



Predicting the degree of surface oxidation on fine coals by measuring the oxygen transfer rate in coal suspensions



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ABSTRACT

Coal surface oxidation plays a dominant role in differential coal flotation and the utilization of coal products. However, a robust and reliable tool to determine coal surface oxidation in coal preparation plants is not currently available. In this study, a novel technique was developed to determine the degree of coal surface oxidation by measuring the adsorption rate of oxygen on coal surfaces after understanding the nature of oxygen transfer in water and oxygen adsorption on oxidized and un-oxidized coal surfaces. In this study, coal samples with different extents of surface oxidation were prepared and the degree of coal surface oxidation was quantified by X-ray photoelectron spectroscopy (XPS) as the percentage of oxidized carbon. Oxygen was purged into the coal suspension at a constant flow rate and the change of dissolved oxygen (DO) concentration was monitored. It was found that the DO concentration increased with oxygen purging time and the rate of increase was dependent on the degree of coal surface oxidation. A faster increase in DO concentration was observed for more oxidized coals, which is related to a slower adsorption of oxygen on oxidized coal surfaces and, therefore, more dissolved oxygen remained in the suspension. The kinetics of the change of DO concentration was calculated using the oxygen transfer equation, based on which the rate of oxygen adsorption on coal surfaces was obtained. A linear relationship was found between the oxygen adsorption rate and the degree of coal surface oxidation. This technique may be implemented in coal preparation plants as a daily tool to closely monitor the coal oxidation status due to its simplicity and accuracy.

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1. Introduction

Coal oxidation commences once it is unearthed and/or removed from the coal seam and proceeds in the subsequent processes during coal production such as stockpiling and beneficiation. Coal oxidation is a complicated process starting with physical adsorption of oxygen on the surface to form an oxy-complex, followed by chemical adsorption of oxygen to form oxygenated species such as hydroxyl, carbonyl and carboxyl groups [1–5]. Physical adsorption is non-specific and requires a relatively weak force to attract oxygen molecules to the coal surface, while chemical adsorption only occurs on particular sites with stronger forces involved. In addition, single or multiple layers of oxygen molecules can form through physical adsorption, while chemical adsorption can only produce a monolayer of oxygen molecules [6].

Coal oxidation needs to be closely monitored in coal preparation plants due to its significant influences on coal beneficiation and the utilization of coal products. In coal preparation plants, fine particles and coarse particles are separated with a cut size of about 200 μm . Fine particles undergo the flotation process while coarse particles undergo the

gravity process. Coal oxidation has a deleterious influence on coal flotation [7–10]. Un-oxidized coals are naturally hydrophobic and can be easily separated by flotation from the gangue minerals which are naturally hydrophilic. However, coals gradually lose their hydrophobicity with an increase in surface oxidation due to the formation of hydrophilic oxygenated groups on the surfaces. The flotation performance of oxidized coals is dependent on the extent of surface oxidation. Minor surface oxidation may only decrease combustible recovery and this can be restored by the addition of a higher dosage of oily collectors. However, heavily oxidized coals cannot be efficiently floated with oily collectors and additional treatments are required for a satisfactory combustible recovery. Fuerstenau et al. found that the flotation rate constant was zero when the percentage of oxygen on coal surfaces reached about 14% [11]. Gutierrez-Rodriguez and Aplan also reported that no flotation occurred when the oxygen content on coal surfaces was more than 11% [12]. Therefore, the characterization and quantification of fine coal oxidation are important in order to optimize coal flotation performance. In addition, oxidation also has a significant influence on coal utilization. It has been found that the oxidation of coking coals results in the loss of their coking properties [13–15]. Coking coals pass through a fluid stage at around 350 °C to 550 °C during carbonization, which is sensitive to the presence of oxygenated groups produced after oxidation. The

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plastic properties and the main quality indexes (mechanical strength and reactivity to CO₂) of coking coals can be impaired by oxygenated groups as well depending on the extent of surface oxidation.

Various methods and instruments including chemical methods, FTIR/DRIFT, UV–Vis, XPS, and NMR have been reported to quantify coal surface oxidation in literature [16]. Chemical methods are based on the determination of oxygenated groups by ion exchange reactions or titration [16]. Each group needs to be determined separately using different chemicals, therefore, the measurement can be time-consuming. In addition, the results obtained from chemical methods are sensitive to impurities in the samples. As a result, chemical methods are not practical to be used in plant operations as a routine measurement of coal surface oxidation. FTIR/DRIFT is the most widely used technique for determining the chemical/structural changes caused by oxidation [17,18]. However, the samples for FTIR/DRIFT analyses need to be finely ground to a size smaller than the wavelength of the incident light, which limits its application in coal processing which deals with coarser particles. The drying and grinding processes for FTIR/DRIFT analyses also change the coal surface property. The UV–Vis method involves the alkaline extraction of oxidation products, followed by the UV–vis analysis of extracts. Although this technique can be easily carried out, it has been found that it does not work well for detecting early stages of oxidation [19]. XPS is a surface-sensitive spectroscopic technique and can quantitatively analyse the surface chemistry of a material in its “as received” state. Furthermore, XPS only analyses the top few monolayers (0–10 nm) of the material and these top layers usually determine the floatability of a particle. Thus, the XPS data can be directly correlated with the flotation behaviour [20,21]. However, XPS cannot be applied in coal preparation plants to regularly monitor coal surface oxidation due to the high cost of purchasing and maintaining the instrument. NMR has been used to measure the change of chemical structures during coal oxidation. However, similar to XPS, it is difficult to apply NMR in coal preparation plants due to the high cost and complicated sample preparation [22,23]. Some other techniques such as zeta potential and surface wettability measurements have also been reported to assess coal surface oxidation indirectly [8,12]. However, the results from these measurements on coal surface oxidation can be misleading because many other factors which do not result from coal oxidation can influence data interpretation.

It has been reported that the oxidation history of coals can have a significant influence on further reactions of coal surfaces with oxygen [5,6]. The oxygen consumption rate of a fresh coal surface was found to be significantly higher than that of an oxidized coal surface. This is mainly caused by the accumulation of oxygenated species at the coal surface and the internal surface of coal pores, resulting in the deactivation of reactive sites responsible for oxygen adsorption [5,24]. Based on this phenomenon, it is possible to predict the oxidation status of a coal sample from its reaction kinetics with oxygen. A slower reaction with oxygen indicates a lower extent of surface oxidation and vice versa. In this study, a novel technique was developed to quantify the extent of

surface oxidation on fine coals based on the oxygen transfer rate after purging oxygen into coal suspensions. Fine coal samples with different extents of surface oxidation were prepared and the degree of coal surface oxidation was determined by XPS analysis. It is expected that this technique can be implemented in the industry as a daily tool to closely monitor the coal oxidation status due to its simplicity and accuracy.

2. Experimental

2.1. Coal samples

The coal sample used in this study was purchased from Geo Discoveries, Sydney and originated from Bulli Mine, New South Wales, Australia. It was a high volatile bituminous coal with an ash content of 7.93%. The mineral matters in this coal sample were mainly quartz and kaolinite as identified by XRD analysis. To simulate the coal processed in coal preparation plants, the raw coal was firstly crushed and then dry ground in a stainless steel rod mill. The P₈₀ of the ground sample is 200 μm. To obtain coal samples with different degrees of surface oxidation, the coal was firstly spread evenly onto a glass dish and then heated in a furnace at 150 °C for different times in an air atmosphere.

2.2. XPS analysis

The degree of coal oxidation was measured using KRATOS Axis Ultra with a monochromatic Al X-ray source operating at 15 kV and 10 mA (150 W). The analysis spot size was 300 × 700 μm. The sample was placed on the stainless steel bar and immediately loaded into the introduction chamber of the spectrometer. The sample was analysed at a pressure of 9 × 10⁻¹⁰ Torr at the room temperature. Each analysis started with a survey scan from 0 to 1200 eV using a pass energy of 160 eV at steps of 1 eV with 1 sweep. High-resolution spectra of O 1s and C 1s were collected at 20 eV pass energy at steps of 100 eV with 2 sweeps. Binding energies were charge-corrected by referencing to carbon at 284.7 eV. The XPS spectra were fitted using Casa XPS software.

2.3. Oxygen transfer rate measurement

The oxygen transfer rate in coal slurry was measured in a specially designed airtight 600 mL glass flask as shown in Fig. 1. It is equipped with a magnetic stirrer to keep the coal particles in suspension. A YSI dissolved oxygen probe with a polarographic sensor was used to monitor the change of dissolved oxygen concentration in the slurry. The probe was calibrated daily in a sodium sulphide calibration solution and air. After turning the dissolved oxygen meter on, it was warmed up for 10 min before taking readings. The probe was placed in the slurry which was stirred all the time and the DO value was recorded. All tests were conducted at 25 °C.

For each test, 50 g coal was added into 450 g DI water to make a slurry with 10% solids. Before starting the measurement, the slurry was

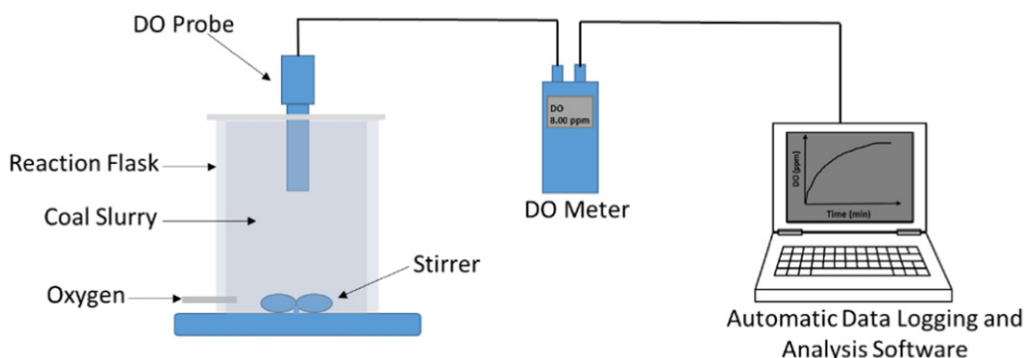


Fig. 1. Schematic diagram of the experimental apparatus for measuring oxygen transfer rate.

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