

Received December 20, 2017; reviewed; accepted February 5, 2018

Effect of oxidation on the wetting of coal surfaces by water: experimental and molecular dynamics simulation studies

Enze Li ¹, Ying Lu ¹, Fangqin Cheng ¹, Xuming Wang ², Jan D. Miller ²

¹ Institute of Resources and Environmental Engineering, State Environmental Protection Key Laboratory of Efficient Utilization Technology of Coal Waste Resources, Shanxi Collaborative Innovation Center of High Value-added Utilization of Coal-related Wastes, Shanxi University, No 92 Wucheng Road, Taiyuan, Shanxi 030006, China

² Department of Metallurgical Engineering, College of Mines and Earth Sciences, University of Utah, 135 S 1460 E 412 WBB, Salt Lake City, UT 84112, USA

Corresponding authors: jan.miller@utah.edu (Jan D. Miller), cfangqin@sxu.edu.cn (Fangqin Cheng)

Abstract: The wettability of coal surfaces by water continues to be one of the key factors which determines the success of coal flotation. Consequently, oxidation of coal surfaces is a fundamental issue of interest. In this work, the effect of oxidation on the wetting of coal surfaces and the interaction between water molecules and oxygen-containing sites at the coal surface were investigated based on advancing/receding contact angle measurements and molecular dynamics simulations. For the simulation studies, a flat coal surface was constructed with the assistance of the molecular repulsion between graphite surfaces and the assembly of Wisser coal molecules. Our results indicated that the simulated advancing and receding contact angles were very similar, and both of them decreased, as expected, with an increase of hydroxyl sites at the coal surface. The good agreement between the simulated advancing/receding contact angles and the experimental receding contact angle values suggested that the configuration of the systems and the set of parameters for the simulation were appropriate. The spreading of water is mainly due to the hydrogen bonds formed between the interfacial water molecules and the hydroxyl sites at the coal surface. The hydroxyl groups exhibit stronger hydration capacity than other oxygen-containing groups according to the calculated hydrogen bonds and interaction energies.

Keywords: oxidation, coal surfaces, wettability, contact angles, molecular dynamics simulation, hydrogen bonding

1. Introduction

Congratulations to Professor Laskowski for 60 years of teaching/research and for his many contributions in the area of mineral flotation chemistry. These contributions are quite significant, including original contributions in the area of coal flotation chemistry and the preparation of his book, *Coal Flotation and Fine Coal Utilization*, published in 2001 (Laskowski, 2001). Much of the fundamental information on coal flotation chemistry is summarized therein and the book provides a valuable resource for education and research. It is appropriate to continue to extend and/or confirm our understanding of coal flotation chemistry and, in this regard, the wetting characteristics of oxidized coal have been studied using molecular dynamics simulation, as reported herein, to help celebrate Janusz's career.

Froth flotation separation is based on control of the surface state of suspended particles and is the preferred process for the recovery of fine coal in plant operations (Boylu and Laskowski, 2007; Fuerstenau et al., 2007; Ding, 2009; Xu et al., 2011; Liang et al., 2015; Xing et al., 2017). In the case of coal flotation, bubble-coal particle attachment during film thinning, rupture and displacement is a fundamental event which depends on the characteristics of interfacial water molecules and their

interaction at the coal surface (Laskowski, 1994; Pan et al., 2012). In order to enhance the air bubble-coal surface attachment, diesel oil or kerosene is usually used as a collector to improve the hydrophobicity of the coal surface (Yesilyurt et al., 2017). However, the collector becomes ineffective to float oxidized coals or low rank coals (Dey, 2012). This is due to the abundance of oxygen-containing hydrophilic functional groups at coal surfaces (Quast and Readett, 1987), which can stabilize the formation of a thin water film, and inhibit the adhesion and spreading of oil droplets at the coal surface. Therefore, understanding the wetting properties of coal surfaces of different rank, with different levels of oxygen content, and having different states of oxidation, is of interest, as discussed in the literature (Ye et al., 1988; Ye and Miller, 1988).

The oxidation of coal surfaces by weathering or during storage and transportation, especially for coals kept at strip mines, is ubiquitous and inevitable (Fuerstenau et al., 1987; Bolat et al., 1998). According to previous reports, the oxygen functional groups at a coal surface after oxidation mainly include OH-phenolic, C=O carboxyl, -C-O-C- etheric, etc (Blom et al., 1957; Yarzab et al., 1979; Pawlik, 2008; Su et al., 2017). The wettability of the coal surface by water, which corresponds to the oxygen content, can be directly determined via contact angle measurements (Sokolović et al., 2006; Arkhipov et al., 2011). However, the experimental contact angle measurements do not provide molecular level information regarding the interaction of water molecules with the extent of surface oxidation and hydrophilic functional groups at coal surfaces. Moreover, understanding of the macroscopic contact angle must consider the relative proportions of hydrophobic groups and hydrophilic groups at the coal surface (Ye et al., 1988; Ye and Miller, 1988). Such understanding can be improved from molecular dynamics simulation (MDS).

Currently, molecular dynamics simulation (MDS) is considered an efficient means to reveal internal atomic interactions for multi-scale systems (Yan and Yuan, 2016; Zhang et al., 2016; Li et al., 2017b; Liu and Guo, 2017; Ou et al., 2017). Several previously reported works have involved analyses of the interfacial interactions at water/mineral surfaces using MDS (Van Niekerk and Mathews, 2011; Du et al., 2012). MDS has been used to simulate contact angles on selected sulfide mineral surfaces by water (Jin et al., 2014), and the simulated contact angles were found to be consistent with the experimental values. More recently, bubble attachment at a hydrophobic surface has been simulated using MDS (Jin et al., 2018). These works provide information on the interaction between water molecules and mineral surfaces and the dynamic properties of interfacial water at the atomic level. However, the mineral surfaces studied are usually crystalline, and the selected surfaces are homogeneous. Little research has been conducted by MDS related to the heterogeneity of amorphous coal surfaces. Although Zhang et al. (2015) systematically investigated the interaction of three different collector oil drops with model surfaces of Wiser coal in the aqueous phase through MDS, the wettability of the coal surfaces, the interfacial water structure, and the interaction between water molecules and oxygen functional groups of the coal surfaces were not discussed.

In order to extend and improve our understanding of the effect of oxidation on coal flotation, the wetting of coal surfaces by water was investigated by employing a combination of contact angle measurements and molecular dynamics simulations. Coal surfaces, with various extents of oxidation, were used for the contact angle experiments. Surface oxidation was achieved by reaction with hydrogen peroxide under different conditions. For MDS analyses, the oxygen content of modeled coal surfaces was varied by tuning the number of -OH groups at the surface. The sessile drop contact angle was simulated with the further analysis of dynamic properties and micro-structural features of interfacial water. This work constitutes a substantial step forward in understanding the flotation of oxidized coal, and provides new insights into means by which flotation performance may be improved.

2. Experimental procedures

2.1 Materials

The coal selected for this work was a high-grade bituminous coal obtained from the Liulin coal field (Taiyuan, Shanxi, China). Demineralization was performed by the float-sink method in heavy liquid at 1.3 g/cm³ to minimize the mineral matter effect during experiments. The ash content of such coal particles (density <1.3 g/cm³) is 2.02%. According to the elemental analyses of the coal samples, the content of C and O were 88.12% and 3.44%, respectively. The hydrogen peroxide (30 wt%) was

purchased from Tianjin Beichen Reagent Co. Ltd. Millipore water (Milli-Q, Millipore Corp., 18.2 M Ω cm) was used in all experiments.

2.2 Oxidation of coal surfaces

For each oxidation experiment, typically, 6.0 g of coal (particle size less than 74 μ m) was added to 20.0 cm³ of H₂O₂ in a round-bottomed flask. Then, the mixture was agitated for 6 h at 40 °C. After the agitation, the final oxidized coal was collected through filtration, and washed at least three times with distilled water followed by anhydrous ethanol. Finally, the obtained oxidized coal sample was dried in a vacuum drying oven at 40 °C for 12 h. The content of oxygen on the surface of fresh coal and oxidized coal was determined by X-ray photo electron spectroscopy (XPS). In order to obtain various coal samples with different extents of oxidation, the concentration of H₂O₂, oxidation times, and oxidation temperatures were varied, as described in Table 1.

Table 1. Different conditions used to oxidize coal surfaces

No.	Concentration of H ₂ O ₂ (wt %)	Volume (cm ³)	Temperature (°C)	Time (h)
1	0	0	0	0
2	10%	20	40	6
3	30%	20	40	6
4	30%	20	80	6
5	30%	20	80	10
6	30%	20	80	16

2.3 Contact angle measurements

A sample of 0.3 g of ultra-fine coal particles was pressed under about 10 atm using a tablet machine for 2 min to form a tablet. In order to reduce the capillary effect generated by small pores in the coal on the contact angle measurements, the tablets were kept in a dryer with saturated NaCl solution for 48 h before making contact angle measurements by the captive-bubble method (Drelich and Miller, 1995; Jin et al., 2014; Marmur et al., 2017) using a DSA100 contact angle analyzer (Krüss, Germany).

As previously reported (Drelich and Miller, 1995), for all measurements, the solid sample was placed in a rectangular glass chamber on two stable supports with flat surfaces. Then, the glass chamber containing the sample was filled with water. A small air bubble was made at the tip of a U-shaped needle using a micro-syringe, and then the bubble was attached at the coal surface. The three-phase contact line of the gas bubble was made to advance or retreat by adding or withdrawing a small volume of air and the advancing and receding contact angles, respectively, were measured on both sides of the gas bubble after 30 sec (the average value was reported). The needle remained in contact with the air bubble during all measurements but no distortion of the bubble shape was allowed to affect the contact angle measurements.

3. Simulation section

3.1 Preparation of coal surface

The previously proposed molecular structure of Wiser coal (Wiser, 1984; Zhang et al., 2015), shown in Fig. 1, was used to build the bituminous coal surface for simulations. The construction of a flat coal surface became very critical for the sessile drop contact angle simulation due to the irregular features of the coal surface. In this work, graphite layers were used to assist in constructing the flat coal surface. First, 15 coal molecules were introduced randomly into the simulation box, and then two three-layer graphite sheets were placed on both sides of the rough coal molecular layers as close to the coal surface as possible (Fig. 2(a)). Then, the Cartesian coordinates of all graphite atoms were fixed and energy minimization of the system was conducted. After energy minimization, the coal layer became denser, and there was a gap between the coal layer and the graphite due to short range repulsive forces. Then, the graphite layers were moved closer to the coal surface, and energy minimization for the system was conducted again (Fig. 2(b)). This energy minimization procedure was repeated several more times until

the thickness of the coal layer was about 13 Å (Fig. 2(c)). After reaching a thickness of 13 Å, dynamics simulation was conducted for 100 ps to relax and equilibrate the coal layer (Fig. 2(d)). Next, the graphite layers were removed, and the flat coal surface was obtained (Fig. 2(e)). The density of the coal layer was about 1.20 g/cm³. Finally, the water drops (diameter 30 Å) (Xu et al., 2011) or water layers (thickness 5 Å), composed of 570 H₂O molecules, were placed on the coal surface to simulate the advancing contact angle (Fig. 2(f-g)) and receding contact angle (Fig. 2(h-i)), respectively.

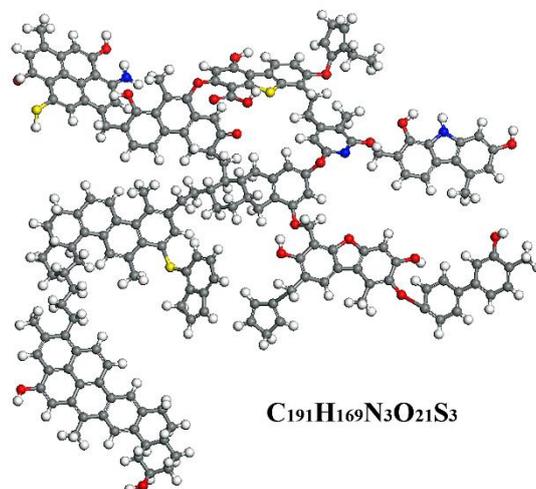


Fig. 1. Molecular structure of Wisser coal. Red: O; yellow: S; blue: N; gray: C; white: H

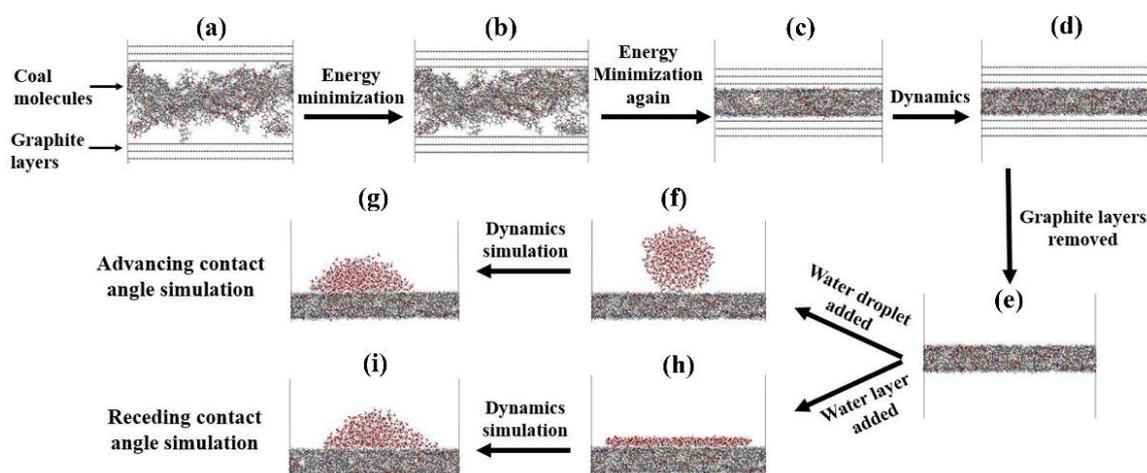


Fig. 2. Preparation of the flat coal surface and configuration of systems for contact angle simulations. Red: O; yellow: S; blue: N; gray: C; white: H

3.2 Simulation systems

In order to study the effect of surface oxidation on the wettability of the coal surface, two coal surface states, each with a different oxygen content, were used for comparison. In one case, all the OH groups of the original Wisser coal molecule were removed and replaced by H atoms. In the second case, 40 of the H atoms connected to carbon atoms in the original Wisser coal molecule were replaced by OH groups. The molecular formula and composition of the above systems are listed in Table 2. It is noted that the first layer of atoms which is exposed to air was considered as the coal surface (< 3 Å). The coal surface was occupied by about 86.4% aromatics and 13.6% aliphatics. Except for the oxygen and carbon content, all the other conditions were the same for both cases. For convenience, we refer to the system in which the coal molecule is the original Wisser coal molecule as 'CA_original' while those in which all the OH groups are removed or more OH groups are added to the original coal molecule as 'CA_no OH' and 'CA_more OH' respectively.

Table 2. Composition of coal and coal surfaces for simulation

Systems	Molecular formula	Coal		Coal surface				Carbon content (%)	Oxygen content (%)
		Carbon content (%)	Oxygen content (%)	No. of oxygen-containing groups					
				-COOH	-C-O-C-	-CO-	-OH		
CA_no OH	C ₁₉₁ H ₁₆₉ N ₃ O ₁₀ S ₃	82.43	6.47	4	9	3	0	81.52	7.09
CA_original	C ₁₉₁ H ₁₆₉ N ₃ O ₂₁ S ₃	78.10	11.45	4	11	3	38	74.14	15.38
CA more OH	C ₁₉₁ H ₁₆₉ N ₃ O ₆₁ S ₃	64.11	27.30	2	19	2	149	62.73	30.41

3.3 Molecular dynamics simulation

All simulations were conducted in orthorhombic simulation cells with the parameters $\alpha=\beta=\gamma=90^\circ$, $a=b=75 \text{ \AA}$, $c=100 \text{ \AA}$, and periodic boundary conditions. After initial configuration, energy minimization was carried out for each system. Then, 1 ns simulation with 100 fs intervals and 1 fs time step in the NVT ensemble (Pacheco-Sánchez et al., 2003; Liang et al., 2016) was performed, and the last 200 ps were used to obtain MD trajectory data for further analysis. The polymer consistent force field (PCFF) (Sun, 1994; Zhang et al., 2015; Li et al., 2017a), the extended simple point charge (SPC/E) water model (Berendsen et al., 1987; Du and Miller, 2007) and the Nosé-Hoover thermostat (298 K) (Nose, 1991; Zhang et al., 2015) were used for all simulations. For all systems, the atomic charges of coal layers were calculated automatically by the force field. In the simulation, all atoms in the coal molecules were fixed.

4. Results and discussion

4.1 Experimental contact angle

Changes in contact angle can directly reflect the variation in wettability of coal surfaces (Drelich et al., 2000). The measured advancing and receding contact angles versus the oxygen content of the coal surfaces at room temperature are plotted in Fig. 3. It can be seen, as expected, from Fig. 3 that the advancing contact angles are obviously larger than the receding contact angles, which can be ascribed to the hysteresis caused by the roughness and heterogeneity of the coal surface (Marmur et al., 2017). These results are consistent with previous reports (Pawlik, 2008). In addition, Fig. 3 also shows that with an increase in oxygen content of the coal surface, the advancing contact angle decreases slightly, while the receding contact angle decreases more significantly. These results indicate that the polarity of the coal surface increases with an increase in oxygen content, and the interaction between water and the coal surface is dominated by the properties of the coal surface.

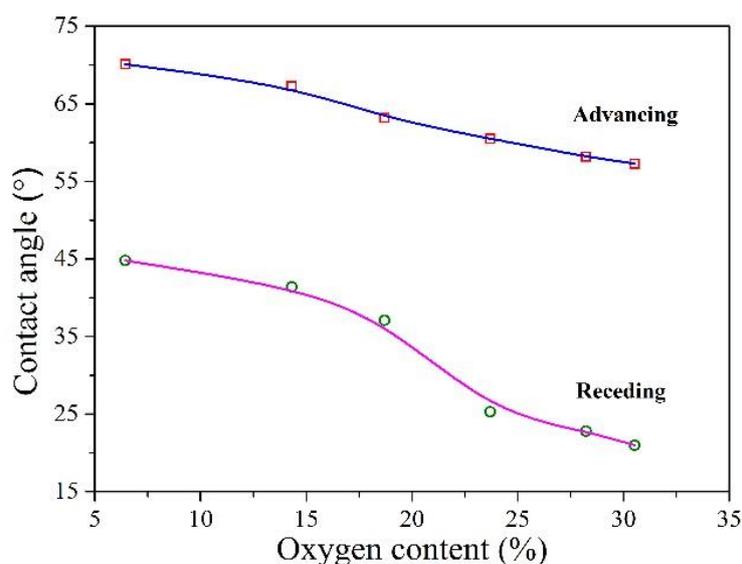


Fig. 3. The measured captive bubble advancing and receding contact angles as a function of the oxygen content of the coal surface as determined by XPS

4.2. Simulated contact angle

Wettability of the coal surfaces with differences in oxygen content were evaluated by simulated contact angle measurements. The spreading of water drops and receding of thin water films at different coal surfaces after simulation are shown in Fig. 4. These simulation results reveal the extent of interaction between the water molecules and the coal surface. It is well known that the contact angle is the angle between the gas-liquid-solid phases according to Young's equation (Young, 1805). In order to determine MDS contact angles, it is critical that the boundaries be defined. All space coordinates of the water molecules were exported and projected on both the xz plane and the yz plane. Then, the edges of these two-dimensional drops were fitted as smooth curves on the basis of the coordinates. The α and β shown in Fig. 5 are contact angles measured from projections on the xz plane and yz plane, respectively. The average of α and β is considered as the contact angle for the advancing and receding sessile drops at the coal surface, and these contact angle values are presented in Table 3. As expected, the wetting of the different coal surfaces varies with hydroxylation of the coal surface as revealed by the contact angles reported in Table 3. The significance of hydroxylation in the wetting of oxide surfaces was published recently (Shrimali et al., 2016).

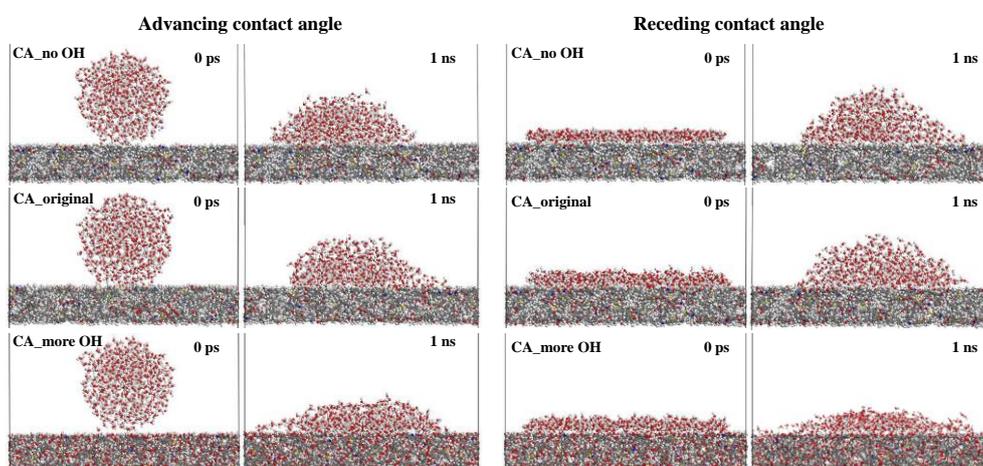


Fig. 4. Snapshots of configurations before and after 1 ns simulation for different coal surfaces

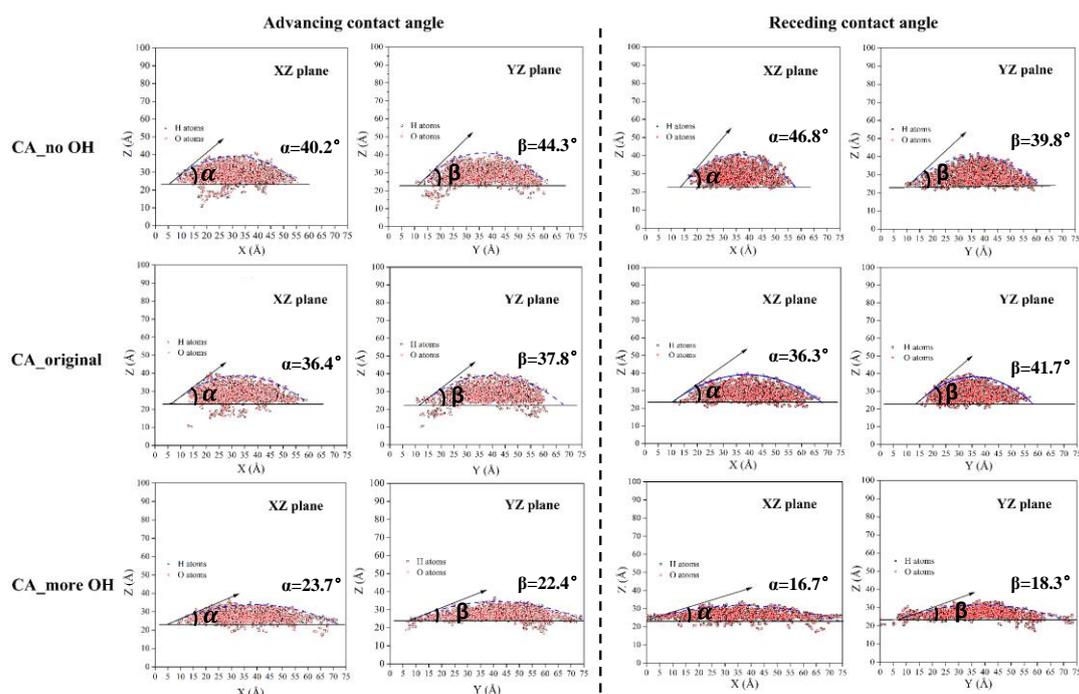


Fig. 5. The contact angles obtained on the xz planes and the yz planes for different systems

Table 3. Simulated and experimental contact angles of water drops at different coal surfaces. The experimental values are interpolated values calculated from the curves shown in Fig. 3

Systems	Simulated						Experimental	
	Advancing			Receding			Advancing	Receding
	α	β	Average	α	β	Average		
CA_no OH	40.2°	44.3°	42.3°	46.8°	39.8°	43.3°	69.9°	44.5°
CA_original	36.4°	37.8°	37.1°	36.3°	41.7°	39.0°	66.0°	40.3°
CA_more OH	23.7°	22.4°	23.1°	16.7°	18.3°	17.5°	57.3°	21.0°

It can be seen from Table 3 that for all systems the MDS advancing and receding contact angles are very similar to each other, suggesting that the coal surfaces for simulation are smooth and homogenous. Although the experimental advancing and receding contact angles (Table 3) are very different, gratifyingly, the MDS advancing/receding contact angles are close to the experimental receding values, which indicates that the simulated coal surfaces are suitable to represent the wettability of the coal surfaces with different oxygen content. The large difference between the simulated and measured advancing contact angle may be ascribed to the roughness and heterogeneity of the true coal surface. The roughness and heterogeneity of the coal surface used for measuring the contact angle can result in hysteresis which does not occur for the smooth and uniform coal surfaces in the simulation. In addition, both the MDS advancing and receding contact angles decrease as the hydroxyl content of the coal surface increases, demonstrating that the increase of hydroxyl content results in a more hydrophilic coal surface.

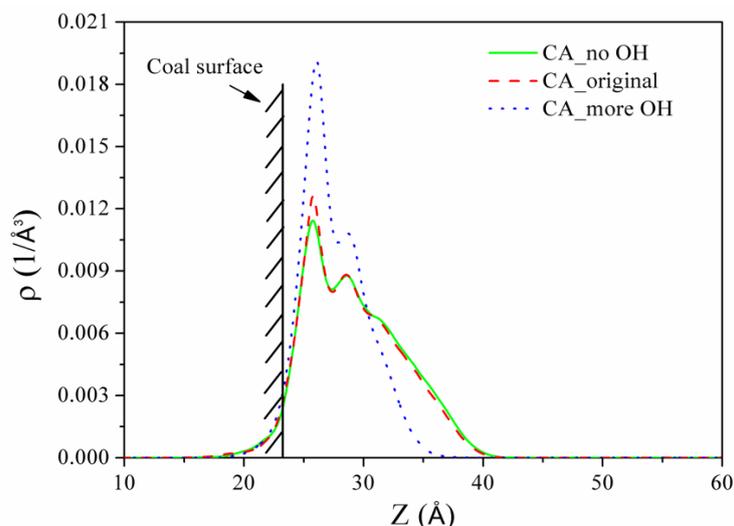


Fig. 6. Density profiles of water molecules along the z-axis for different coal surfaces

4.3 MDS interfacial water structure

4.3.1 Density profile of water molecules

In order to obtain the distribution of water molecules at different coal surfaces, the density profiles of water molecules in the entire water drop for different coal surfaces were calculated along the z-axis, and the results are shown in Fig. 6. These density profiles reflect the interfacial water structure at different coal surfaces. It is apparent from Fig. 6 that all the profiles have one distinguishable peak near the coal surface followed by one weak peak. The first peak for the 'CA_more OH' system is much stronger than that for the other two systems, suggesting that a larger number of water molecules are polarized at the hydroxylated coal surfaces having the highest content of oxygen. These results explain the higher wettability of the coal surface for the 'CA_more OH' system due to the largest number of polar OH groups. In addition, the water molecules located in the range of the first peak are considered as the interfacial water molecules, which are examined in subsequent discussions.

4.3.2 Dynamic properties of water molecules

Mean square displacement is always used to reveal the dynamic properties of molecules/atoms. Fig. 7 shows the displacement curves for molecules in water drops at different coal surfaces. These results were calculated from Eq. 1 (Xu et al., 2011; Li et al., 2015):

$$\text{Mean square displacement (t)} = \frac{1}{N} \sum_{i=1}^N \langle |r_i(t) - r_i(0)|^2 \rangle \quad (1)$$

where N is the number of water molecules, and $r_i(t)$ denotes the position of molecule i at time t . It is clear that mean square displacement indicates the motion of molecules with respect to their original position, and the mean square displacement value is related to the diffusion coefficient (D) as follows:

$$D = \frac{1}{6} \lim_{t \rightarrow \infty} \frac{d}{dt} \sum_{i=1}^N \langle |r_i(t) - r_i(0)|^2 \rangle. \quad (2)$$

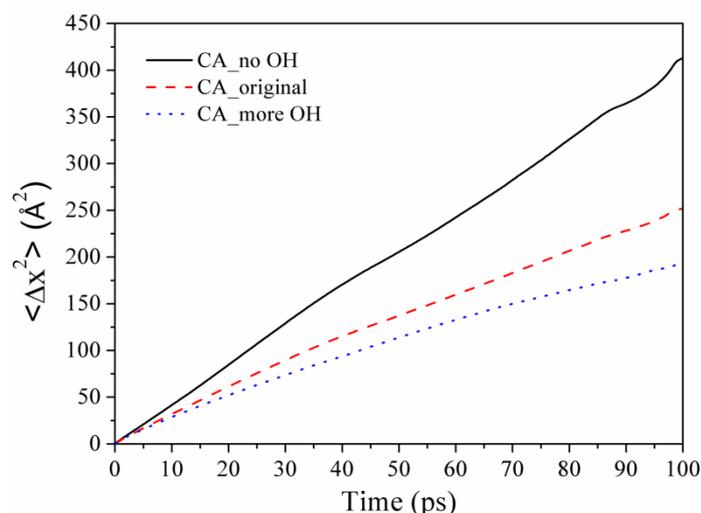


Fig. 7. Mean square displacement (the mean square displacement of the particles with respect to their original position is obtained as the second moment of their distribution at $t > 0$) of water molecules in different systems

Table 4. Diffusion coefficient (D) for interfacial water molecules at different coal surfaces as obtained from their mean square displacements

System	D (10^{-5} cm ² /s)
CA_no OH	6.697±0.001
CA_original	4.072±0.001
CA_more OH	3.145±0.001

From the mean square displacement curves shown in Fig. 7, it is obvious that the mobility of water molecules significantly slows down with an increase in the hydroxyl content of the coal surface. The displacement and motion of interfacial water molecules are related to the existence of hydroxyl sites at the coal surface, which interact with water molecules through hydrogen bonds and slow the water motion. The diffusion coefficients (D) obtained from their mean square displacements are listed in Table 4, and support the previous statements. The diffusion coefficients of water molecules are consistent with the strength of the wetting characteristics of the coal surface (Xu et al., 2011). The higher the hydroxyl content of the coal surface, the more slowly the interfacial water molecules spread.

4.3.3 Radial distribution functions

The structure and ordering of water molecules in water drops at different coal surfaces can be observed from the radial distribution function (RDF) (Li et al., 2013; Chong and Dutt, 2014). Fig. 8 shows the oxygen-hydrogen radial distribution functions for interfacial water molecules at different coal surfaces. It is observed that all the curves have one notable peak at a distance of 0.98 Å, after which several broad

weak peaks appear (Fig. 8). The first peak represents the first tight layer of hydrogen atoms from other water molecules around one oxygen atom. It is clear from Fig. 8 that the peak for the 'CA_no OH' system is about the same as that for the 'CA_original' system, and both of these cases are significantly higher than that for the 'CA_more OH' system, elucidating that the structure and ordering of the interfacial water layer is dramatically influenced by the density of oxygen atoms at the coal surfaces.

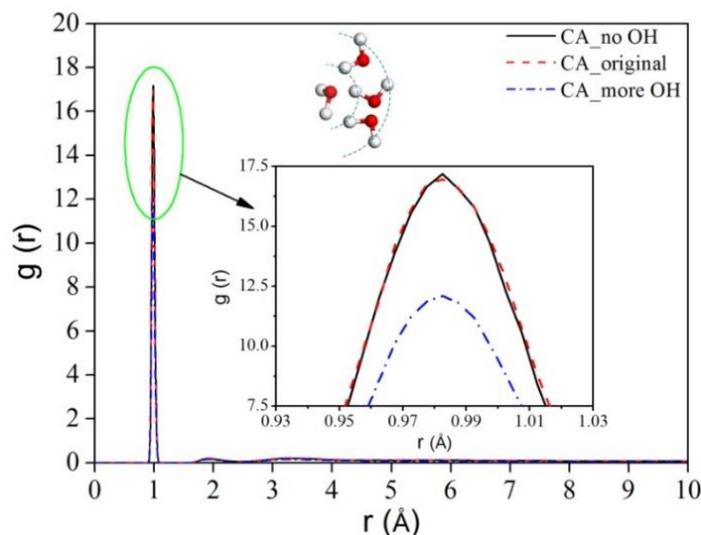


Fig. 8. Intermolecular oxygen-hydrogen radial distribution functions for the interfacial water layer in different systems. The inserted figs. are enlarged observations of the first peaks and the illustration of the calculated RDF

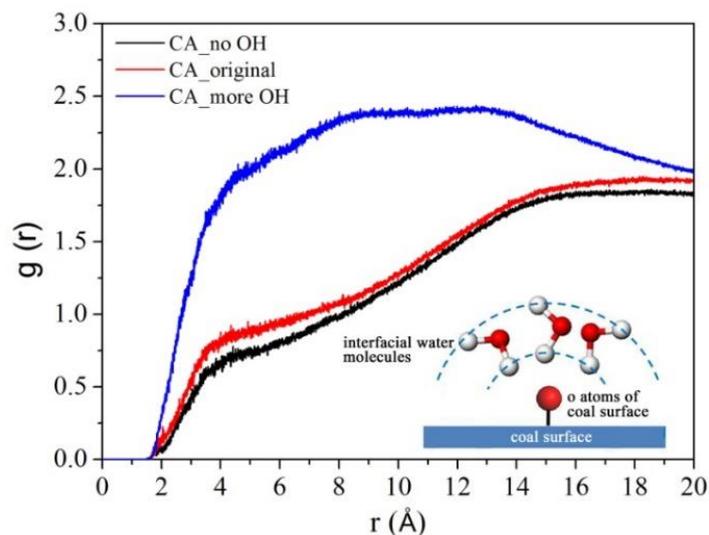


Fig. 9. RDFs of water hydrogen atoms from coal surface oxygen sites. The inserted schematic diagram is used to illustrate the calculated RDF. The online version of this paper has the Fig. in color for clarification of data

In order to obtain more information about the influence on interfacial water structure by the oxygen content of the coal surfaces, the RDFs of water hydrogen atoms from coal surface oxygen sites were calculated, and are shown in Fig. 9. Although the RDF for the 'CA_no OH' system is similar to that for the 'CA_original' system, the RDF increases with the hydroxyl content of the coal surface, suggesting that many more hydrogen atoms of interfacial water molecules prefer to be around the hydroxyl groups at coal surfaces, resulting in the disruption of the original water structure. It is noted that there are no notable peaks for the results presented in Fig. 9. It appears that the hydrogen atoms of interfacial water molecules cannot form a tight layer around the oxygen atoms at the coal surfaces. This may be because the area of the coal surface is much larger than the spreading area of the water droplet and partial hydroxyl groups of coal surfaces are exposed to air which cannot interact with the water molecules.

4.3.4 Hydrogen bonds

The hydrogen bond (HB) network can also provide further information about the structural topology of interfacial water layers at coal surfaces. In this study, the geometric description was used to define hydrogen bonding: a hydrogen bond is considered to be formed if the distance between the donor and acceptor is less than 3.5 Å, and the donor-hydrogen-acceptor angle is greater than 120° (Jorgensen et al., 1983; Hower et al., 2006). The number of hydrogen bonds formed between interfacial water molecules and each oxygen-containing functional group at the coal surfaces are calculated and listed in Table 5, which shows that the number of hydrogen bonds is mainly related to the number of hydroxyl sites at the coal surfaces (see Table 2). In particular, it can be seen that the number of hydrogen bonds formed between water molecules and hydroxyl groups at the coal surface significantly increases with an increase in the hydroxyl content of the coal surface. In order to evaluate the interaction between water molecules and each oxygen-containing functional group, the hydration number of each surface functional site was calculated, and listed in Table 6. The results show that the average number of hydrated water molecules per hydroxyl group is significantly larger than that of the other oxygen-containing groups, showing that the interaction between water molecules and surface hydroxyl groups is the greatest for all these surface sites considered.

Table 5. Number of hydrogen bonds (HBs) formed between interfacial water molecules and different oxygen-containing functional groups at coal surfaces

Systems	-COOH	-C-O-C-	-C=O	-OH
CA_no OH	5	4	1	0
CA_original	6	6	1	75
CA_more OH	4	9	0	326

Table 6. The hydration number per surface site and the corresponding interaction energy

Surface sites	Hydration Number (water molecules per surface site)	Interaction Energy (KJ/mol)
-OH	~2	3.517
-COOH	~1	0.304
-C-O-C-	~1/2	0.156
-C=O	~1/3	1.443

4.3.5 Interaction energy

Further insight into the interaction between water molecules and surface sites can be described by consideration of interaction energies. The energy profile between water molecules and each surface site is usually expressed by potential of mean force (PMF), which is calculated by the radial distribution function, $g(r)$, through the equation $E(r) = -k_B T \ln g(r)$ in this work (Ghosh et al., 2001; Yan et al., 2010), where k_B is Boltzmann's constant, and T is the simulation temperature (K). The RDF and PMF obtained for each surface site in the 'CA_more OH' system are shown in Fig. 10. From Fig. 10(a), the stronger peaks of RDF also indicate that more water molecules are accumulated around the hydroxyl sites when compared to the other surface sites. For the PMF curves shown in Fig. 10(b), the first peak relates to the interaction energy between the water molecules and each surface site. Points A, B, and C in Fig. 10(b) represent the contact minimum (CM), the barrier of solvent layer (BARR) and the solvent-separated minimum (SSM), respectively (Li et al., 2017a). As previously reported (Yan et al., 2010), the binding energy barrier for the water molecule-surface site corresponds to the SSM and BARR, $\Delta E = E_{BARR} - E_{SSM}$, which is also related to the interaction energy between the water molecules and surface sites. The obtained interaction energies for different surface sites are also listed in Table 6. It can be seen from Table 6 that the interaction energy between water molecules and hydroxyl groups is larger than that for other oxygen-containing groups.

The analysis with respect to hydrogen bonds and interaction energies suggests that the wetting of the coal surface by water is determined by the hydroxyl content of the coal surface, and the process is driven via hydrogen bonds formed between the water molecules and hydroxyl sites at the coal surface.

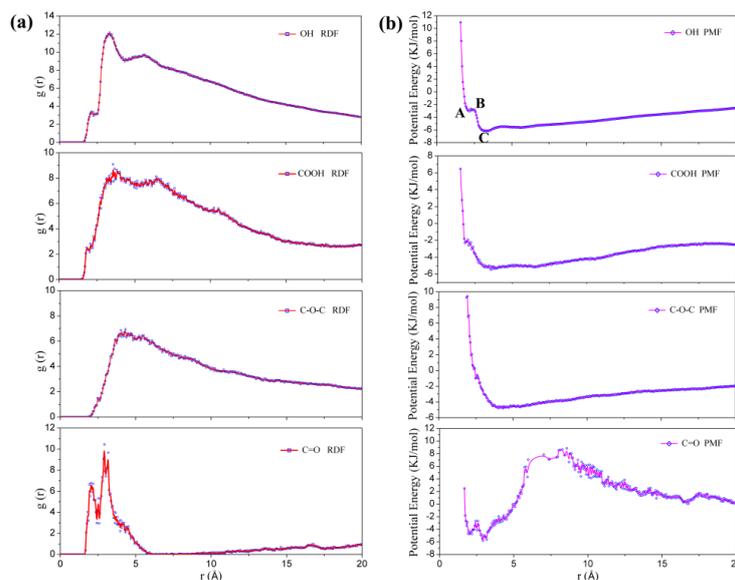


Fig. 10. (a) RDFs for water at different surface sites, (b) the corresponding PMF curves calculated from the RDFs. The online version of this paper has the Fig. in color for clarification of data

5. Conclusions

In summary, the effect of oxidation on the wetting of coal surfaces by water was investigated by contact angle measurements combined with molecular dynamics simulations. Different coal surfaces each with a different oxygen content were obtained by using hydrogen peroxide as an oxidant under different oxidation conditions. A new strategy using graphite was employed to construct a flat coal surface for simulation. The oxygen content of the coal surface was changed by varying the number of hydroxyl groups. Our results showed that the simulated advancing and receding contact angles were very similar, and are consistent with the experimental receding contact angle values, indicating that both the configuration of the systems, and the set of parameters were appropriate to simulate the wettability of coal surfaces by water. Both advancing and receding contact angles notably decreased when the hydroxyl content of the coal surface increased. The coal surface with the higher hydroxyl content was strongly hydrophilic, resulting in more water molecules being accommodated at the coal surface and the mobility of water molecules being restricted. Compared with other oxygen-containing functional groups (-COOH, -C-O-C-, -C=O), the hydroxyl group sites could hydrate more water molecules through hydrogen bonds and exhibited a much higher interaction energy. Therefore, an extended understanding of the effect of oxidation on the wetting of coal surfaces by water is provided at the atomic/molecular level. Additional MDS study will involve more coal surfaces with different oxygen content adjusted through varying the number of functional groups, -COOH, -C-O-C-, etc. In this way fundamental details will be further established, and the design of improved fine coal flotation should be possible.

Acknowledgments

This work was financially supported by the National Nature Science Foundation of China (Grant No. U1610254), the Program for Sanjin Scholars of Shanxi Province and by the Division of Chemical Sciences, Geosciences, and Biosciences, Office of Basic Energy Sciences of the US Department of Energy through Grant No. DE-FG03-93ER14315.

References

ARKHIPOV, V., PALEEV, D.Y., PATRAKOV, Y.F., USANINA, A., 2011. Determination of contact angle on the coal surface. *Journal of Mining Science*, 47(5), 561-565.

- BERENDSEN, H., GRIGERA, J., STRAATSMA, T., 1987. *The missing term in effective pair potentials*. Journal of Physical Chemistry, 91(24), 6269-6271.
- BLOM, L., EDELHAUSEN, L., VANKREVELEN, D., 1957. *Chemical structure and properties of coal, 18. Oxygen groups in coal and related products*. Fuel, 36(2), 135-153.
- BOLAT, E., SAĞLAM, S., PIŞKIN, S., 1998. *The effect of oxidation on the flotation properties of a Turkish bituminous coal*. Fuel Processing Technology, 55(2), 101-105.
- BOYLU, F., LASKOWSKI, J.S., 2007. *Rate of water transfer to flotation froth in the flotation of low-rank coal that also requires the use of oily collector*. International Journal of Mineral Processing, 83, 125-131.
- CHONG, L., DUTT, M., 2014. *Computer simulations of fluid flow over catalytic surfaces for water splitting*. Applied Surface Science, 323, 96-104.
- DEY, S., 2012. *Enhancement in hydrophobicity of low rank coal by surfactants-A critical overview*. Fuel Processing Technology, 94(1), 151-158.
- DING, L.P., 2009. *Investigation of bituminous coal hydrophobicity and its influence on flotation*. Energy & Fuels, 23(11), 5536-5543.
- DRELICH, J., LASKOWSKI, J.S., PAWLIK, M., 2000. *Improved sample preparation and surface analysis methodology for contact angle measurements on coal (heterogeneous) surfaces*. Coal Preparation, 21, 247-275.
- DRELICH, J., MILLER, J.D., 1995. *A systematic comparison of sessile-drop and captive-bubble contact angle methods*, in: 124th SME Annual Meeting, Denver, CO, USA.
- DU, H., MILLER, J.D., 2007. *Interfacial water structure and surface charge of selected alkali chloride salt crystals in saturated solutions: A molecular dynamics modeling study*. The Journal of Physical Chemistry C, 111(27), 10013-10022.
- DU, H., YIN, X., OZDEMIR, O., LIU, J., WANG, X., ZHENG, S., MILLER, J.D., 2012. *Molecular dynamics simulation analysis of solutions and surfaces in nonsulfide flotation systems*, in: Molecular Modeling for the Design of Novel Performance Chemicals and Materials, CRC Press, Boca Raton, FL, USA, 107-156.
- FUERSTENAU, M.C., JAMESON, G.J., YOON, R.-H., Froth flotation: A century of innovation. 2007, SME, Littleton, CO, USA.
- FUERSTENAU, D.W., YANG, G.C.C., LASKOWSKI, J.S., 1987. *Oxidation phenomena in coal flotation. Part 1, correlation between oxygen functional group concentration, immersion wettability and salt flotation response*. Coal Preparation: A Multinational Journal, 4, 161-182.
- GHOSH, T., GARCIA, A.E., GARDE, S., 2001. *Molecular dynamics simulations of pressure effects on hydrophobic interactions*. Journal of the American Chemical Society, 123(44), 10997-11003.
- HOWER, J.C., HE, Y., BERNARDS, M.T., JIANG, S., 2006. *Understanding the nonfouling mechanism of surfaces through molecular simulations of sugar-based self-assembled monolayers*. The Journal of Chemical Physics, 125(21), 214704.
- JIN, J., DANG, L.X., MILLER, J.D., 2018. *Molecular dynamics simulations study of nano bubble attachment at hydrophobic surfaces*. Physicochemical Problems of Mineral Processing, 54(1), 89-101.
- JIN, J., MILLER, J.D., DANG, L.X., 2014. *Molecular dynamics simulation and analysis of interfacial water at selected sulfide mineral surfaces under anaerobic conditions*. International Journal of Mineral Processing, 128, 55-67.
- JORGENSEN, W.L., CHANDRASEKHAR, J., MADURA, J.D., IMPEY, R.W., KLEIN, M.L., 1983. *Comparison of simple potential functions for simulating liquid water*. The Journal of Chemical Physics, 79(2), 926-935.
- LASKOWSKI, J.S., 1994. *Coal surface chemistry and its role in fine coal beneficiation and utilization*. Coal Preparation, 14, 115-132.
- LASKOWSKI, J.S., 2001. Coal flotation and fine coal utilization, Vol. 14, Developments in mineral processing, D.W. Fuerstenau (adv. ed.), Elsevier, Amsterdam, NL.
- LI, E., DU, Z., LI, D., CHENG, F., 2017a. *Specific ion effects of salt solutions on colloidal properties of octadecylamine hydrochloride*. Journal of Surfactants and Detergents, 20(2), 483-491.
- LI, E., DU, Z., YUAN, S., 2013. *Properties of a water layer on hydrophilic and hydrophobic self-assembled monolayer surfaces: A molecular dynamics study*. Science China Chemistry, 56(6), 773-781.
- LI, E., DU, Z., YUAN, S., CHENG, F., 2015. *Low temperature molecular dynamic simulation of water structure at sylvite crystal surface in saturated solution*. Minerals Engineering, 83, 53-58.
- LI, L., HAO, H., YUAN, Z., LIU, J., 2017b. *Molecular dynamics simulation of siderite-hematite-quartz flotation with sodium oleate*. Applied Surface Science, 419, 557-563.
- LIANG, L., LI, Z., PENG, Y., TAN, J., XIE, G., 2015. *Influence of coal particles on froth stability and flotation performance*. Minerals Engineering, 81, 96-102.
- LIANG, Y.H., WANG, F., ZHANG, H., WANG, J.P., LI, Y.Y., LI, G.Y., 2016. *A ReaxFF molecular dynamics study on*

- the mechanism of organic sulfur transformation in the hydrolysis process of lignite.* Fuel Processing Technology, 147, 32-40.
- LIU, J., GUO, X., 2017. *ReaxFF molecular dynamics simulation of pyrolysis and combustion of pyridine.* Fuel Processing Technology, 161, 107-115.
- MARMUR, A., DELLA VOLPE, C., SIBONI, S., AMIRFAZLI, A., DRELICH, J.W., 2017. *Contact angles and wettability: Towards common and accurate terminology.* Surface Innovations, 5(1), 3-8.
- NOSE, S., 1991. *Constant temperature molecular dynamics methods.* Progress of Theoretical Physics Supplement, 103(103), 1-46.
- OU, X., WANG, X., LIN, Z., LI, J., 2017. *Heterogeneous condensation of water on the mica (001) Surface: A molecular dynamics simulation work.* The Journal of Physical Chemistry C, 121(12), 6813-6819.
- PACHECO-SANCHEZ, J.H., ZARAGOZA, I.P., MARTINEZ-MAGADAN, J.M., 2003. *Asphaltene aggregation under vacuum at different temperatures by molecular dynamics.* Energy & Fuels, 17(5), 1346-1355.
- PAN, L., JUNG, S., YOON, R.-H., 2012. *A fundamental study on the role of collector in the kinetics of bubble-particle interaction.* International Journal of Mineral Processing, 106, 37-41.
- PAWLIK, M., 2008. *The surface properties of coal,* in: Handbook of Surface and Colloid Chemistry, Third Edition, K.S. Birdi (ed.), CRC Press, Boca Raton, FL, USA, 655-680.
- QUAST, K.B., READETT, D.J., 1987. *The surface chemistry of low-rank coals.* Advances in Colloid and Interface Science, 27(3-4), 169-187.
- SHRIMALI, K., JIN, J., VAZIRI HASSAS, B., WANG, X., MILLER, J.D., 2016. *The surface state of hematite and its wetting characteristics.* Journal of Colloid and Interface Science, 477, 16-24.
- SOKOLOVIĆ, J., STANOJLOVIĆ, R.R., MARKOVIĆ, Z.S., 2006. *Effect of oxidation on flotation and electro kinetic properties of coal.* Journal of Mining and Metallurgy A: Mining, 42(1), 69-81.
- SU, H., ZHOU, F., LI, J., QI, H., 2017. *Effects of oxygen supply on low-temperature oxidation of coal: A case study of Jurassic coal in Yima, China.* Fuel, 202, 446-454.
- SUN, H., 1994. *Force field for computation of conformational energies, structures, and vibrational frequencies of aromatic polyesters.* Journal of Computational Chemistry, 15(7), 752-768.
- VAN NIEKERK, D., MATHEWS, J.P., 2011. *Molecular dynamic simulation of coal-solvent interactions in Permian-aged South African coals.* Fuel Processing Technology, 92(4), 729-734.
- WISER, W.H., 1984. *Conversion of bituminous coal to liquids and gases: chemistry and representative processes,* in: Magnetic Resonance, Springer, L. Petrakis, J.P. Fraissard (eds.), Dordrecht, NL, 325-350.
- XING, Y., XU, X., GUI, X., CAO, Y., XU, M., 2017. *Effect of kaolinite and montmorillonite on fine coal flotation.* Fuel, 195, 284-289.
- XU, Z., SONG, K., YUAN, S., LIU, C., 2011. *Microscopic wetting of self-assembled monolayers with different surfaces: A combined molecular dynamics and quantum mechanics study.* Langmuir, 27(14), 8611-8620.
- YAN, H., YUAN, S., 2016. *Molecular dynamics simulation of the oil detachment process within silica nanopores.* The Journal of Physical Chemistry C, 120(5), 2667-2674.
- YAN, H., YUAN, S.L., XU, G.Y., LIU, C.B., 2010. *Effect of Ca²⁺ and Mg²⁺ ions on surfactant solutions investigated by molecular dynamics simulation.* Langmuir, 26(13), 10448-10459.
- YARZAB, R.F., ABDEL-BASET, Z., GIVEN, P.H., 1979. *Hydroxyl contents of coals: new data and statistical analyses.* Geochimica et Cosmochimica Acta, 43(3), 281-287.
- YE, Y., JIN, R., MILLER, J., 1988. *Thermal treatment of low-rank coal and its relationship to flotation response.* Coal Preparation, 6(1-2), 1-16.
- YE, Y., MILLER, J.D., 1988. *Bubble/particle contact time in the analysis of coal flotation.* Coal Preparation, 5(3-4), 147-166.
- YESILYURT, Z., VAZIRI HASSAS, B., KARAKAS, F., BOYLU, F., 2017. *Ultrafine coal flotation and dewatering: Selecting the surfactants of proper hydrophilic-lipophilic balance (HLB).* International Journal of Coal Preparation and Utilization, DOI:10.1080/19392699.2017.1383246.
- YOUNG, T., 1805. *An essay on the cohesion of fluids.* Philosophical Transactions of the Royal Society of London, 95, 65-87.
- ZHANG, L., LU, X., LIU, X., YANG, K., ZHOU, H., 2016. *Surface wettability of basal surfaces of clay minerals: Insights from molecular dynamics simulation.* Energy & Fuels, 30(1), 149-160.
- ZHANG, Z., WANG, C., YAN, K., 2015. *Adsorption of collectors on model surface of wiser bituminous coal: a molecular dynamics simulation study.* Minerals Engineering, 79, 31-39.