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Aerial and subaquatic oxidation of coal by molecular oxygen

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ABSTRACT

The oxidation behaviour of three coal types towards molecular oxygen was investigated both in aerial and subaquatic conditions. The effects of time, temperature and coal grain size were studied and compared as basic parameters influencing the oxidation process. The obtained results showed that the influence of these factors can be similar both on aerial and subaquatic coal oxidation. Among the samples, subbituminous coal was primarily found to differ with respect to oxidation in aerial and subaquatic environment. A possible explanation for this is a change in its porous system when immersed in water. For aerial oxidation of the studied coal, oxygen consumption rates R_{O2} (40 °C, grain size 0.06–0.15 mm) in the range of $1{\cdot}10^{-6}$ to $5{\cdot}10^{-6}$ mol O_2.(kg.s)$^{-1}$ were found, which is approximately 2–4 times higher in comparison with R_{O2} for the subaquatic oxidation of the coal samples.

1. Introduction

Oxidation of coal has been intensively studied mainly in relation with spontaneous heating processes (e.g., [1–7]) and/or deterioration of coal quality during its storage in air (e.g., [8–10]). Much less attention is given to possible interactions occurring between coal and oxygen dissolved in water although practical situations when coal is totally immersed in water are not so scarce, e.g. wet coal milling [11,12], coal-water slurries [13,14], underwater coal mining [15]. In addition, considerations about the geochemical carbon cycle are in question when oxidative weathering of coal both below and above water is known to take place [16].

Chen et al. [17] recently published an experimental procedure to evaluate the degree of surface oxidation of coal using measurements of the consumption rate of oxygen dissolved in water. However, wet oxidation of coal has preferably been studied to produce carboxylic acids or with respect to coal desulphurisation using oxidative agents like permanganate potassium [18], hydrogen peroxide [19,20] or dissolved oxygen in the presence of catalysts [21,22].

This paper is aimed at the comparison of oxidation behaviour of three coal samples towards molecular oxygen both in aerial and subaquatic conditions. The effects of time, temperature and coal grain size were studied and compared as basic parameters influencing the oxidation process. It will be shown that the influence of the factors can be similar both on aerial and subaquatic coal oxidation. Moreover, the oxygen consumption rate of coal under subaquatic conditions will be recognised as quite comparable with that for the aerial oxidation of coal.

2. Material and methods

2.1. Coal samples, characterisation

Two bituminous coals (denoted as TX, PV) from the Upper Silesian Coal Basin and a sample of subbituminous coal (HN) of the North Bohemian Coal District were investigated. The coals were taken as fresh samples from mine and stored in airtight bags in a refrigerator until analysed and measured. Sample PV represents a type of oxidative altered bituminous coal, the occurrence of which is connected with changes in the development of coal seams in the post-sedimentary geological past [23]. The oxidative altered bituminous coal is distinctive for its increased concentration of oxygen, and, simultaneously, it exhibits a high propensity to spontaneous combustion [24].

The self-heating susceptibility of the studied coal was assessed according to the oxidation heats (q^{30}) ascertained from the pulse flow calorimetric method, and applying boundaries valid for bituminous and/or subbituminous coals [25].

The surface characteristics of the coal was evaluated by the adsorption isotherms of nitrogen at −196 °C (Hiden Isochema, Great Britain) and carbon dioxide at 30 °C (PCTPro HyEnergy, Setaram, France). From the adsorption isotherm of nitrogen, the surface area S^{BET} was calculated according to the BET theory, using a molecular area of 0.162 nm^2 for the calculation. The surface area of micropores S_{mi} was determined of the carbon dioxide isotherm by applying the Dubinin-Radushkevich (D-R) model and Medek equation [26].

Mercury porosimetry (Porosimeter 2000, Carlo Erba) was then used to determine pore volume. From the porosimetric experiments, the

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Table 1
Analyses and properties of the studied samples.

	Sample PV	Sample TX	Sample HN
Proximate analysis			
Ash content (%, dry basis)	11.4	4.4	5.9
Volatile matter (%, dry, ash-free basis)	32.7	29.1	57.8
Elemental composition			
C (%, dry, ash-free basis)	75.2	83.9	73.0
H (%, dry, ash-free basis)	2.7	5.1	5.3
N (%, dry, ash-free basis)	2.1	1.0	1.0
S_{total} (%, dry basis)	2.6	0.36	1.1
$(O + S)_{dif}$ (%, dry, ash-free basis)	20.0	10.0	20.7
Surface characteristics, self-heating propensity			
BET surface area, S^{BET} ($m^2\ g^{-1}$)	1.5	0.8	27
Surface of micropores, S^{CO2} ($m^2\ g^{-1}$)	170	135	280
Pores volume, V^{poro} ($mL\ g^{-1}$)	0.093	0.031	0.114
Self-heating susceptibility	high risk	low risk	medium risk

volume of meso and macropores, in the range of pore diameters from 10 nm to 10 µm, V^{poro}, was calculated.

The quality characteristics of the studied samples as well as their propensity to spontaneous heating and surface characteristics are shown in Table 1.

2.2. Investigations of aerial oxidation of coal

2.2.1. Continuous flow reactor

Aerial oxidation of the samples was monitored using a continuous flow reactor operating under air at temperatures of 40–120 °C [27]. A weighed sample (70–80 g) was packed in the reactor and the temperature was set at a starting level of 40 °C, with air flowing at a rate of ca. 20 ml min^{-1}. After a "stabilisation" period of 20 min, the gas flow of the reactor was collected in a tedlar bag for 30 min. The temperature was then set at a level 20 °C higher, followed again by the stabilisation and gas collecting periods. The cycle was repeated until a temperature of 120 °C was reached. During the measurements, the air flow was repeatedly checked both at the entry and exit of the reactor using a bubble flow meter. The collected gas samples were immediately analysed. The content of CO_2 and CO were measured by infrared analysers (Unor, Maihak), the concentration of O_2 was determined by a paramagnetic analyser (Servomex OA 250). Other (minor) gaseous compounds were analysed using a Master GC gas chromatograph a Master GC (Dani Instruments).

From the gas analyses and measured flow velocities, the oxygen consumption rate R_{O2} was evaluated at the given temperature, expressed in units mol O_2 $(kg.s)^{-1}$. The basic coal grain size was 0.4–2 mm for the measurements; investigations with coal fractions of 0.2–0.35 mm and 1.8–2.0 mm were also performed.

2.2.2. Flow calorimetric method

Using a C80 calorimeter (Setaram, France), the amount of evolved heat during the oxidation of coal by gaseous oxygen was measured. A discrete amount (pulse) of oxygen was introduced into the flow of inert gas and the heat of the *chemical* reaction between the oxygen and the investigated sample was evaluated [25]. The flow rate of helium (as an inert carrier gas) was about 2.5 ml per minute. The volume of the oxygen pulse was 80 ml and thus passage of oxygen through the sample took about half an hour. The basic temperature of the experiments was 30 °C; however, measurements up to 120 °C were also performed. The weight of the coal was approximately 2.5 g. In addition to usual grain size (0.063–0.15 mm), fragmentation of 0.8–1.0 mm was also measured.

From the calorimetric tests, oxidation heat q^{30} was determined (J $(kg.s)^{-1}$, equivalent to W kg^{-1}), with the index 30 indicating the residence time of the coal oxidation (30 min).

2.3. Measurements of subaquatic coal oxidation

2.3.1. Batch reactor

To study subaquatic coal oxidation, a batch reactor was used thermostatted at temperatures between 25 and 50 °C. The ratio between the sample mass (g) and volume of the glass reactor (ml) was ca 2/100. The primary coal grain size was 0.4–0.8 mm, however, measurements with fragmentations of 0.063–0.15 mm and/or 0.8–1.0 mm were also performed. After inserting the sample into the glass reactor, it was filled with pre-thermostatted distilled water with an equilibrated content of oxygen. The plug with the oxygen probe was then fixed in the neck of the flask. The excess water of the reactor was expelled through a metal capillary passing through the plug. Thus, an exclusively aqueous environment was restored in the reactor. A magnetic stirrer was then immediately switched on rotating at 700 r.p.m.

2.3.2. Dissolved oxygen measurement

For the measurements of water dissolved oxygen, an InoLab Oxi Level 2P (WTW, Germany) equipped with a CellOx 325 membrane oxygen sensor was used. Before each experiment, the oxygen probe was calibrated using an OxiCal calibration vessel. The maximum measurement error is estimated to be ± 0.1 $mgO_2.L^{-1}$.

During the measurements, the working electrode reduces oxygen molecules to hydroxide ions; some amount of oxygen is thus consumed, possibly interfering with experimental data. Corrections for the *blank* electrode oxygen consumption were ascertained from tests with the reactor filled with oxygen equilibrated water at the given temperatures. The true electrode oxygen consumption proved to be negligible in comparison with the amount of oxygen consumed by the coal.

2.4. Evaluation of coal oxidation kinetics

Regarding coal oxidation simply as a heterogeneous reaction between oxygen and coal (forming a solid "oxy-coal" and gaseous products), the basic kinetic equation can be written as [2,3]:

$$-\frac{dc}{dt} = k'.\ c^n.\ c_c^m \tag{1}$$

where c is the concentration of oxygen, c_c is the concentration of reacting sites on coal, t is time, k' represents the kinetic constant and n, m denote the reaction orders to oxygen and coal, respectively. At low temperatures, the concentration of coal reacting sites can be involved to the kinetic constant [7], thus simplifying Eq. (1) to the form:

$$-\frac{dc}{dt} = k.\ c^n. \tag{2}$$

In this case, the value of k is implicitly related to the ratio between the volume of the reactor and mass of the coal including the coal grain size and its oxidation history. Such relation (2) was used here as a basis to describe the kinetics of the subaquatic oxidation of coal, with the time dependence of oxygen concentration being directly measured.

In principle, Eq. (2) is an analogy with formulation (3), which is frequently used to express the kinetics of aerial oxidation of coal (e.g., [5,6]), and which is also applied in the study:

$$R_{O2} = k.\ c^n. \tag{3}$$

R_{O2} is the rate of oxygen consumption usually expressed in "mol O_2 $(kg.s)^{-1}$", thus related to the "mol.kg^{-1}" unit for oxygen concentration. In addition, oxygen consumption rate in mol O_2 $(m^3.s)^{-1}$ is also used [4] corresponding to oxygen concentration in "mol m^{-3}". The value of R_{O2} is dependent (through kinetic constant k) on the coal grain size and oxidation history of coal that implicitly reflects the influence of time. To keep the oxidation history of the studied samples unified, "fresh" coal was used here for the experiments. Specifically, coal samples were stored in a refrigerator in plastic bags and were crushed and sieved to the desired grain size just before the measurements.