

TITLE: Use of Molecular modeling to determine the interaction and competition of gases within coal for carbon dioxide sequestration

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ABSTRACT

1. Objectives

Sequestration of CO₂ within coal seams that are too deep, thin, or uneconomic has been suggested to slow the rate of climate change. Additionally, coal can hold twice as much CO₂, (from sorption isotherm studies) as it can hold methane(1). Sequestered CO₂ also displaces CH₄ within coal, a valuable fossil fuel, to help offset the sequestration cost. The objective is to carry out first time molecular dynamics simulations to provide useful information on accessible pore volumes, energy of interactions between host and guest molecules, self-diffusion coefficients, identification of likely sorption sites, impact of carbon dioxide sorption/methane exchange upon the coal matrix (expansion/contraction), and competitive adsorption isotherms. The molecular modeling approach essentially permits us to investigate the complex interactions at the molecular level to define and explain the issues relating to sequestration of CO₂ within coal. The structural model is being revised to better represent the structural alignment in a coal of this rank which has implications for the shape of pores, diffusion, and swelling anisotropy. The objective is to construct a reasonable molecular representation of Pocahontas No. 3 coal which is representative of both the physical and chemical composition, *and behavior* of this low volatile bituminous coal.

2. Accomplishments to date

We have utilized computational molecular modeling to generate a state-of-the-art large scale structural representation of a bituminous coal of lower bituminous rank. This structure(s) has been used to investigate the molecular forces between the bituminous coal structure (or idealized pores) and the molecular species CH₄ and CO₂. We have created a new force field for these simulations and are currently carrying out molecular dynamics simulations. An initial step performed is to help define the issues with sequestration utilizing the molecular modeling approach. Once defined, advanced molecular modeling techniques can be utilized in investigating sorbent and host behavior.

The complex interconnection, distribution, and shapes of the pores are the controlling features with regard to capacity and kinetics of uptake. From our advanced model we can predict the relative scale of macro, meso, and micropores, (shown as spheres.) The dual porosity nature of the coal means for the most part that mesoporosity is limited. From our model, we find that the distribution, size and shape of the micropores limits access to the methane molecules while permitting carbon dioxide to enter (molecular sieving). Our interpretations are based upon 32 molecules of methane that a structure of this size (C_{3,538}H_{2,061}O₃₂N₄₅S₆) should contain (based on average methane content values for this coalseam) and the 64 carbon dioxide molecules that can displace the methane (assuming 2:1 ratio).

3. Future Work

Further characterization of the shape, distribution, and interconnectivity of the pores within the structural model. Molecular dynamics to observe effective open and closed porosity to the sorbents: methane, carbon dioxide, water, and nitrogen. Determine the degree of swelling with each sorbent. Reproduce the adsorption isotherm utilizing molecular modeling techniques. Investigate the methane/carbon dioxide 2:1 ratio, and methane displacement for the pore surface(s) of the coal. Determine relative diffusion rates for sorbents within the structure. Investigate coal behavior upon sorbent exposure.

4. Lists of Papers and Conferences

Mathews, J. P., Halleck, P., Narkiewicz, M. R., and Hile, M., 2003, Presentation: "CO₂ sequestration: What we know about bituminous coal", North American Coalbed Methane Forum, Washington, PA, April 16th 2004

Horn, H.W., Swope, W.C., Pitera, J.W., Madura, J.D., Dick, T.J., Hura, G.L., and Head-Gordon, T., *Development of an improved four-site Water model for bio-molecular simulations: TIP4P-Ew*. J. Chem. Phys., 2004 *in press*.

5. Students supported under this grant

Orlando Acevedo, Thomas Dick, and Patrice Pique are graduate students at Duquesne University, and Marielle R. Narkiewicz is a graduate student at the Pennsylvania State University.