{\frac{N_a}{N} + \left(1-\frac{N_a}{N}\right)K_i}$$



Algorithm 1

Initial guess: x_i, y_i, ω $\Longrightarrow$ $K_i = \dfrac{y_i}{x_i} = \dfrac{Z_a \overset{\frown}{\phi}_i^{a} \omega}{k_i \phi_i^g P}$

$$F\left(\frac{N_a}{N}\right) = \sum_i \frac{(1-K_i)z_i}{\dfrac{N_a}{N} + \left(1-\dfrac{N_a}{N}\right)K_i} = 0$$

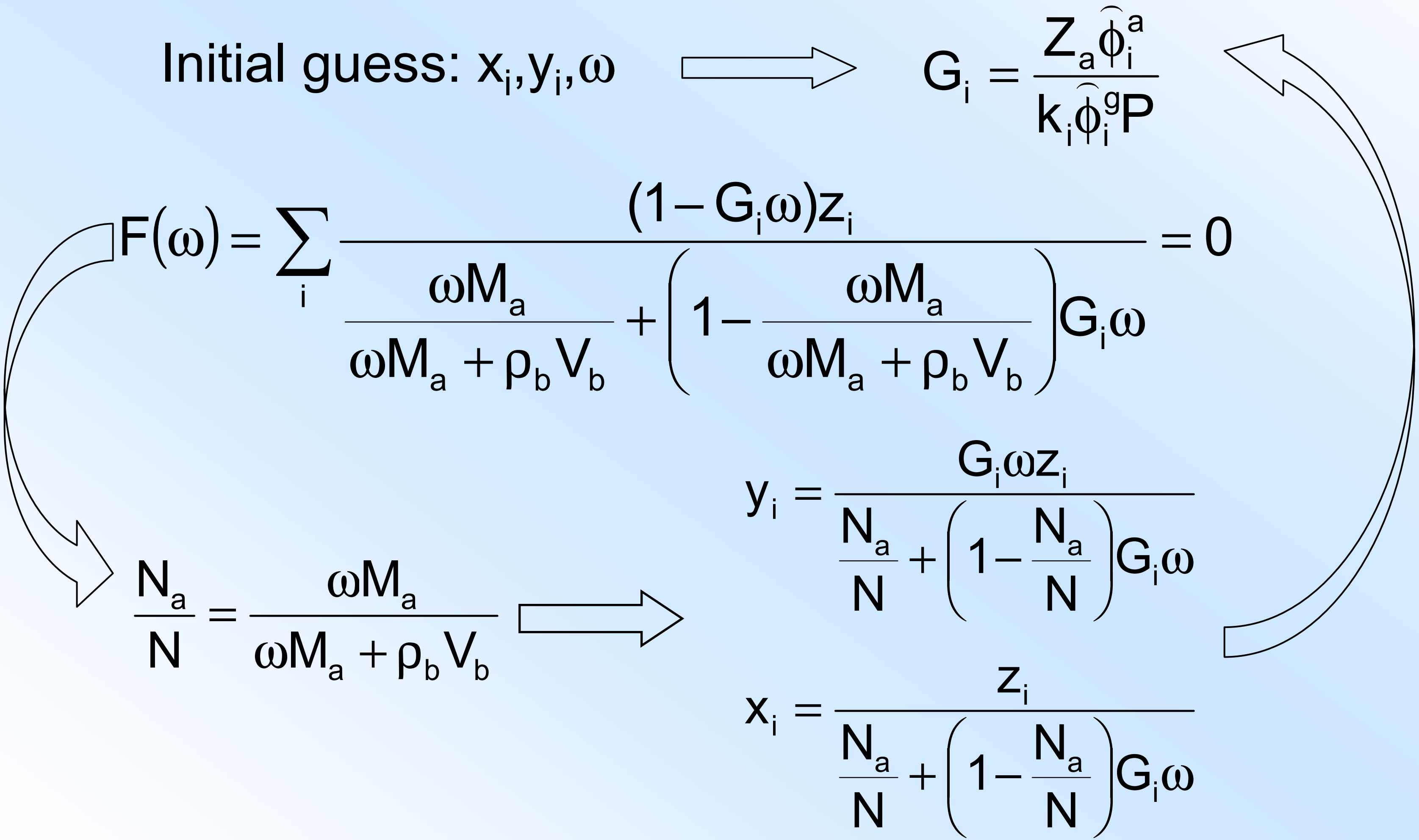
$$y_i = \frac{K_i z_i}{\dfrac{N_a}{N} + \left(1-\dfrac{N_a}{N}\right)K_i}$$

$$x_i = \frac{z_i}{\dfrac{N_a}{N} + \left(1-\dfrac{N_a}{N}\right)K_i}$$

$$\frac{N_a}{N} = \frac{\omega M_a}{\omega M_a + \rho_b V_b}$$

(Solve ω)

Algorithm 2



Initial guess: x_i, y_i, ω

$$G_i = \frac{Z_a \hat{\phi}_i^a}{k_i \hat{\phi}_i^g P}$$

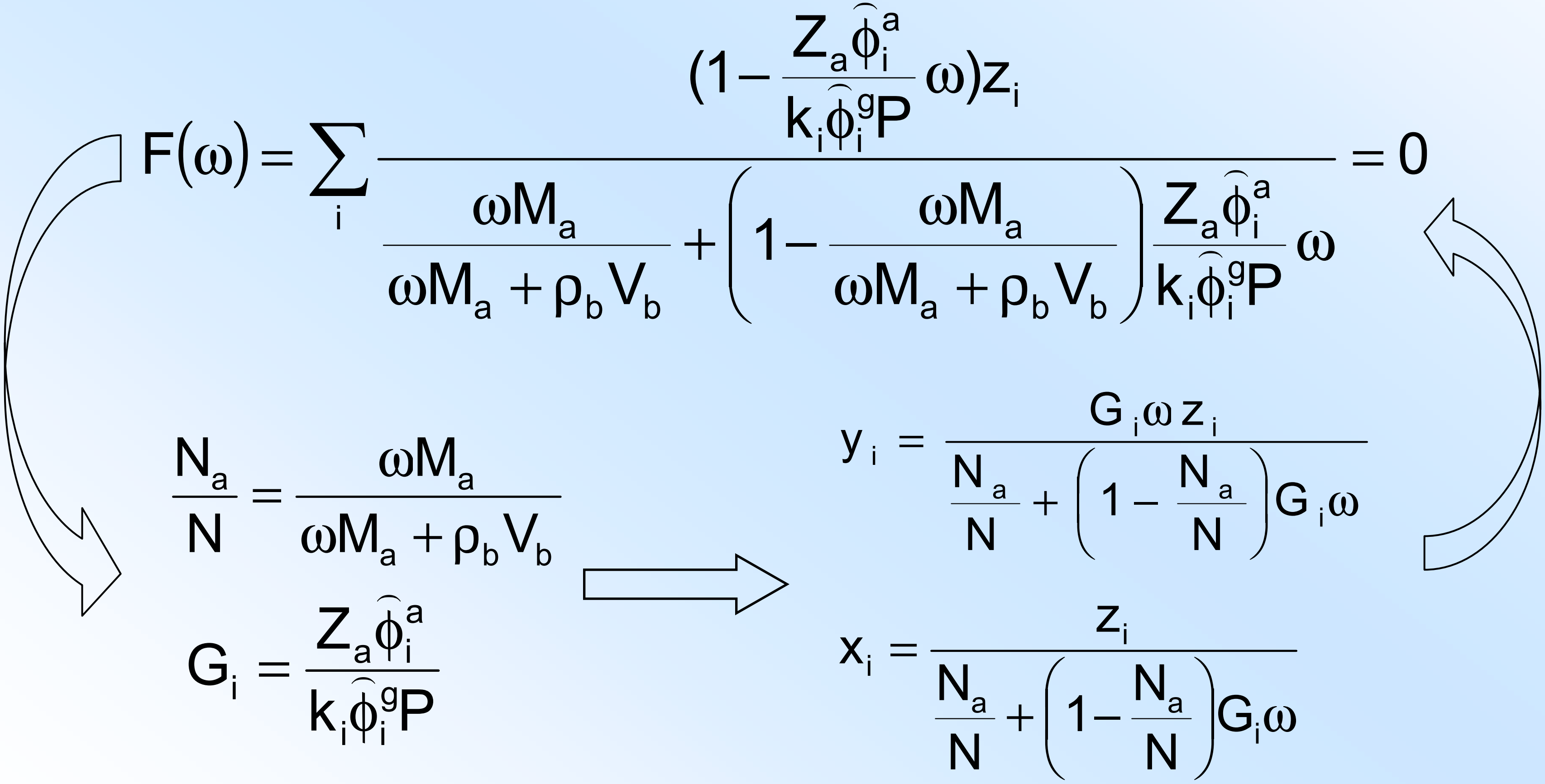
$$F(\omega) = \sum_i \frac{(1 - G_i \omega) z_i}{\dfrac{\omega M_a}{\omega M_a + \rho_b V_b} + \left(1 - \dfrac{\omega M_a}{\omega M_a + \rho_b V_b}\right) G_i \omega} = 0$$

$$\frac{N_a}{N} = \frac{\omega M_a}{\omega M_a + \rho_b V_b}$$

$$y_i = \frac{G_i \omega z_i}{\dfrac{N_a}{N} + \left(1 - \dfrac{N_a}{N}\right) G_i \omega}$$

$$x_i = \frac{z_i}{\dfrac{N_a}{N} + \left(1 - \dfrac{N_a}{N}\right) G_i \omega}$$

Algorithm 3



Initial guess: x_i, y_i

$$F(\omega) = \sum_i \frac{\left(1 - \dfrac{Z_a \hat{\phi}_i^a}{k_i \hat{\phi}_i^g P}\omega\right) z_i}{\dfrac{\omega M_a}{\omega M_a + \rho_b V_b} + \left(1 - \dfrac{\omega M_a}{\omega M_a + \rho_b V_b}\right)\dfrac{Z_a \hat{\phi}_i^a}{k_i \hat{\phi}_i^g P}\omega} = 0$$

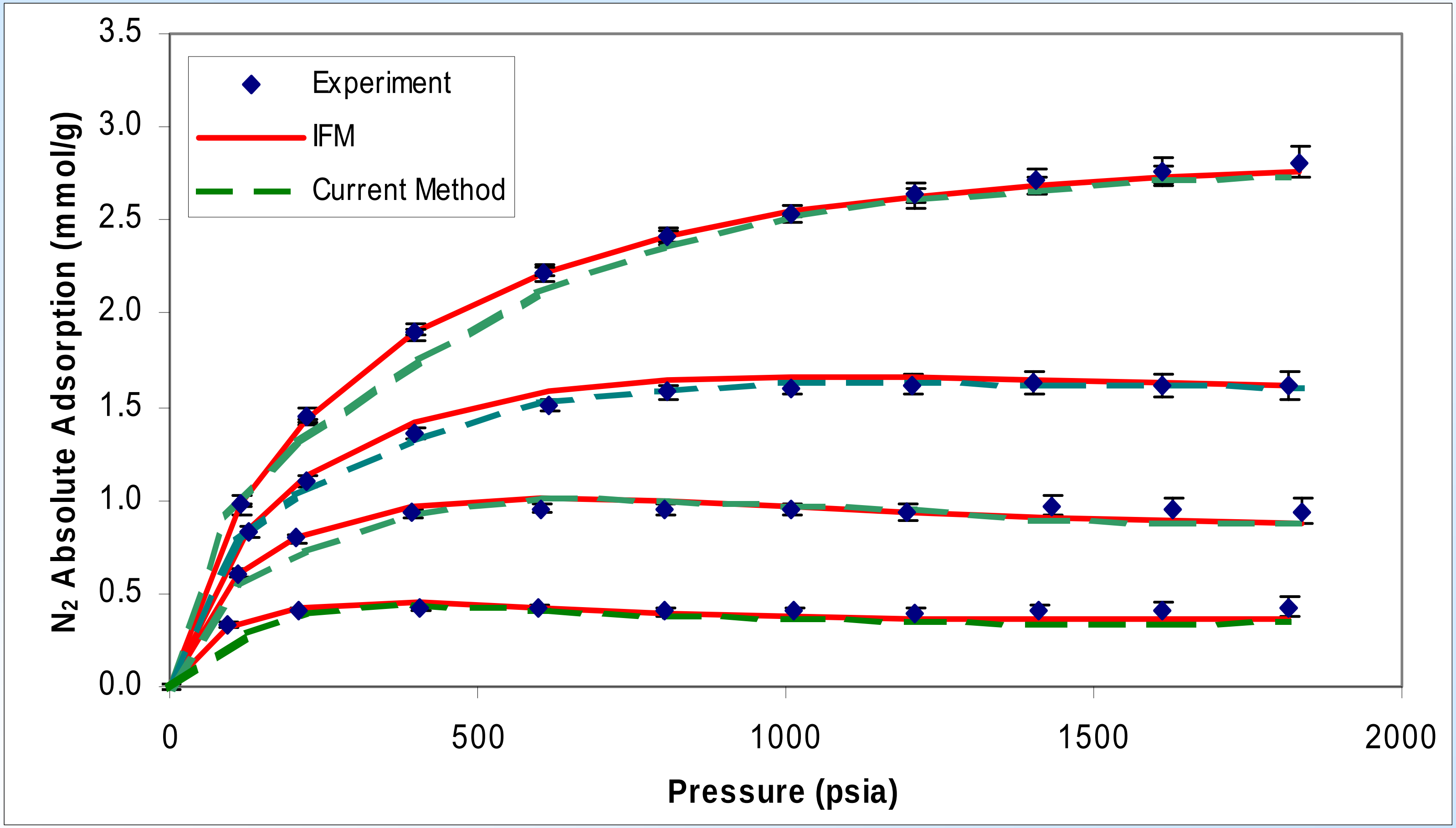
$$\frac{N_a}{N} = \frac{\omega M_a}{\omega M_a + \rho_b V_b}$$

$$G_i = \frac{Z_a \hat{\phi}_i^a}{k_i \hat{\phi}_i^g P}$$

$$y_i = \frac{G_i \omega z_i}{\dfrac{N_a}{N} + \left(1 - \dfrac{N_a}{N}\right) G_i \omega}$$

$$x_i = \frac{z_i}{\dfrac{N_a}{N} + \left(1 - \dfrac{N_a}{N}\right) G_i \omega}$$

Results: N_2+CO_2 on Activated Carbon at 113 °F



Conclusions: Algorithms

- The proposed adsorption IFM algorithm is robust
- The proposed flash calculations produce consistent computational results

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Approach

- Investigate the effect of each factor on our ability to simulate accurately CBM production and CO_2 sequestration processes
- Assess the potential economic impact of the uncertainty associated with each factor
- Rank order the issues to be resolved
- Identify the required resources for resolving the priority issues
- Develop research plans to resolve the priority issues

Moisture Effects

Current Working Assumption

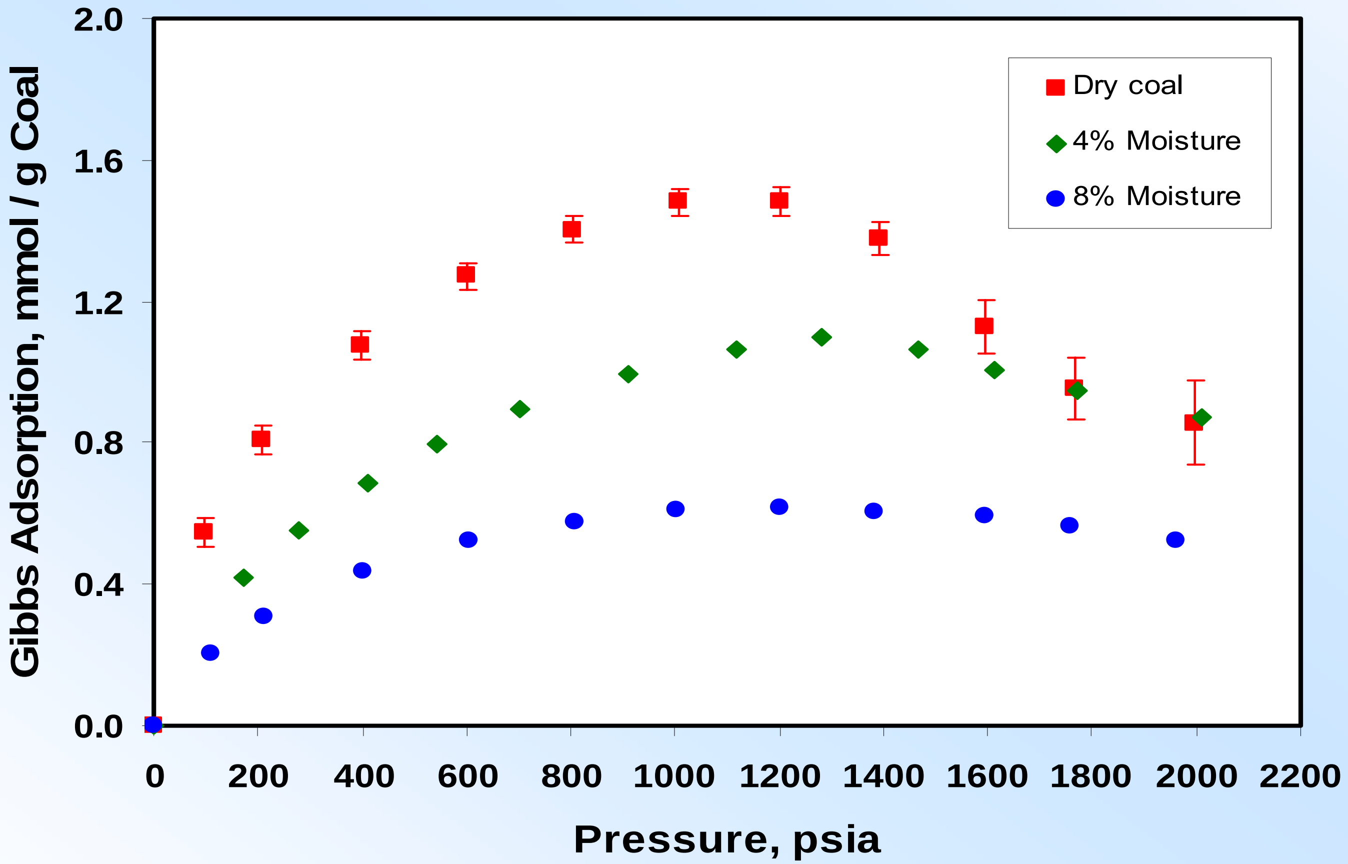
Operations occur in super-saturated water conditions; therefore, adsorption isotherms involving super-moist adsorbents are sufficient for the purpose.

In Reality

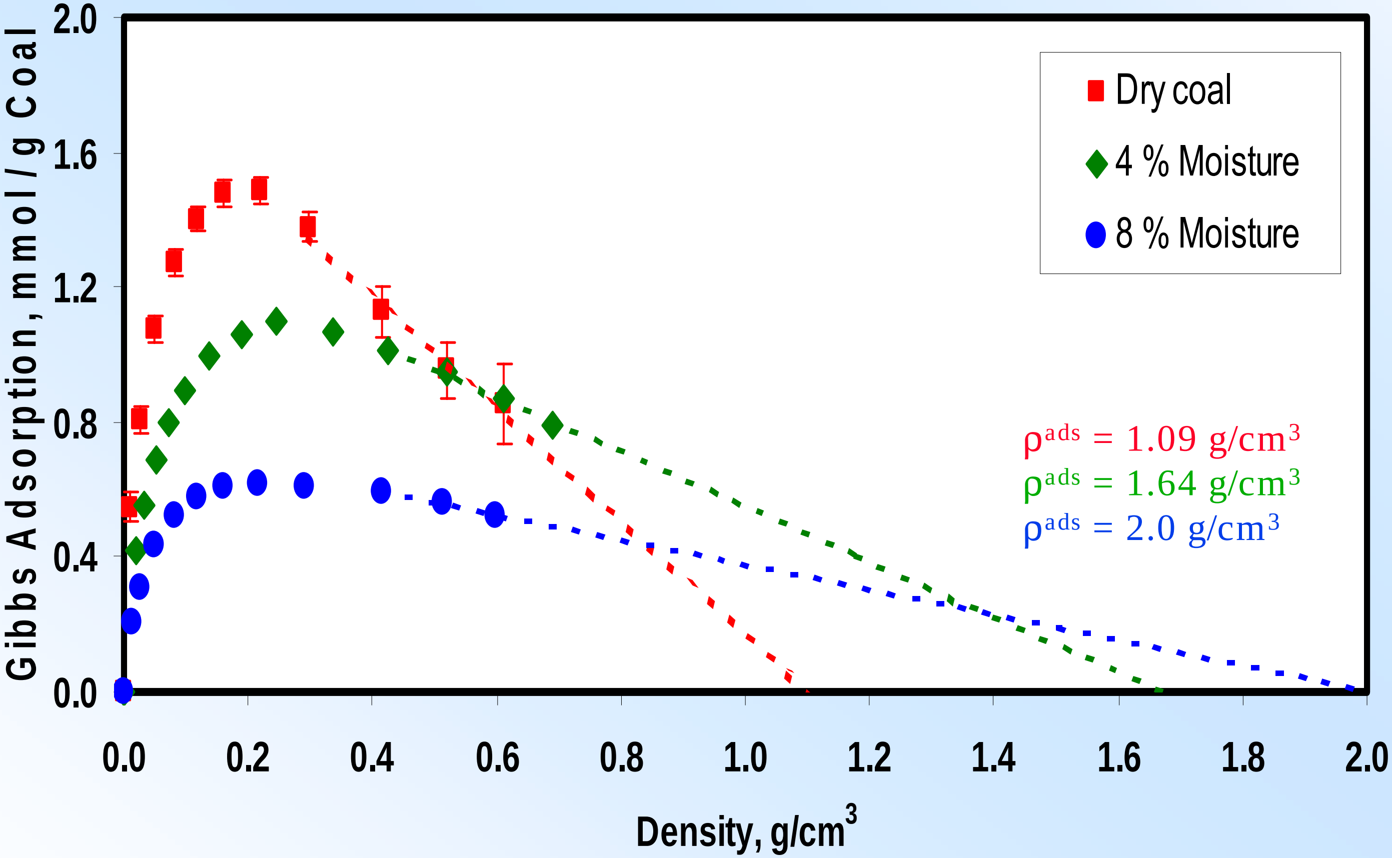
- Moisture content may affect significantly the:
    - Adsorption capacity
    - Adsorbed-phase density
    - Mixture adsorption behavior
    - Data interpretation and reconciliation
- The current accounting for moisture effects is not adequate

We need more rigorous modeling of wet adsorption behavior!

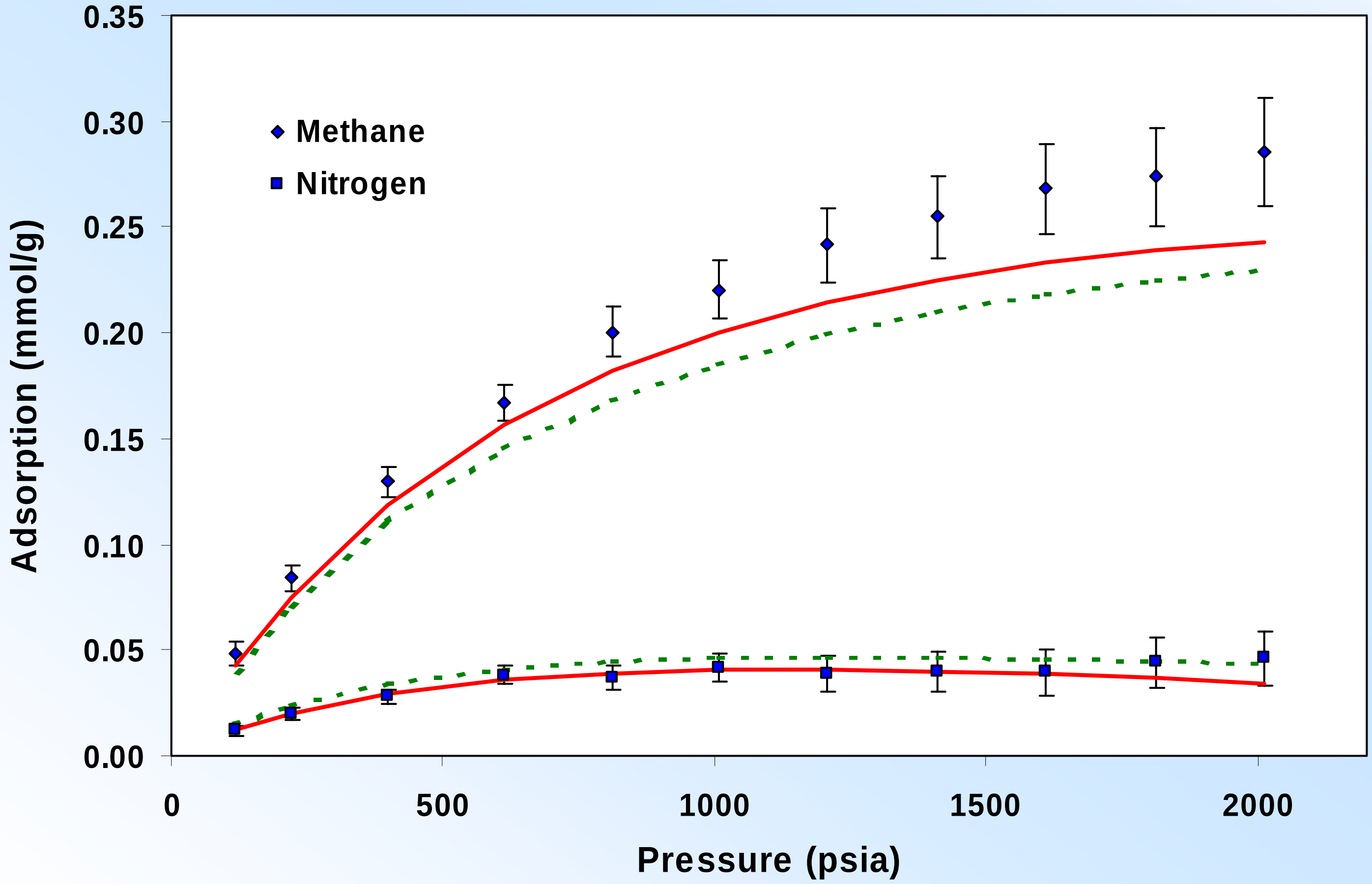
Moisture Effect on CO_2 Adsorption Isotherms: Illinois-6 at 131 °F



Moisture Effect on CO_2 Adsorbed Phase Density: Illinois-6 at 131 °F



SLD Modeling of Wet Methane/Nitrogen Adsorption on Tiffany Coal at 131 °F

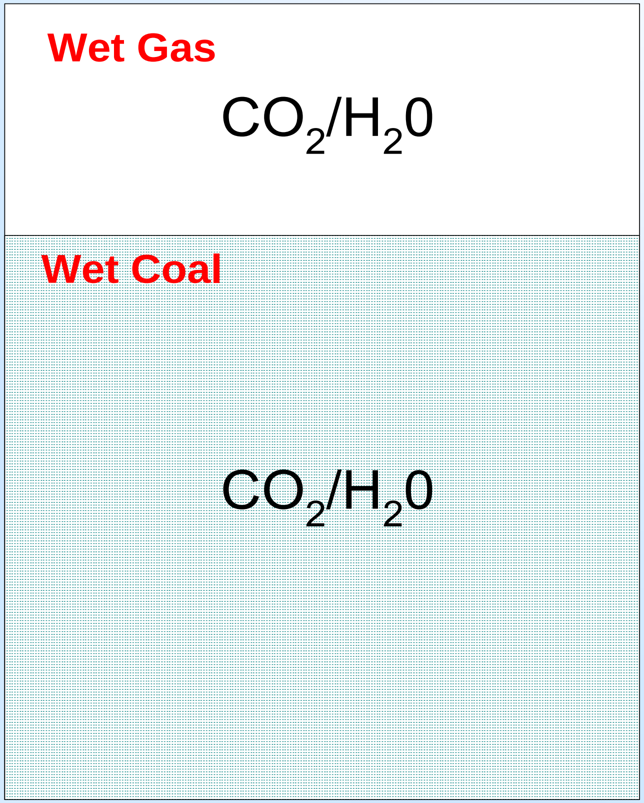


Moisture Effects: Case 1

- ***Assumptions***

  No standing water, no salts

- ***Approach***
  - Treat the situation as an **AD/Gas** equilibrium problem
  - Develop an adsorption model to cover the full pTx diagram for CBM gas/water systems

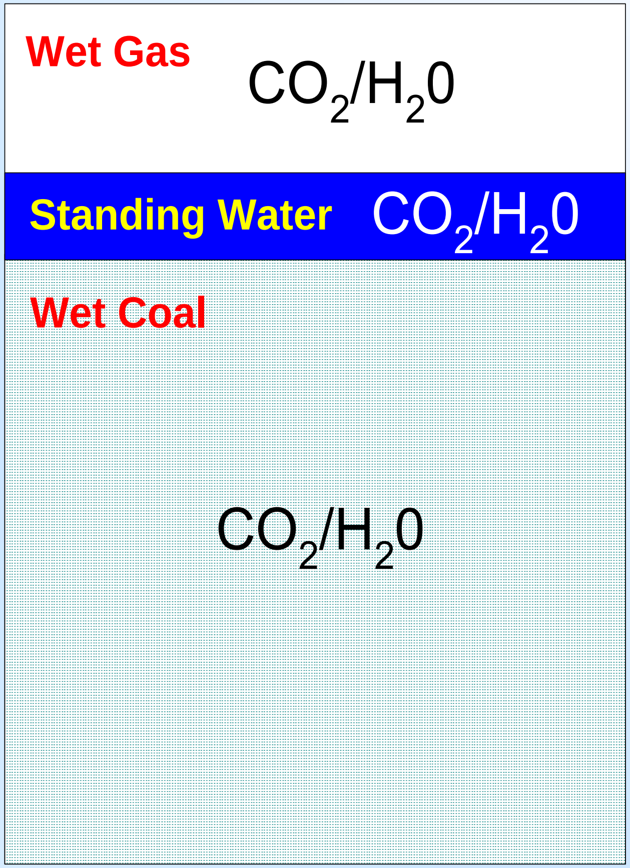


Moisture Effects: Case 2

- ***Assumptions***

  Standing water, no salts

- ***Approach 1***
  - Treat the situation as an **AD/Liq/Gas** equilibrium problem
  - Develop an accurate 3D EOS for CBM gas/water systems
  - Develop an adsorption model to cover the full pTx diagram for CBM gas/water systems



Wet Gas CO_2/H_20

Standing Water CO_2/H_20

Wet Coal

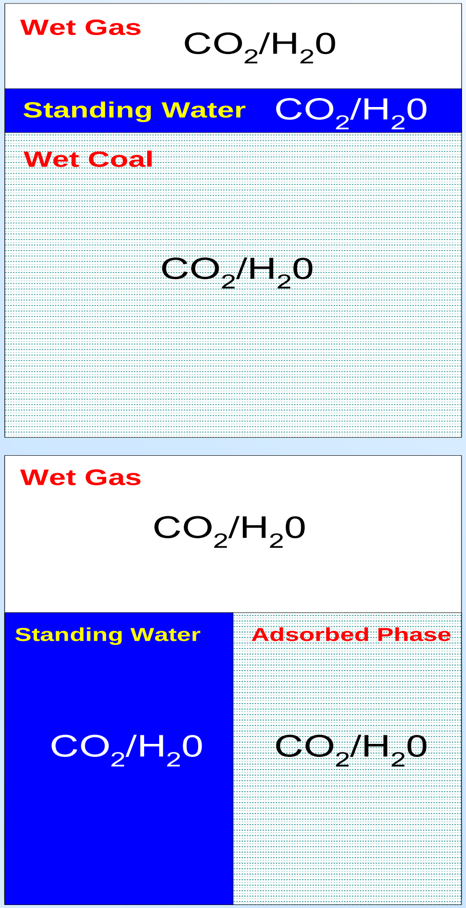
CO_2/H_20

Moisture Effects: Case 2 - continued

- ***Assumptions***

  Standing water, no salts

- ***Approach 2***
  - Develop an accurate EOS for CBM gas/water systems
  - Conduct a VLE calculation for CBM gas/water system
  - Use the VLE gas composition to conduct **AD/Gas** calculation for the gas mixture
  - Repeat the procedure until component fugacities are equal across the three phases



Moisture Effects: Case 3

- ***Assumptions***

  Standing water, with salts

- ***Approach 3***
  - Develop an accurate 3D EOS for CBM gas/water systems
  - Conduct a **electrolyte** VLE calculations for gas/water system
  - Use the VLE gas composition to conduct **AD/Gas** calculations for the gas mixture
  - Repeat the procedure until component fugacities are equal in the three phases

Moisture Effects: Experimental Measurements

- **Apparatus**

  Install density meter for increased accuracy of mixture data

- **Measurements**

  Conduct equilibrium adsorption measurements involving
  a) the targeted gases
  b) on activated carbon and two well characterized coals
  c) for at least three levels of moisture content

Closure

Fundamental Theory - OSU

Improved mixture modeling	*done*
Computational algorithms	*done*
Effect of moisture on adsorption behavior	2003
Model parameter generalizations	2003

Matrix Characterization - PSU

Coal characterization	2003/4
Coal structure-based generalizations	2003/4