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Research article

The effect of bituminous additives on the carbonization of oxidized coals

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ABSTRACT

Two bituminous coals of different rank and coking characteristics were oxidized at low temperature for two months. Bituminous additives obtained in-situ in the coking plant were used to improve the thermoplastic properties of the oxidized coals. The Gieseler fluidity test was applied to evaluate their coking properties. A thermogravimetric analysis (TGA) of the fresh, oxidized coals and their blends with the bituminous additives was carried in order to evaluate the interaction between the blend components. In addition, carbonization tests of the fresh and oxidized coals and the blends with the additives were carried out in a movable wall oven of 17 kg capacity and the quality of the cokes tested by means of standardized methods generally used by the steel industry. The additives increased coal fluidity but the original fluidity values could not be recovered. From TGA it was concluded that the blend components behave independently of one another during co-carbonization. The oxidation of coal leads to an increase in the dangerousness of the low volatile coal which was related to the porous texture of the cokes. In addition, it was found that the decrease in the quality of the coke produced from low rank oxidized coal can be partially recovered by using bituminous additives.

1. Introduction

The natural oxidation of coal (weathering) is a complex process involving several chemical processes, which are accompanied by physical changes [1,2]. Cokemaking is an important technological process that is adversely affected by coal oxidation [3]. This is directly reflected in a reduction in carbonization rate, coke yield, and coke quality [4–8], effects which reduce the productivity of the coke plant and undermine the economic feasibility of coke production. In the carbonization process the coal softens, melts and then resolidifies to form coke when heated in the absence of air. The fluid stage is very sensitive to the presence of oxidized coal because oxidation causes a decrease in the thermoplastic properties of coking coals. It is therefore necessary to develop efficient methods to restore the coking properties of oxidized coals in order to counteract the deleterious influence of oxidation on the coking process.

Many studies have been published on the modification of coal thermal decomposition by the use of additives. The effect of additives on the coking process includes modifications to the thermoplastic properties of the coal, the generation of coking pressure [9,10] and a deterioration of the quality of the resultant cokes [11–13].

Several authors have studied the effect of aerial oxidation by using artificial oxidation as a model of coal weathering [14,15] and have assessed the effect of different additives on the thermoplastic properties of oxidized coals. The results obtained vary depending on the type of additive used. For instance, the co-carbonization of oxidized coals with pitches and decacyclene can reduce the effects of mild oxidation. In this case the role of the additives is to replace the hydrogen lost during oxidation, which in turn influences coal fluidity [16,17]. The addition of small amounts of coal tar, diesel fuel and high-density polyethylene increases or preserves the fluid characteristics of weathered coals (as measured by rheometry), whereas the addition of sugar beet roots, bio-oil and lignin reduces coal fluidity [18].

In this work two bituminous coals of different rank were investigated in order to study the effect of mild oxidation on their coking properties and the effectiveness of adding carbonaceous additives as a means of restoring these properties without impairing the quality of the resulting cokes. The effect of the additives on coking pressure was also studied.

2. Experimental

2.1. Materials

Two coals of different rank were selected for the study, a high-volatile bituminous coal (HV) and a low-volatile bituminous coal (LV). Oxidation was performed in a drying chamber for two months in two ways: i) in trays (64 cm long, 40 cm wide and 3 cm high) where the coals were uniformly spread out in a thin layer in order to ensure that air exposure was similar for all the particles and ii) in baskets (48 cm high and 56 cm in diameter). Coal oxidized in trays and baskets will be labelled O and OB, respectively, after their name. Representative samples were collected before the carbonization process for analysis. Two bituminous additives were used, a high temperature coal tar (T) obtained as a by-

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product in the cokemaking industry and a coal tar sludge (CTS), a waste material extracted from the tar decanter of a by-products coking plant, made up of a blend of coal tar with coke fines from the coking ovens. To prepare the coal/additive blends, each bituminous additive was physically mixed with the corresponding coal in amounts of 2 wt%. The main characteristics of the pristine coals, oxidized coals and additives are shown in Table 1.

Proximate analyses were performed following the ISO562 and ISO1171 standard procedures for volatile matter and ash content, respectively. The elemental analysis was carried out using a LECO CHN-2000 device for C, H and N (ASTM D-5773), a LECO S-144DR instrument (ASTM D-5016) for sulphur and a LECO VTF-900 device for direct oxygen determination.

2.2. Thermoplastic properties

The thermoplastic properties of the fresh coals, oxidized coals and blends were assessed by means of the Gieseler test in a R.B. Automazione Gieseler plastometer PL 2000 following the ASTM D2639-08 standard procedure [19]. The characteristic temperatures in the development of coal fluidity i.e. softening temperature (Ts), maximum fluidity temperature (Tf) and resolidification temperature (Tr) were recorded together with the maximum fluidity value. The plastic/fluid range defined as the difference between the resolidification and softening temperatures was also recorded.

2.3. Thermogravimetric analysis (TG/DTG)

The TG/DTG analysis of the coals and coal/additives blends was carried out using a TA Instruments STD 2960 thermoanalyser. Samples (10 mg) with a particle size of <0.212 mm were heated to 1000 °C at a rate of 3 °C/min under a nitrogen flow of 100 ml/min. From the data obtained by thermogravimetric analysis the volatile matter evolved up to specific temperatures (VMT) and the derivative weight loss curve (DTG curve) were calculated. The volatile matter evolved over a specific temperature range was calculated as the difference between the volatile matter evolved up to two specific temperatures (VMT1-VMT2). In addition, Tmax, the temperature of maximum volatile matter evolution was derived from the TG/DTG curves [19,20]. The precision in the measurement of the DTGmax value is ±0.02%/min.

2.4. Carbonization test

Carbonization tests were carried out in a movable wall oven of approximately 17 kg capacity (MWO17). The dimensions of the oven are 250 mm *L* × 165 mm *W* × 790 mm *H*. A load cell was mounted on the movable wall to measure the force exerted on the wall during carbonization. A programmable controller was used to control the oven temperature. The temperature at the centre of the coal charge was monitored by means of a thermocouple connected to a computer. The coal was charged when the oven walls reached 1100 °C. The temperature of the wall was kept constant throughout the test. The coke was pushed after 3 h and 30 min [21]. As bulk density varies as a function of grain size and moisture content, both parameters were kept as close as possible in each series of carbonizations to give mean values of 791 and 771 kg/m^3 for LV and HV respectively.

Table 1
Proximate and ultimate analyses of the fresh coals (LV, HV), the oxidized coals in baskets (LVOB, HVOB) and trays (LVO, HVO), coal tar (T) and coal tar sludge (CTS).

Coals	LV	LVOB	LVO	HV	HVOB	HVO	T	CTS
Ash (wt% db[a])	8.5	9.2	9.2	7.0	7.6	9.8	0.8	2.2
VM[b] (wt% db[a])	20.3	20.6	20.1	34.2	30.6	30.5	61.9	44.9
C (wt% db[a])	81.7	80.8	80.9	80.8	80.3	77.9	90.3	89.1
H (wt% db[a])	4.3	4.4	4.3	5.1	5.0	4.8	4.7	4.2
N (wt% db[a])	1.8	1.8	1.8	1.8	1.7	1.7	0.8	1.1
S (wt% db[a])	0.71	0.73	0.66	0.98	0.83	0.88	0.38	0.52
O (wt% db[a])	2.8	3.5	3.9	4.3	5.0	4.8	2.8	1.9
C/O[c]	39	31	37	25	22	22	43	61

[a] Dry basis.
[b] Volatile matter.
[c] Atomic ratio.

2.5. Semicoke contraction

The Koppers-INCAR test was used to assess the variation in charge height during heating. A coal sample of 80 g was heated from the sole in a stainless steel crucible for 2 h. The change in charge height compared to the initial state of the coal sample was recorded on a graph and expressed in mm. Contraction is expressed by negative values, while positive values indicate expansion.

2.6. Textural characterization

Rectangular prism pieces of semicokes produced at 575 °C with the following sizes: a height of 10 mm, a width of 5 mm and a length of 8 mm, were used for the textural characterization. The pore size distribution was determined on a Micromeritics autopore IV 9500 mercury porosimeter by increasing the pressure up to 227 MPa in order to determine pore sizes in the range between 140 μm to 5.5 nm. Porosity was grouped into three categories: coarse porosity (dp > 12 μm), macroporosity (12 μm > dp > 50 nm) and mesoporosity (50 nm > dp > 5.5 nm).

FE-SEM images were obtained on a Quanta FEG650 microscope (FEI Company) at 25 kV.

2.7. Coke quality

The cold mechanical strength of the cokes produced was assessed by applying the JIS test (JIS K2151 standard procedure). After the test the coke was sieved and the DI150/15 and D150/5 indices were calculated from the amount of coke with a particle size >15 mm and smaller than 5 mm respectively. Coke reactivity and mechanical strength after reaction were assessed by means of the NSC test (ASTM D5341 standard procedure). A coke destined for use in blast furnaces must have a CRI index value in the 20–30% range and a CSR index value of above 60–65% [22].

3. Results and discussion

The fresh coals were oxidized and then different additives were used to restore the properties of the oxidized coals to their original state. The main characteristics of the fresh and oxidized coals together with those of the bituminous additives are shown in Table 1. The effect of the oxidation on the proximate and ultimate analyses is slightly more noticeable in the high volatile coal than in the low volatile one. In relation to oxidation, the proximate analyses reveal an increase in ash content for both coals but a reduction in VM content only in HV (Table 1). These trends are accompanied by a very slight decline in elemental carbon, elemental hydrogen and sulphur content and a slight increase in oxygen content, confirming the findings of a previous study [23].

3.1. Recovery of coal thermoplastic properties with the use of additives

To study the thermoplastic properties of the coals, a Gieseler plastometer was used. This method is employed in the steel industry and is considered to be a very sensitive indicator of the degree of oxidation in coals.

The plastic properties of the fresh and oxidized coals and their blends with the additives, T and CTS, are shown in Table 2. In accordance with its rank, the low volatile coal has higher temperature of maximum fluidity, a lower maximum fluidity and a narrower plastic range.