

Influence of coal forced oxidation on technological properties of cokes produced at laboratory scale

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Abstract

The effect of coal oxidation in air at 140 °C on the technological properties of cokes obtained at laboratory scale from two medium volatile bituminous coals has been studied. The proximate and ultimate analyses do not show important changes with coal oxidation time. However oxidation clearly has a strong effect on the plastic properties of the coals in view of the fact that the Gieseler fluidity eventually disappears. From this point variations in plastic properties can still be detected by FSI. Other changes, such as a shortening of the length of the saturated fragments of the aliphatic chains, a decrease in the aliphatic hydrogen content and an increase in the oxygen-containing groups are detected by PA-FTIR. It was also found that the main coke quality indices (mechanical strength and reactivity to CO₂) of both coke series are impaired with coal oxidation. A close relationship between reactivity to CO₂ and the micropore specific surface area of the cokes has been corroborated.

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1. Introduction

Weathering (natural oxidation) is a process that takes place when coal is exposed to the atmosphere after being mined and, in some instances, while it is still in the seam (outcropping). Strictly speaking, this phenomenon occurs when coal is exposed to the atmosphere under natural, uncontrolled climatic conditions involving rain, snow, humidity, temperature, etc. Oxidation can occur during weathering and also during storage (controlled conditions) when the coal is exposed to air. Most of the studies on oxidation have attempted to simulate the weathering process in a laboratory. However, weathering and low or moderate-temperature oxidation (simulated weathering) differ in these conditions because the weathering processes for coal involve aerial oxidation of organic and mineral matter (chemical weathering), microbial oxidation of pyrite (biological weathering), and changes in moisture content that may result in an appreciable slackening or particle size degradation (physical weathering). In other words: coal weathering is a complex phenomenon involving several simultaneous and interacting chemical processes, which are sometimes accom-

panied by physical changes [1–4]. Coke making is the most important technological process that is adversely affected by bituminous coal oxidation due to the dramatic changes experienced by the thermoplastic properties of coking coals. Such changes can seriously affect the quality of the blast furnace coke used in industry.

The plastic properties of bituminous coals, especially the Gieseler fluidity, are very sensitive to oxidation and undergo important changes even before other properties experience modifications. The dependence of coke quality on the plastic properties of the coals in terms of reactivity and strength indices is well known [5]. The aim of this work is to study the effects that air oxidation has on the properties of a coal and on the ones of the resulting cokes. This evaluation is based on the mechanical strength and reactivity to CO₂ of the coke samples.

2. Experimental

The present work was carried out using two medium volatile bituminous coals which are usually employed by the Spanish steel industry in preparing complex blends for use in the production of blast furnace coke. The most important characteristics of the parent coals are given in Table 1.

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Table 1
Characteristics of the parent coals used

	Coal A	Coal B
Ash (% db) ^a	9.3	5.7
Volatile matter (% db)	23.0	22.8
C (% daf) ^b	88.8	89.5
H (% daf)	4.6	4.9
N (% daf)	1.3	1.3
S (% daf)	0.6	0.6
O (% daf, by diff.)	4.7	3.6
<i>Petrographic characteristics</i>		
Mean reflectance, R_o (%)	1.03	1.21
Standard deviation of R_o	0.09	0.10
Vitrinite (% vol. mmf) ^c	71.4	89.0
Liptinite (% vol. mmf)	1.2	0.4
Semifusinite (% vol. mmf)	17.6	5.1
Fusinite (% vol. mmf)	9.8	5.5
<i>Gieseler test</i>		
T_s (°C) ^d	425	404
T_f (°C) ^e	464	466
T_r (°C) ^f	488	502
MF (ddpm) ^g	17	1386
Free Swelling Index	7	8 1/4

^a db: dry basis.

^b daf: dry ash free.

^c mmf: mineral matter free.

^d T_s : softening temperature.

^e T_f : temperature at which maximum fluidity is attained.

^f T_r : resolidification temperature.

^g MF: maximum fluidity; ddpm: dial divisions per minute.

Coal oxidation was carried out in trays which were placed in an oven of air forced convection at a temperature of 140 °C in all cases. The samples were uniformly distributed on the trays so that they formed a layer with an average thickness of 3 mm. The particle size was less than 1 mm. The oxidation time was varied in order to obtain different degrees of oxidation.

Throughout the study, proximate and ultimate analyses of the coals were performed at fixed periods of time. Gieseler fluidity and the Free-Swelling Index (FSI) tests of both coals were carried out in accordance with the ASTM D2639-74 and ASTM D720-91 procedures, respectively.

Coal samples with a particle size of less than 0.15 mm were used for the PA-FTIR spectroscopy. Prior to spectroscopic examination, the coal samples were stored in a desiccator with P₂O₅ and argon as inert gas for 5 days to minimize humidity and avoid coal oxidation that may result from drying the coals at high temperatures. To avoid the appearance of H₂O bands in the spectra, the samples were studied by introducing a desiccant (silica gel) in the sample chamber. Finally, the samples were placed in a cup which was inserted above the desiccant. The PA spectra were measured with a Nicolet Magna-IR System 560 equipped with an MTEC-300 detector. The nominal resolution of the spectra was 4 cm⁻¹. Purging was carried out using 5 mL s⁻¹ of dry nitrogen. 800 spectra were recorded for each sample and ratioed against a carbon black spectrum recorded under the same experimental conditions to correct for the frequency dependency of the incident intensity. From these spectra a semi-quantitative analysis was carried out,

using the aromatic carbon content as an internal standard representative of the macromolecular network of the coal. This type of analysis was preferred as aromatic carbon remains constant during the weathering process (natural oxidation) [6].

A previous article [7] presented the results corresponding to the study of the weathering process of the same two medium volatile bituminous coals stored at the INCAR open stockyard for several months, using Gieseler plastometry, the Free-Swelling Index (FSI) test and photoacoustic Fourier transform infrared spectroscopy (PA-FTIR). The effects of subjecting these two coals to weathering on the technological properties of the cokes obtained at three different scales (laboratory, pilot plant and semi-industrial) were also studied [8]. The results showed that the procedure developed at laboratory scale is useful for studying the evolution of coke quality, because the trends of the main coke quality indexes (mechanical strength and reactivity to CO₂) are in agreement with those of the cokes produced at larger scales. Consequently, in this work carbonisation tests were carried out at laboratory scale in a 400 g sole heated oven [9]. The coking conditions were kept constant in all the tests. Coking time was approximately 3 h, which was long enough for the temperature of the top of the coke to reach 900 °C. The bulk density (dry basis) used was 820 kg m⁻³.

To evaluate the quality of the coke, the samples were characterized in terms of mechanical strength and reactivity to carbon dioxide. The coke cold mechanical strength was assessed by means of the abrasion index, evaluated according to the INCAR-MITREM method and defined as the weight percentage of the initial sample as it passes through a 1-mm sieve after 3000 revolutions in a mini-MICUM drum test at 31.5 rpm [5]. Coke reactivity to carbon dioxide was measured by means of the ECE-INCAR method [10]. In this procedure, 7 g of coke with a particle size of 1–3 mm are heated to 1000 °C for 1 h in an atmosphere of CO₂ at a flow rate of 120 mL min⁻¹. Reactivity is expressed as the percentage of mass loss.

Coke microporosity was assessed by means of CO₂ adsorption at 273 K. CO₂ adsorption at relative pressures <0.04 was analysed using the Dubinin-Radushkevich (D-R)

Table 2
Evolution of the main characteristics of coal A with oxidation time at 140 °C

Oxidation time (h)	0	0.5	1	3	6	9
Moisture (wt.%)	1.2	0.5	0.6	0.7	0.8	0.7
Ash (% db)	9.3	9.1	9.2	9.3	9.3	8.9
Volatile matter (% db)	23.0	22.8	22.7	23.0	22.7	22.6
C (% daf)	88.8	87.3	88.5	87.2	87.6	86.9
H (% daf)	4.6	5.1	5.0	5.2	4.7	5.5
N (% daf)	1.3	2.1	1.2	1.2	1.2	1.2
S (% daf)	0.6	0.6	0.6	0.6	0.6	0.6
O (% daf)	4.7	4.9	4.8	5.8	5.9	5.7
Calorific value (MJ kg ⁻¹)	32.67	32.45	32.39	32.20	32.16	32.13
<i>Gieseler test</i>						
T_s (°C)	425	431	434	–	–	–
T_f (°C)	464	464	459	–	–	–
T_r (°C)	488	483	480	–	–	–
MF (ddpm)	17	5	3	0	0	0
Free Swelling Index	7	6 3/4	5 1/2	5 1/2	3 1/2	2 1/4

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