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

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ABSTRACT

Molecular modeling was employed to both visualize and probe our understanding of carbon dioxide sequestration within a bituminous coal. A large-scale (>20,000 atoms) 3D molecular representation of Pocahontas No. 3 coal was generated. This model was constructed based on a the review data of Stock and Muntean[1], oxidation and decarboxylation data for aromatic clustersize frequency of Stock and Obeng[2], and the combination of Laser Desorption Mass Spectrometry data with HRTEM[3], enabled the inclusion of a molecular weight distribution. The model contains 21,931 atoms, with a molecular mass of 174,873 amu, and an average molecular weight of 714 amu, with 201 structural components. The structure was evaluated based on several characteristics to ensure a reasonable constitution (chemical and physical representation). The helium density of Pocahontas No. 3 coal is 1.34 g/cm^3 $(dmmf)^4$ and the model was 1.27 g/cm^3. The structure is microporous, with a pore volume comprising 34% of the volume as expected for a coal of this rank. The representation was used to visualize CO_2, and CH_4 capacity, and the role of moisture in swelling and CO_2, and CH_4 capacity reduction. Inclusion of 0.68% moisture by mass (ash-free) enabled the model to swell by 1.2% (volume). Inclusion of CO_2 enabled volumetric swelling of 4%.

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INTRODUCTION

This research employs molecular modeling to describe the relationships of CO_2, CH_4, and water within the pore system of a large-scale structural representation of coal. The modeling effort will aid in understanding and defining the molecular process of interest for CO2 sequestration. The coal is a representation of the Argonne Premium low-volatile bituminous coal, Pocahontas No. 3. The Energy Information Agency (1999) estimated the U.S. identified coal resources (measured, indicated and inferred), to a depth of 6,000 ft, at 1.7 trillion short tons with around 84% being unmineable[5]. Unmineable U.S. coalbeds are those that are too deep (eastern coalbeds are generally less than 4,000 ft deep, while western coalbeds can be as deep as 10,000 ft[6]), too thin, unsafe to mine, have a high sulfur content, or mineral matter content, or are low in BTU value[7]. Sequestration of CO_2 in coalbeds, is considered a near-term option[8]. Once injected into the coal, CO_2, a greenhouse gas, if sequestered will not contribute to climate change. Additionally, CH_4 that may be held within the coal can be displaced, extracted and utilized giving additional climate change mitigation benefits[8]. The transport, of CO_2, CH_4 and H_2O, is dependent on the size, distribution, connectivity and shape of the pores, and the sorption or diffusion processes that occur. Coal behavior will contribute to these processes. For example, additional sorption sites may be made available with coal swelling.

EXECUTIVE SUMMARY

Recent experimental and computational advances have the potential to produce a first-time reasonable constitutional model (chemical and physical structure) and enable its use. 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. First, structural diversity was incorporated through the combination of image analysis of high-resolution transmission electron microscopy (HRTEM), laser desorption mass spectroscopy, and known coal chemistry which has not been previously included into a three-dimensional structural model of coal. Secondly, methodological advances in molecular simulations that have been successfully applied to biomolecular systems and new engineering materials coupled with available high capacity and high speed parallel super computers make the molecular modeling of CO_2 sequestration within coal a realistic and practical research. A major focus of the presented research is in the modification and creation of appropriate force field parameters to model accurately the structure and properties of coal with small molecules such as CO_2 and CH_4. Molecular models of CO_2 have been evaluated with water to analyze which classical molecular force-field parameters are the most reasonable to predict CO_2 interactions with water. A large-scale molecular representation of Pocahontas No. 3 coal was constructed based on average structural parameters, but also included a reasonable molecular weight distribution obtained from the combination of LDMS, and HRTEM lattice images. This structure was then used to visualize the inclusion of CO_2, CH4, and water. The pore size distribution of the model was determined using the POR program. POR was also used to evaluate accessibility of CO_2 and CH_4.

EXPERIMENTAL

In terms of super computing facilities, we have used a SGI Altix 3700 system (32 processors @ 1.5 GHz with 64 GB of memory and 1.6 TB of disk); SGI Altix 350 (16 processors @ 1.5 GHz with 16 GB of memory and 1.6 TB of disk); IBM RISC System/6000 SP Supercomputer Model 3A8 (four nodes @ 160 MHz each w/256 Mb ECC memory, twelve nodes @ 120 MHz each w/1 GB ECC memory); 2 IBM RISC System/6000 (77 MHz and 66 MHz w/512 Mb ECC memory); and 2 Dec Alpha Beowulf Clusters containing Master-node (600 MHz w/512 MB ECC memory and 24 GB of disk space) and 16 nodes (600 MHz w/256 MB ECC memory) were utilized. Twenty 1.8-3.2 GHz Pentium IV computers with molecular computation and data processing software were utilized to visualize and setup larger computations.

RESULTS AND DISCUSSION

Data Reduction

We have made progress in carrying out large scale molecular dynamics simulations using the CHARMM force field in order to refine our coal model. First, we have had to create a completely new topology and parameter definition for coal. This means that each of the force field parameters much be explicitly defined and parameterized. This specific approach has several draw backs. First, the created force field will be of use on only the system for which it was designed. Second, the number of force field elements and parameters will be applied to systems of over 250 K particles. As such, it will be difficult to create and manage such a database with any degree of accuracy. Therefore, we have adopted the strategy of treating coal composed of individual common fragments based upon mass, composition and bonding. Our procedure is similar to treating a protein as being composed of the discrete set of amino acids. Second, we have had to incorporate the quality CO_2 parameters that we have developed over the last two years. There are the geometric and arithmetic procedures, which we have successfully implemented.

We are building upon our previous results from quantum chemical computations. The CO_2 parameters were derived from *ab initio* calculations for a CO_2 molecule, a single water molecule, and the CO_2-H_2O complex at multiple levels of theory and basis sets in order to calculate the interaction energy of the complex. For the interaction energies, they were calculated as the energy of the complex minus the energies of the individual CO_2 and water molecules. This can be shown below:

$$\Delta E = E(AB) - E(A) - E(B) \qquad (1)$$

where delta E is the energy of interaction, E(AB) is the energy of the complex, and E(A) and E(B) are the energies of the CO_2 and water molecules.

A thorough evaluation of the CO_2-H_2O complex was achieved by using different theory and basis sets. Hartree-Fock (HF), density functional theory (DFT), Möller-Plesset perturbation theory (MPPT), and coupled clusters with single and double excitations (CCSD) were used with the following basis sets: 3-21G, 6-31G, 6-31G(d),

aug-cc-pvdz, and aug-cc-pvtz. The density functional theory used in the calculations was the Becke3 exchange functional with the Lee, Yang, and Parr non-local functional corrections. For the most complete QM study of the complex, the use of polarized split-valence basis sets were employed to allow the molecular orbitals to change shape by adding basis functions to higher than ground state levels to increase angular momentum and efforts were made to keep a balanced basis set in the calculations. The investigation with the increasing levels of theory was in an attempt to converge the interaction energies and the *ab initio* calculations were done using Gaussian98 and Gaussian03.

The zero point energy calculations were obtained by releasing the constraints of the system until all degrees of freedom were free. The minima were obtained and frequency calculations were completed and evaluated with all of the above mentioned methods and basis sets. The energetic minima were found to have no negative frequencies, concluding that the true minimum was found for both the T-structure and the H-structure of the complex. The T-structure was also constrained to C_{2V} symmetry, as had been done in previous *ab initio* calculations and frequency calculations on the minimized structure for comparison.

For the classical simulations, including both the MM minimizations and MC simulations, a classical force field was used to model the CO_2-H_2O interactions; the waters in the bulk phase simulations were modeled in the same fashion. The potential energy function of the force field is given as follows.

$$U(R) = U(R)_{bonded} + U(R)_{non-bonded} \tag{2}$$

where

$$U(R)_{bonded} = \sum_{bonds} K_b(b - b_0)^2 + \sum_{angles} K_\theta(\theta - \theta_0)^2 + \sum_{dihedrals} K_\chi[1 + \cos(n\chi - \sigma)] \tag{3}$$

and

$$U(R)_{non-bonded} = \sum_{\substack{non-bonded \\ pairs}} \left(\varepsilon_{ij} \left[(\frac{R_{min.ij}}{r_{ij}})^{12} - (\frac{R_{min.ij}}{r_{ij}})^6 \right] + \frac{q_i q_j}{\varepsilon_D r_{ij}} \right) \tag{4}$$

where U(R) is the potential energy of the system. For the CO_2-H_2O complexes, the only parameters that will be evaluated will be the non-bonded terms, since the CO_2 and water will be treated as rigid molecules. The standard mixing rules for the mixing of the LJ terms between molecules was observed. The mixing rules can be shown as:

$$\sigma_{AB} = \frac{\sigma_{AA} + \sigma_{BB}}{2} \tag{5} \quad \text{and} \quad \varepsilon_{AB} = \sqrt{\varepsilon_{AA}\varepsilon_{BB}} \tag{6}$$

The DYNAMO program was used to perform the MM minimizations and BOSS was used in the MC simulations. The MM minimizations were done using several steps of steepest decent followed by conjugate gradient, in order to find the lowest energy

structures; the complexes interaction energies were calculated using the same methods in the *ab initio* calculations shown in *Equation 1*. The MC simulations were standard done using the standard acceptance/rejection ratio of 0.40/0.60, which has been shown to give reasonable sampling in simulations.

The force-field parameters used in the molecular mechanics calculations were taken from the literature and developed here. The water molecules used in the simulations the TIP3P and TIP4P water models from Jorgensen *et. al*. Several CO_2 models from the literature were studied along with a newly developed model, the TJDM1 model (named from the authors initials). All the CO_2 models used in the calculations are 3-site electrostatic models with the charges and LJ 12-6 terms centered on the atoms.

Experimental and Operational Data

The structural representation of Pocahontas No. 3 was constructed in a similar manner to that already discussed[9]. Here the bulk data were obtained from the literature review of Stock and Muntean[1], and the oxidation decarboxylation data to determined aromatic cluster-size relative abundance[2], along with the molecular weight distribution determined from the combination of HRTEM and laser desorption mass spectrometry (LDMS) data. The details of the elucidation of the molecular weight distribution using the complimentary HRTEM and LDMS data are available elsewhere[3]. Essentially, image analysis of 1,000 fringes from the HRTEM produced the same molecular weight distribution curve, assuming parallelogram catenation, as a LDMS offset by several hundred amu. Construction and cross-linking these 1,000 fringes with the appropriate aliphatic content and aliphatic and aromatic bridges generated the 201 (mostly unique) structural components used to construct the model. The structure was minimized using Cerius[2] software (Accelrys[10]) with an applied stress to force preferential alignment. The stress field is removed and the structure is then minimized producing a partially aligned model. Highrank coals are expected to have preferential alignment; this was confirmed via image analysis of the lattice fringe orientation from the HRTEM[11]. The "squashing" of the model to force orientation is an unsophisticated yet necessary approach, if swelling anisotropy is to be reproduced. It was not an attempt to represent realistic stress conditions within the seam but rather a brute force approach to force some structural orientation.

The sorption module of Cerius2 was used to probe the pore space and to "load" CO_2 and CH_4 molecules into the coal structure. Sorption generates random configurations by translating and rotating, and creating and destroying sorbate molecules in the model framework[12]. Configurations are accepted or rejected based on near neighbor distances and a Lennard-Jones 12-6 interaction[10]. This energy is calculated based on the interaction between the sorbate molecules to the structure. Each subsequent configuration is generated by either a random translation or random rotation of that sorbate molecule[12]. If the energy change from the random translation or rotation is negative, then the configuration is accepted. If the energy change is positive, then the molecule's Boltzmann factor is calculated and compared to a randomly generated number between zero and one; if the Boltzmann factor is greater than the random number, the configuration is kept, but if the Boltzmann factor is less than the random number the configuration is destroyed[12]. Loading was controlled in these experiments by specifying

the sorbate content. The POR program was used to calculate the helium density, the open porosity, and the closed porosity of the model[13]. This program immerses the structure in a grid of 1Å^3 cells and calculates the atomic occupied volume as well as the accessible and inaccessible pore volumes. It was used to investigate the pore size distribution of the model.

Model Structure

This structural representation of the Pocahontas No. 3 coal can be seen in *Figure 1*. This model has a helium density of 1.27 g/cm^3 in reasonable agreement with the 1.34 g/cm^3 value for the Argonne Premium coal. The model contains C13471 H8143 O113 N181 S23 atoms and is contained within a box of dimensions 63 x 60 x 112 Å. The calculated the accessible micropore volume is 151,218 Å^3, representing 34% of the volume. The closed porosity to helium (5.08 Å) is 0.003 cm3/g and as expected is small, less than 0.5 %. The capacity ratio of 2 CO_2 molecules for every 1 CH_4 molecule with coal is a function of gas pressure, and is rank and coal specific. Isotherms presented by Stanton *et al.* it can be seen that for dry lignites, this ratio can increase to 10:114. A 2:1 ratio for bituminous Pocahontas No. 3 coal, was reproduced by Busch *et al.* at 10 bar gas pressure[15]. We selected data at 10 bar as a reasonable gas content, close to that found in the seam. That work obtained 5.84 x 1020 molecules of CO_2/gram of coal, and 2.89 x 1020 molecules of CH_4/gram of coal, which equates to 169 CO_2 or 84 CH_4 molecules in this structure. The 10 bar gas pressure adsorption capacity for CO_2 can be seen in *Figure 2*. A similar visualization of CH_4 at adsorption capacity can be seen in *Figure 3*. At 48 bar gas pressure, the ratio is 229:138 molecules and represents the maximum capacity. The simulations employed here were low-level, computationally inexpensive, and do not adequately recreate the behavior of these sorbates and the coal structure. There are however useful in probing our understanding of the sequestration process and the influence of certain specific contributions to that process. Future work will employ higher-level approaches.

Carbon   Hydrogen   Oxygen   Nitrogen   Sulfur
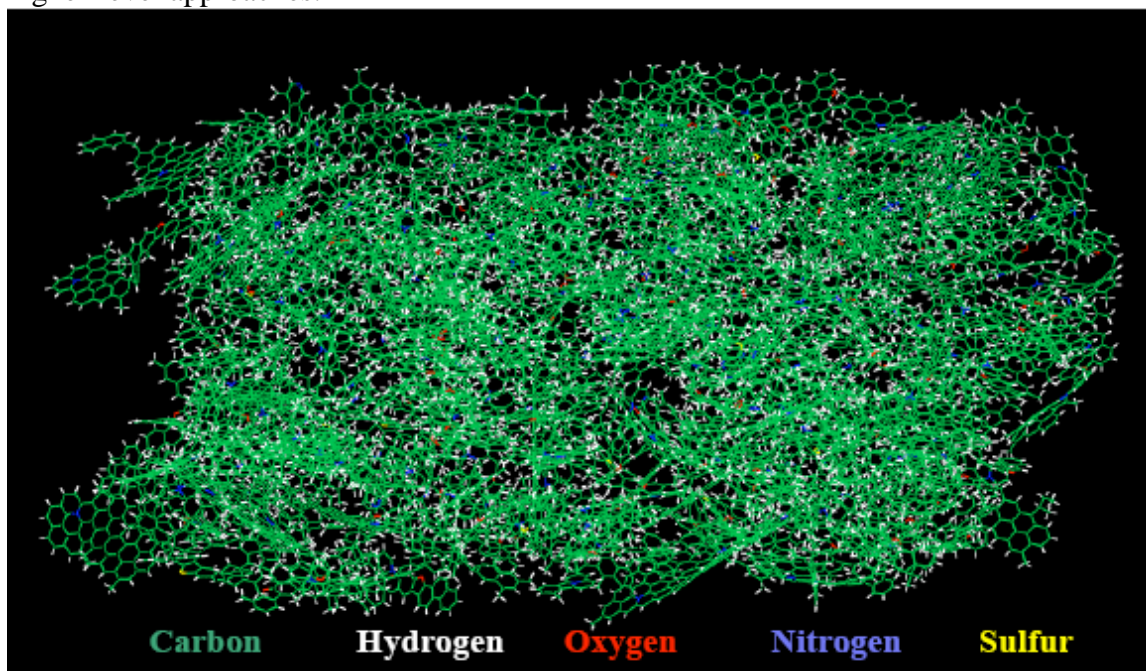
Figure 1: The molecular representation of Pocahontas No. 3 bituminous coal.
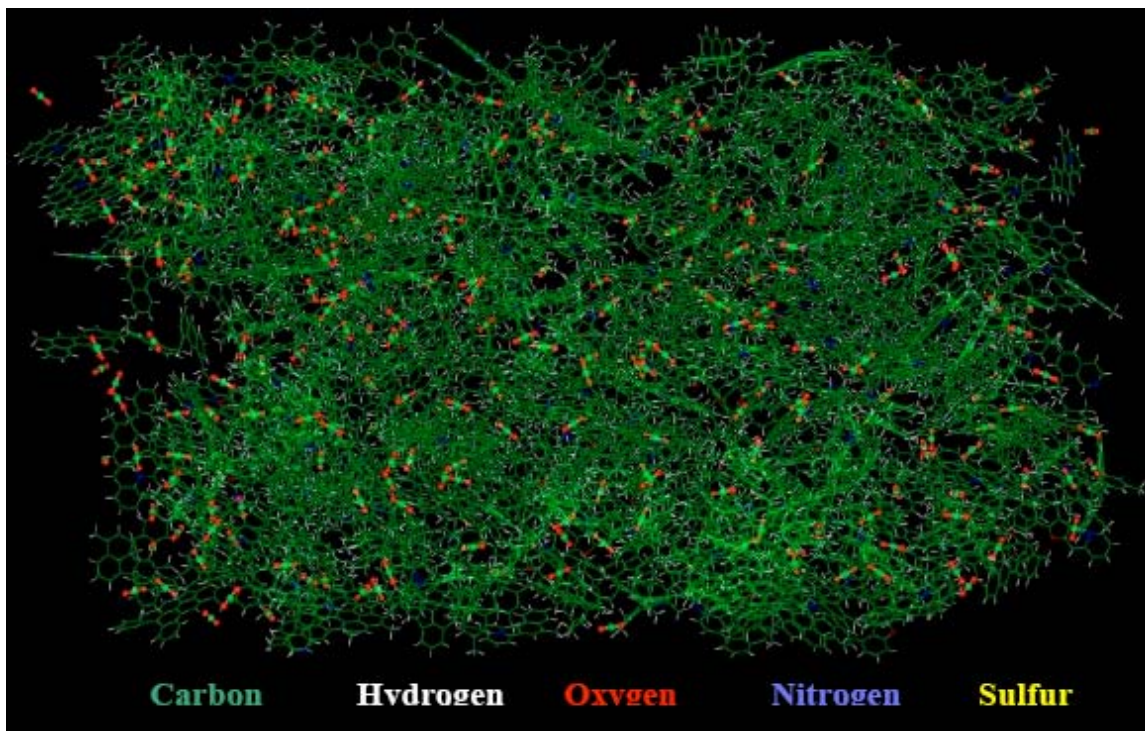
Figure 2: Visualization of CO₂ adsorption at capacity representing the Pocahontas No. 3 adsorption isotherm.
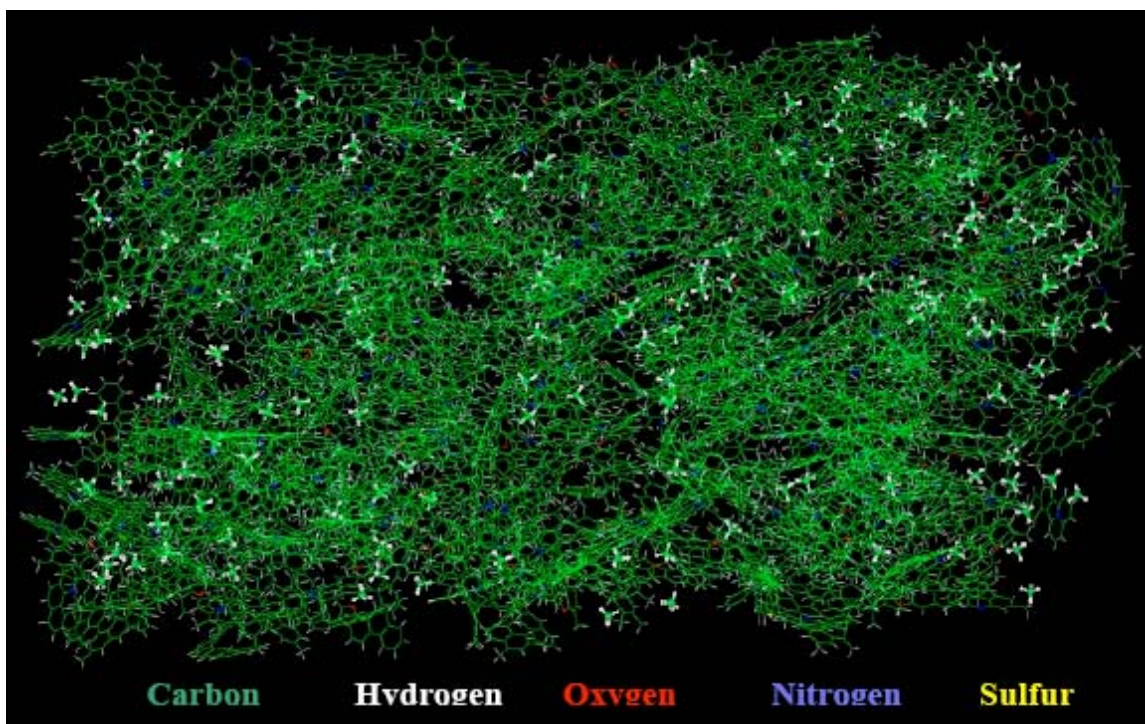
Figure 3: Visualization of CO₂ adsorption at capacity representing the Pocahontas No. 3 adsorption isotherm.

Pore Access

Access to pores is dependent on the size and shape of the sorbate, temperature, pressure, chemical interaction, and the size, shape, and interconnectivity of the pores. This study investigated CO_2, CH_4, and water. Two sizes are of interest in probing accessibility of these gases, the kinetic diameter (for spherical molecules such as methane), and the minimum distance approach (for non-spherical molecules such as CO_2)[16]. Walker *et al.* calculated that diffusion of a sorbate into pores becomes activated once the pore wall spacing becomes less than the species kinetic diameter plus 1.6 Å[17]. This 1.6 Å is the radius of the p-p clouds surrounding the carbon basal plane (assuming micropores are due to parallel graphitic-like layers). The resulting value is termed the critical pore dimension for spherical molecules. The Lennard-Jones potential is used to describe the kinetic diameter. While this approach is considered accurate for slit-shaped carbon pores[16, 18-20] for spherical gaseous molecules, it is not for linear molecules where shape influences energetic interactions. Transport of non-spherical molecules through relatively narrow pores involves loss of rotational freedom and thus cannot accurately be described solely through the kinetic diameter[18]; therefore, they should be described by parameters that define the species. For example, in a study by Heuchel *et al.* on pore access within graphitic layers, CH_4 was treated as a one-center Lennard Jones interaction expression while CO_2 as a two-center Lennard-Jones expression plus a single point quadrupole[21]. Our initial approach using the sorption module is a lower-level modeling simulation based on Lennard Jones interactions and did not include quadrupole or other interactions.

We investigated the coal model pore size distribution utilizing the POR program with narrow minimum and maximum entrances ranges, in the same manner to that described previously[13]. The pore size distribution is shown in *Figure 4*. Helium (5.08 Å) was able to access essentially 100% of the micropore volume (less than 0.5% of the pores within the model are closed to helium, in this case, determined using POR). Ninety percent of the pores were smaller than 8 Å. Using critical pore dimensions, as defined by Heuchel *et al.* the smallest pore in which CO_2 and CH_4 can enter (the critical pore dimension) was 5.7 Å and 6.1 Å, respectively in a activated carbon modeled using slit-shaped pores[21]. Carbon dioxide is thus able to access 122,184 $Å^3$ or 80.8% of the pore volume. Methane is able to access 102,519$Å^3$, 67.8% of the pore volume. Thus, in a rigid representation CO_2 can access 13% more volume than the CH_4, or if sorbate density within the pore is assumed to be the same this is a 1.2:1 ratio for CO_2:CH_4. Expectations are that for a dry bituminous coal, at capacity, twice as much CO_2 can be within the structure as CH_4 at the same conditions. Walker *et al.* have concluded that uptake of CO_2 into coal is due to both sorption within pores, and imbibition of the sorbate in the structure itself[22]. The coal swelling being attributed 1.9 % due to pore access, and 1.9% due to imbibition. Here we confirm simply accessing the pore structure in a rigid model does not approach the expected 2:1 ratio, confirming the importance of imbibition and swelling.
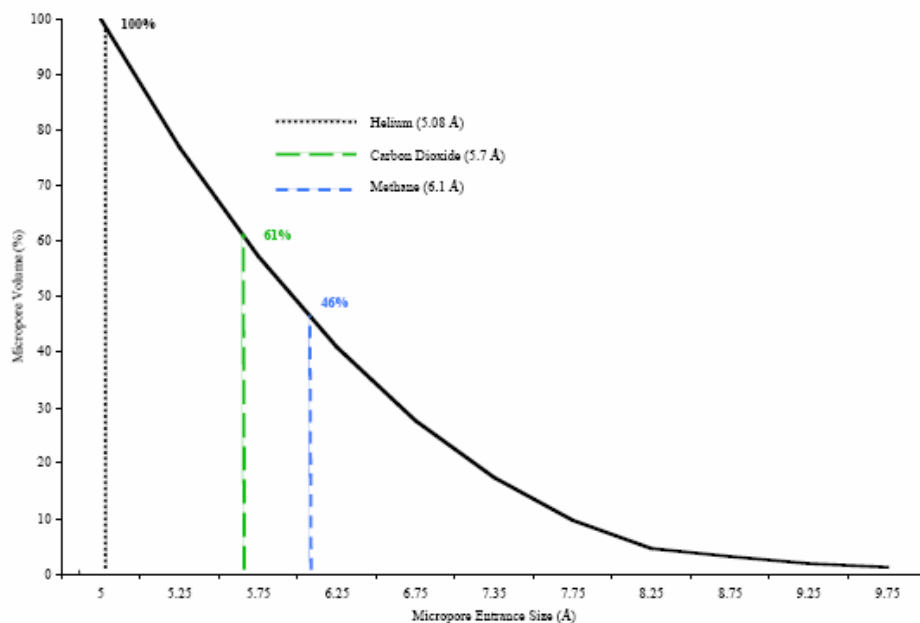
Figure 4: The volume of porosity that is accessible (and inaccessible) to different sorbates sizes, specifically carbon dioxide and methane.

Role of Moisture

Water is known to reduce the sorption capacity of CO_2 [23] and CH_4 [24] in coal. With increasing water content, *up to a certain coal-specific (rank) loading*, decreases capacity. Additional water does not further reduce the ability to store these gases. As little as 1.4% moisture reduced the methane capacity for a sample from the Pocahontas seam by 26.5% [24]. As little as 0.1%, increase (0.54 % to 0.63%) decreased CO_2 capacity 14% [23]. This implies that CO_2 is more sensitive (at this rank) to moisture content than CH_4. To better define the influence of moisture on capacity reduction, the appropriate moisture content of 0.65% [25] as received was added to the coal model. Sixty-six water molecules were manually placed close to (2 Å) oxygen atom, as it is expected that the water is associated with the oxygen functionality of the coal [24]. Fifty-eight percent of the oxygen atoms in the coal are associated with a water molecule. The structure was minimized and allowed to swell. This structure is shown in *Figure 5*. The POR program was again employed to determine the open porosity with water molecules present. There is a generalization that water competes for adsorption sites on the coal surface, resulting in reduced capacity for sorbate adsorption [26]. Also, capacity can be reduced due to a reduction of pore size, due to water adsorption, or due to coal swelling [27]. Inclusion of 0.65% moisture by mass (66 molecules) resulted in a volume change of +1.2% and a decrease of available pore volume of 2.6% for CO_2 (a reduction of an estimated 6 CO_2 molecules) and 3.7% for CH_4 (a reduction of an estimated 5 CH_4 molecules) based on Heuchel's *et al.* critical pore sizes. It is important to note that this pore volume reduction is due to a static water molecule physically blocking entry into pore space or simply by occupying pore volume. The chemical influence of the water molecule will extend beyond the van der Waals radii. The finding implies that water molecules do not effectively compete with CO_2 or CH_4 for adsorption sites at this rank. Rather the presence of water, swelling, or an influence on the transport of CO_2 into the pore system is

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responsible for the moisture influence. We plan on using higher-level molecular modeling approaches, which are likely to shed more light on the issues.
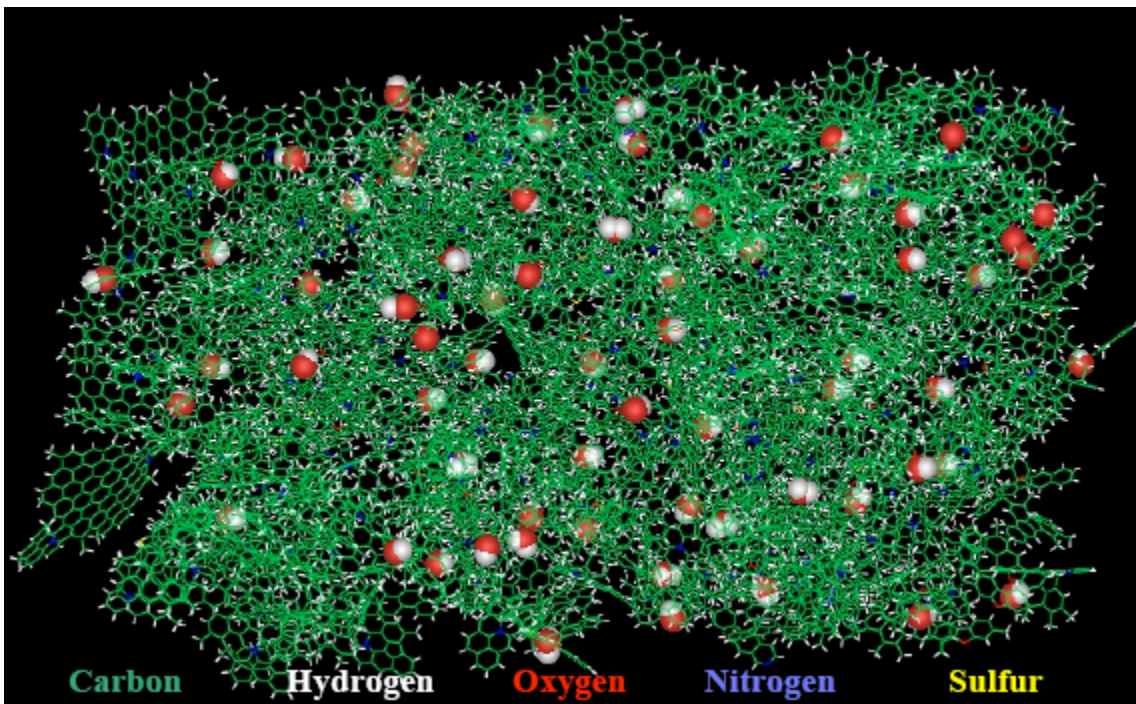
Figure 5:The molecular representation of Pocahontas No. 3 bituminous coal with 66 water molecules added. This is the as-received moisture found in Argonne Pocahontas No. 3 coal.

CONCLUSIONS

A large-scale molecular representation of Pocahontas No. 3 coal was constructed based on average structural parameters, but also included a reasonable molecular weight distribution obtained from the combination of LDMS, and HRTEM lattice images. This structure was then used to visualize the inclusion of CO_2, CH_4, and water. The pore size distribution of the model was determined using the POR program. POR was also used to evaluate accessibility of CO_2 and CH_4. The following was determined.
  i) At 10 bar gas pressure CO_2 capacity is 229 molecules (calculated from literature data), the coal swelled 4% volumetrically and the swelling was anisotropic, greatest in the direction perpendicular to the alignment/bedding plane.
  ii) Porosity closed to helium was small (0.5% of the pore volume)
  iii) Ninety percent of the pores were smaller than 8 Å in size.
  iv) Carbon dioxide can access 81% of the pore volumes in a rigid model, while CH_4 can access 68% of the pore volume.
  v) Inclusion of 0.68 wt% moisture resulted in a 1.2% volume increase due to swelling.
  vi) With 0.68% moisture there is a decrease of approximately 2.6% of accessible pores to CO_2, thus moisture is not effectively competing for sorption sites and the

influence of moisture is expected to be swelling, transport related, and or pore blocking.

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LIST OF ACRONYMS AND ABBREVIATIONS

CCSD	coupled clusters with single and double excitations
DFT	density functional theory
HF	Hartree-Fock
HRTEM	high-resolution transmission electron microscopy
MC	Monte Carlo
MM	Molecular Mechanical
MPPT	Möller-Plesset perturbation theory
QM	Quantum Mechanical

TJDM1   Tom Jeffry David Madura 1 water model