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# Chemically bound water in brown coal and impact of ambient oxidation on its characteristics

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ABSTRACT

This study adopted a molecular dynamics simulation technique to investigate characteristics of chemically bound water in brown coal and effects of ambient oxidation and temperature at varying total system water contents (TSWC). The Hatcher's brown coal model structure was utilized to simulate a non-altered lignite-water system. An oxidized system was created by modifying the Hatcher's model structure with an application of oxidation reaction pathways that have been reported to be spontaneous at ambient condition. Elemental analysis indicated that the oxidized system was equivalent to about 103-day aerial oxidation of the Victorian brown coal at 35 °C. Three types of chemically bound water, namely $W_H$, $W_{LH}$ and $W_{NF}$ were defined from the molecular dynamics perspective considering hydrogen(H)-bonding and distance from lignite surface. Effects of ambient oxidation and temperature on contents of each type of chemically bound water, defined as percentage of corresponding water molecules with respect to TSWC (e.g., $P_H$ and $P_{NF}$), were analyzed separately. Shear viscosity and diffusion of water in brown coal were investigated and linked to chemically bound water contents. Results indicate that characteristics of chemically bound water are influenced by ambient oxidation, temperature and TSWC. The property of $W_H$ governs the viscous characteristics of water in brown coal.

## 1. Introduction

Coals are declining energy resources in the world due to their high pollution levels and ever-falling costs for renewable energy technologies. In Australia, open-cut coal mines are subject to gradual closure followed by rehabilitation that may as well affect the surrounding environment of the coal and hence its behaviour. It has been recognized since the earliest mine operation that mining activity gives rise to changes in coal properties due to extensive exposure of coals to atmospheric air (i.e., oxidation). Mine closure and rehabilitation processes may be accompanied by re-wetting process of such altered brown coals as mined holes are likely to be inundated (e.g., rehabilitated as a lake) [1]. However, little study has been reported on interactions of water with the altered coal and resulting characteristics. Lack of understanding on such alteration will bring about geotechnical engineering problems (e.g., long-term land subsidence or swelling behaviour of major geological formations including the coal) that risks to infrastructure in the vicinity [2].

A lignite-water system, so-called brown coal, is a colloidal system containing up to 230 wt% moisture relative to the dry solids mass [3]. From the geotechnical engineering perspective, interactions between geomaterial and water are critical for determining many engineering properties related to strength and deformation [4,5]. For example, shear strength of geomaterials depends on a cohesion term which is influenced substantially by the characteristics of water-solid interaction [4]. Due to the viscous characteristics, chemically bound water is especially important when it comes to time-dependent behaviour such as creep [6,7]. However, chemically bound water in brown coal has not been defined clearly from the molecular dynamics perspective and a range of reported values is wide, i.e., 36 ~ 78% of total water [8–11].

Furthermore, brown coal has a high propensity to irreversibly adsorb oxygen at ambient temperatures when exposed to oxygen-containing environment [12]. The oxidation of brown coal is known to affect the coal-water interactions and such effects are accompanied by a marked micro-structural deformation and hence engineering property alteration [13,14]. However, the effects of oxidation are controversial – some reports have concluded that oxidation enhances coal-water interactions evidenced by swelling behaviour upon oxidation [15,16], while others have reported oxidation-induced volumetric shrinkage [17,18]. Such inconsistency may be caused by failure in isolating factors of interest and therefore unanimous explanation is in demand.

This study investigated characteristics of chemically bound water in brown coal and effects of ambient oxidation and temperature. Chemically bound water was defined from the molecular dynamics perspective and then effects of temperature and ambient oxidation on its content, diffusion coefficient and shear viscosity were studied at

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varying total system water contents. A computational technique, molecular dynamics simulation was utilized in this study to capture dynamics of hydrogen bonding. Because of the complex heterogeneous nature of brown coal, it is not practical to investigate such molecule-level changes in a laboratory. Computational techniques have the advantage of isolating factors of concern in a cost-effective time-efficient way, and have successfully been applied for a broad range of coal study including interactions between gas/liquid and coal structure [19,20], chemical reactions in coals [21], and the deformation behaviour of coals [22].

## 2. Molecular model structure of lignite

Brown coal consists mainly of carbon, oxygen, and hydrogen. For example, the Victorian brown coal presents approximately 67% C, 28% O and 5% H and 50 ~ 70% of the oxygen is in the form of carboxylic acid and phenolic acid groups [10,23]. Many model structures of brown coal have been developed based on elemental analysis and further characterization such as $^{13}$C-NMR, FTIR, and analytical pyrolysis [21,22,24]. For instance, the Hatcher's model structure has the chemical formula of $C_{108}H_{102}O_{34}$ constructed using data from analytical pyrolysis and $^{13}$C-NMR spectroscopy. Among many other model structures, the Hatcher's one has elemental composition similar to the Victorian brown coal and the molecular size well represents a major fraction of the coal [25]. Hence, this study utilized the Hatcher's brown coal model structure in simulating lignite-water interactions.

Brown coals often exist in oxygen-free-groundwater-saturated environments. Any disturbance of such environments, including mining activities and cracking, will trigger weathering processes. Such an ambient weathering process consists mainly of oxidation of the coal [26]. Oxidation can proceed until the carbon and hydrogen contents reach 60 ~ 65% and 2 ~ 3%, respectively [27]. Below 70 °C however, rates of oxidation are generally low enough not to proceed much beyond forming acid functional groups [28,29].

Hence, an oxidized lignite molecule was generated by converting aliphatic groups of the Hatcher's model structure into acidic functional groups in the form of hydroxyl, carbonyl, and carboxylic groups as shown in Fig. 1. Deliberately chosen reaction pathways of brown coal oxidation and their thermodynamic data are tabulated in Table 1. Those were selected as they have been known to be spontaneous at ambient temperature [28,29]. Aromatic carbons remained unchanged because they are very stable upon oxidation [30]. According to oxygen balance before and after coal oxidation experiment on the Victorian brown coal [12], each reaction had different number of occurrence and thus similar mass balance of products was reproduced. All free radicals on the coal molecule were terminated by capturing H or OH from water [31].

The oxidized structure has approximately 7% loss of carbon, 5% loss of hydrogen, and 18% more organically bound oxygen than the original coal, which is equivalent to about 103-day aerial oxidation of Victorian brown coal at 35 °C [12]. In specific, one mole of carboxylic group, three moles of carbonyl group, and four moles of hydroxyl group were generated by the addition of 19 mol of $O_2$. As a result of oxidation, the original lignite molecule was degraded into four smaller molecules.

## 3. Chemically bound water in brown coal

Water in the brown coal is an essential part of the system. The Victorian brown coals contain up to 230 wt% moisture, relative to the dry solids mass, due to their good hydrophilicity caused by abundant oxygen-containing functional groups which interact with water molecules via hydrogen bonds [3,33]. The water in brown coal is generally classified into four types of water [11,34]: bulk, capillary, multilayer, and monolayer water. Bulk water has the properties of free water while the properties of capillary, multilayer, and monolayer water are influenced by surface forces (i.e., lignite-water interactions). Thus, a total of monolayer, multilayer and capillary water should be defined as chemically bound water. The amount of chemically bound water in brown coal has been reported to be 36 ~ 78 wt%, that increases with increasing oxygen content of the coal [8–10].

Such chemically bound water is often referred to as "non-freezing water" and is known to be adsorbed on the internal surface of the coal and/or in micropores through specified interactions such as hydrogen (H)-bonds [10,35]. Water becomes non-freezing when the number of water molecules involved in a molecular cluster is less than around ten [10,36]. If ten water molecules in a cluster are uniformly dispersed, water molecules surrounding an oxygen atom on a lignite molecule, with about 6 Å cutoff distance, represent non-freezing water. This cutoff distance also represents the farthest distance between the coal surface and a water molecule located in the middle of a spherical micropore, i.e., the maximum radius of the micropore [37]. Advanced laboratory techniques allowed to find that water molecules just within about two layers of water (6 ~ 7 Å) from a hydrophilic surface present greater viscosity and heat capacity than bulk water, i.e., chemically bound [38,39]. Therefore, coal oxygen is chemically associated with monolayer and bilayer water and a total of them can be categorized as non-freezing water.

However, H-bonding must be considered to explain the non-freezing characteristic [39,40] and a better definition of such chemically bound water is required. From the molecular dynamics perspective, water molecules can be defined to be H-bonded if distances and an angle simultaneously satisfy the following criteria [41,42]: $R_{OO} \leq 3.60$ Å, $R_{OH} \leq 2.45$ Å, $\phi \leq 30^{\circ}$ where $R_{OO}$ is the distance between acceptor oxygen ($O_a$) and donor oxygen ($O_d$), $R_{OH}$ is the distance between $O_a$ and donor hydrogen ($H_d$), and $\phi$ is the valence angle $H_d$–$O_d$···$O_a$. From the radial distribution function between coal oxygen and water oxygen, water molecules in the first solvation shell with a 3.7 Å cutoff distance depicted monolayer water ($W_{mono}$) containing the water molecules H-bonded to lignite ($W_H$).

In this study, chemically bound water was divided into three types of water, namely $W_H$ (blue $H_2O$ in Fig. 1), $W_{LH}$ (red $H_2O$ in Fig. 1) and $W_{NF}$. $W_{NF}$ (non-freezing water) was defined as a total of $W_H$ (water molecules H-bonded to lignite) and $W_{LH}$ (water molecules, within the bilayer ($W_{bi}$) with a 6.6 Å cutoff distance, linked to at least one of $W_H$ via H-bonds). Hereafter, the term "chemically bound water" refers to the non-freezing water. Water molecules beyond the bilayer could be chemically bound, but the quantity and bonding strength are insignificant as compared with $W_{bi}$ [39,40]. Hence, this study did not consider chemically bound water molecules beyond the second solvation shell from the coal surface.

## 4. Simulation details

This study investigated effects of ambient oxidation and temperature on lignite-water interactions and resulting characteristics utilizing molecular dynamics simulations on the non-altered (i.e., the original Hatcher's model structure) and the oxidized lignite molecules at varying water contents (0.3, 0.7, 1.1, 1.5, 1.9, and 2.3 by weight). The water contents of 1.1 ~ 2.3 represent a typical range of natural moisture contents of the Victorian brown coal [8]. A lignite molecule was placed in a three-dimensional box with periodic boundary conditions that eliminate edge effect [43]. Water molecules were then added to surround the lignite molecule as uniformly as possible. The number of placed water molecules and the initial size of simulation box varied with each water content. For example, 249 water molecules were added to a simulation box of 24 Å by 31 Å by 13.5 Å for water content of 2.3.

The system was first equilibrated in a constant pressure and temperature (NPT) ensemble using a Berendsen thermostat and barostat [44]. The pressure and temperature of the system were maintained at 1 atm and 298 K, respectively. A time step of 1 fs was used to integrate the equation of motion. Cutoff distances of 10.5 Å and 15.5 Å were employed for van der Waals and long-ranged electrostatic interactions, respectively. The electrostatic interactions were simulated with the