

Effect of pre-oxidation on the porosity development in a heavy oil fly ash by CO₂ activation

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Abstract

The effect of pre-oxidation on the porosity evolution in heavy-oil fly ash subjected to activation with CO₂ has been investigated. After preliminary acid leaching, used to reduce the mineral matter content, the leached fly ash has been oxidised in air at 250 °C for 36 h. Pyrolysis was conducted on the unoxidised and oxidised leached fly ash at 900 °C for 2 h and the resultant chars were activated with CO₂ at 900 °C for different times. The activated samples have been characterised as regards the surface area and the pore volume.

The pre-oxidation enhances the porosity development mainly in terms of mesoporosity leading to obtain activated products with higher surface area (about 270 m²/g at a 40% burn-off).

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1. Introduction

In previous works [1,2], the possibility of converting heavy-oil fly ashes, after acid leaching to reduce the mineral matter content, into porous matrices by CO₂ activation has been investigated. The resultant activated products showed structures mainly mesoporous with a maximum in surface area of about 160 m²/g.

A considerable amount of work on the conversion of coals and other carbonaceous materials into activated carbons has shown that the pre-oxidation plays an important role in the development of highly microporous structures [3–10] by formation of oxygen groups which reduce the thermoplastic properties of the material [4].

In the present note, the pre-oxidation has been introduced in the activation process of a heavy-oil fly ash.

2. Experimental

2.1. Starting material

A heavy-oil fly ash collected from electrostatic precipitator of an Italian power electric plant has been used. The as-received fly ash has been sieved and the particle size fraction less than 300 μm has been chosen for this study.

The acid leaching was conducted in accordance with the operative conditions used in previous works [11,12] regarding the recovery of vanadium from heavy-oil fly ashes. The solid residue, after filtration and washing, has been dried in an oven at 105 °C and then placed in a desiccator before being submitted to pre-oxidation and/or to pyrolysis/activation.

2.2. Pre-oxidation, pyrolysis and activation

Oxidation at temperature below 200 °C is a slow and time-consuming process for developing a reasonable pore structure in coals [6] and at temperature higher than 270 °C, the combustion of the carbonaceous matrix occurs markedly leading to significant changes in the composition and in the structure [5]. Consequently, oxidation has been carried out

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on the leached fly ash at 250 °C in an oven with forced circulation of air (30 ml/min at STP) for 36 h. The sample has been placed in ceramic crucibles with a layer height of 3–4 mm.

Unoxidised and oxidised leached fly ashes have been pyrolysed in nitrogen at 900 °C for 2 h in a laboratory horizontal quartz tube. In the same reactor, the chars have been activated with CO₂ at 900 °C for different exposure times. Details of the pyrolysis and activation runs can be found elsewhere [1,2].

Porosimetric characteristics of the samples were determined by an automated adsorption–desorption apparatus (Carlo Erba Sorptomatic 1900). The surface area and porosity have been determined from the application of the BET equation (in the relative pressure range of 0.05–0.35) and the Dollim–Heal method [13] (considering the complete 77 K nitrogen desorption isotherm), respectively.

A JEOL 5600 LV scanning electron microscope (SEM) in conjunction with an energy dispersive spectrometer (EDS) has been used for observing the morphology and the presence of various elements in the particles.

3. Results and discussion

The chemical analyses and porosimetric characteristics of the raw fly ash are shown in Table 1. The low values of surface area and pore volume are typical for these residues [1,2,14] and are the result of their formation path [15].

The SEM morphological analysis shows that the raw fly ash consists of well-distinct spongy and hollow particles (cenospheres) and aggregates. The SEM–EDS microanalysis reveals that the cenospheres contain mainly unburned carbon (85–90 wt%) and organic sulphur and the

inorganic components are prevailing in the aggregates. Besides, the presence of adherent inorganic matter on the external surface of the cenospheres has been observed (Fig. 1).

The characteristics of the leached fly ash are compared to those of the raw fly ash in Table 1. The H₂SO₄ leaching reduces the mineral matter content from 22.8 to 4.5 wt%. The decrease of volatile matter (VM) observed may be mainly attributed to the removal of inorganic compounds that decompose at high temperature. The leaching removes the inorganic matter from both the surface and inside of the cenospheres; only the residual organically bound sulphur is again present (see Fig. 2).

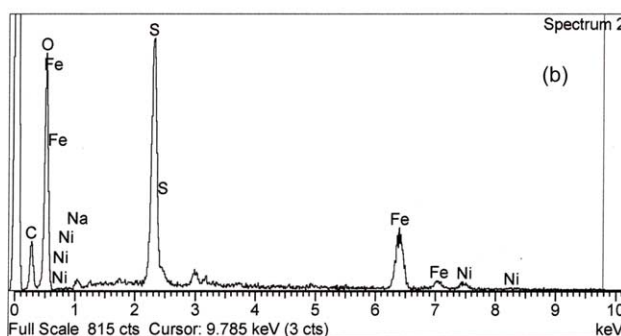
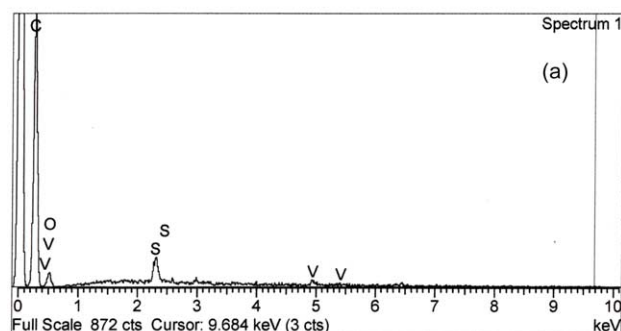
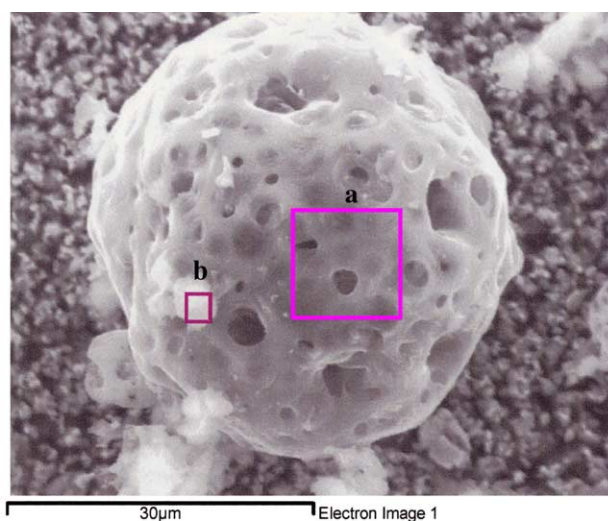


Table 1
Chemical analyses and porosimetric characteristics of the raw and leached fly ashes

Sample	Raw fly ash	Leached fly ash	Oxidised leached fly ash
<i>Proximate (dry basis, wt%)</i>			
Volatile matter ^a	46.0	2.8	9.0
Fixed carbon	31.2	92.7	86.5
Ash	22.8	4.5	4.5
<i>Ultimate (dry ash free, wt%)</i>			
Carbon		97.6	98.0
Hydrogen		0.1	~0
Nitrogen		0.7	0.4
Sulphur		1.2	~0
O (by difference)		0.4	1.6
Atomic ratio O/C		0.003	0.012
BET surface area, m ² /g	10	111	114
Pore volume ^b , cm ³ /g	0.04	0.08	0.120
Micropore volume ^c , cm ³ /g	~0	0.009	0.010

^a Value determined in N₂ at 900 °C.

^b Width less than 2 nm.

^c Width between 2 and 50 nm.

Fig. 1. SEM–EDS microanalysis on the surface of a particle of the raw fly ash.

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