Microporosity Development in Coal-Based Carbon Foams

Elena Rodríguez, Roberto García*

Instituto Nacional del Carbón, INCAR-CSIC, C/ Francisco Pintado Fe, 26,
33011 Oviedo, Spain

ABSTRACT: This paper presents a novel method of manufacturing carbon foams from coals with a bimodal porosity structure (macro- and microporosity), by means of a carbonisation process at 450 or 475 °C that produces the carbon foam, followed by chemical activation with zinc chloride at 500 °C. The activation agent influences the development of macroporosity during the foaming step and gives rise to microporosity (major pore sizes in the 0.6-1.1 nm range) and a specific surface area (up to 762 m² g⁻¹) in the activation step. A coal with a lower volatile matter content and less fluidity gives rise to carbon foams with a higher macropore volume but a lower macropore size. A higher gas flow and a longer soaking time in the activation step lead to a larger micropore volume and a higher surface area. Foams with a still significant micropore network can be obtained by performing simultaneous chemical (with ZnCl₂) and physical (with CO₂) activations at 800 °C. Presumably, such foams would display higher mechanical strength and electrical conductivity.

Keywords: Carbon foams; Chemical activation; Physical activation

*Corresponding author

E-mail: robo@incar.csic.es. Phone: +34 985 118963. Fax: +34 985 297662

1. INTRODUCTION

Since carbon foams were first developed by Ford in 1964 from thermosetting organic polymers,¹ many new precursors and synthesis methods have been reported.^{2,3} Recent studies have revealed that carbon foams can be obtained from coal by means of a controlled carbonization process under pressure, without having to use foaming agents or stabilization steps.⁴ It is already known that the plastic behaviour of raw coal and the synthesis conditions (temperature and pressure) to which it is subjected determine the properties of the resultant foam.⁵ Coal offers an interesting economical alternative for carbon foam manufacture to other conventional precursors such as polymers or pitches.

Coal based carbon foams are light weight materials with large interconnected pores (mainly macropores), that display tailorable thermal, mechanical and electrical properties. Such materials can be used in a wide range of industrial applications, including insulation materials,⁶ reinforcing phases for structural composite materials,⁷ anodes for ion-lithium batteries⁸ and many others. However, their poor textural parameters (in terms of microporosity volume and surface area) prevent them from being employed as catalyst supports, as hydrogen storage materials or in supercapacitor applications.

The most common methods to develop microporosity in carbons are chemical and physical activation. Chemical activation involves the pyrolysis of the precursor at a relatively low temperature in the presence of a dehydrating agent (e.g., ZnCl_2 , H_3PO_4 , KOH , NaOH), whereas physical activation involves the carbonization of the precursor followed by heat treatment in the presence of a mildly oxidizing gas, such as carbon dioxide or steam. A combination of both methods is also a possibility. The final pore structure of the activated materials

depends largely on the nature of the precursor.⁹ Thus, in some cases, the activation method selected might not be effective. Moreover, multiple variables in the activation process, such as the amount of activating agent, the gas flow rate, heating rate, temperature, etc., can also influence the final properties of the activated carbon.¹⁰⁻¹²

This work describes a simple method to prepare coal-based carbon foams with a bimodal porosity (macro and microporosity) by means of chemical activation with zinc chloride, without the need of combining two different materials (coating procedures).¹³ The microporosity, added to the typical macroporous texture of the carbon foams made from coal, will enhance these materials with the potential capacity of being used as catalysts supports or adsorbent materials. The parameters involved in the foaming and activation processes have been evaluated in order to determine their effect on the porous texture of the resultant foams. Subsequent physical activation with CO₂ at 800 °C was also carried out. Presumably, the resultant activated foams would have improved mechanical and electrical properties.

2. EXPERIMENTAL SECTION

2.1. Precursors. Two bituminous coals, Pondfork (P) and Fenxi (F), were used as carbon foam precursors. The analytical results in Table 1 show that these coals have a different volatile matter content and plastic behaviour, characteristics that have a huge influence on the properties of the resultant foam.⁵ The coals were ground to < 212 µm before being treated.

2.2. Activated foam preparation. The chemical activation of the coal-based carbon foams was carried out using ZnCl₂ as chemical reagent. This was

initially mixed with the precursor coal by impregnation. Before the foaming process, 15 g of the precursor coal was added to a solution of 15 g ZnCl_2 in 100 ml EtOH, (coal/ ZnCl_2 mass ratio, 1/1 in most of the experiments, 1/2 in one experiment for comparative purposes). The mixing step was performed at 60-75 °C for 2 h, by means of magnetic stirring and the resultant mixture was dried at 105 °C for 2 days in order to remove as much solvent as possible. After that, the impregnated coal was loaded into a cone trunk shaped stainless steel reactor coated with aluminium foil. The loaded reactor was purged with argon to obtain an inert atmosphere, and subsequently the valves were closed to prevent the volatile matter from leaving the reactor during carbonisation. The foaming process was carried out in a fluidised sand bed oven at the temperature of coal maximum fluidity (450 °C for P and 475 °C for F), for 2 h. The "green" foams obtained after this step, were carbonised in a horizontal tubular furnace under Ar flow by heating at a rate of 4 °C/min up to the reaction temperature (500, 600 or 800 °C).

The experimental conditions employed and the corresponding sample designations are listed in Table 2. The activation temperature is indicated in the names of the samples. Other variables studied during the foaming and activation processes are indicated in parenthesis and brackets, respectively.

It is important to note that foaming and activation were carried out in two sequential steps, the reason being that the activation temperature exceeds the re-solidification temperature of the coal. If the foaming process was carried out at 500 °C, the resultant foams would possess an irregular morphology with cracks in the pore walls.⁴

After carbonization, the samples were washed with a 0.5 M HCl solution to eliminate any ZnCl_2 residue. The samples were then washed in Soxhlet extractors with Milli-Q water for 5 days to remove the chloride ions. Finally, the cleansed samples were dried at 110 °C overnight.

Foams PZ500 and PZ were also subjected to physical activation with CO_2 . In the case of PZ, chemical and physical activation were carried out simultaneously in the same step. The process consisted in heating them from room temperature up to 800 °C under an Ar flow of 100 ml/min. Once the temperature of 800 °C was reached the samples were subjected to a carbon dioxide stream at the same flow rate for 20 h. The products were labelled as PZ500-PA, and PZ-PA, respectively. This treatment was also carried out on a non-activated foam, which had not been impregnated with ZnCl_2 , the resultant foam being designated as P500-PA.

2.3. Characterization techniques. The morphology of the activated foams was examined by scanning electron microscopy (SEM) using a Zeiss microscope (model DSM 942), equipped with an OXFORD EDS detector (model Link-Isis II).

The true density (ρ_{He}) was measured by means of a Micromeritics Accupyc 1330 pycnometer, using helium as probe gas. The samples were outgassed at 120 °C overnight prior to analysis. The apparent density (ρ_{Hg}) was determined with mercury on a Micromeritics AutoPore IV apparatus. The samples were previously dried at 120 °C in an oven for 1 h. The pore volume distributions were evaluated with a mercury porosimeter that is able to provide a maximum operating pressure of 227 MPa. The total pore volume (V_{Hg}) was

calculated with equation (1), and the percentage of open porosity (s) with equation (2).

$$V_{Hg} = (1/\rho_{Hg}) - (1/\rho_{He}) \quad (1)$$

$$s = [1 - (\rho_{Hg}/\rho_{He})] \cdot 100 \quad (2)$$

The porous texture was analyzed by the physical adsorption of N₂, measured at -196 °C in a Micromeritics ASAP 2420 semiautomatic adsorption apparatus. Adsorption isotherms of CO₂ at 0 °C were evaluated using a Quantachrome NOVA 1200 system in order to determine the narrow porosity (<0.7 nm) where N₂ adsorption may be kinetically restricted.¹⁴ In both cases all the samples were outgassed overnight at 120 °C under vacuum right up to the beginning of the adsorption run.

The apparent surface areas (S_{BET}) were calculated from the N₂ adsorption data, according to the Brunauer-Emmett-Teller (BET) equation, using data in the 0.01–0.2 relative pressure range. The total pore volume, V_t , was obtained from the amount of N₂ adsorbed at a relative pressure of 0.975, and the micropore volume, V_{DR-N_2} , was determined using the Dubinin–Radushkevich (DR) equation. The pore size distributions (PSD) based on the nitrogen isotherms were obtained by applying the nonlocal density functional theory (NLDFT), with Micromeritics DFT plus software. The mesopore volume, V_{mp} , was calculated as the difference between V_t and V_{DR-N_2} . The micropore volume, V_{DR-CO_2} , was determined from the CO₂ adsorption isotherms, using the

DR equation. Medium pore sizes were calculated with the equation of Stoeckli and Ballerini, from both N₂ and CO₂ isotherms.¹⁵

3. RESULTS AND DISCUSSION

3.1. Microporosity development. SEM micrographs of the surface morphology of foams PZ500 and P500 are shown in Fig. 1. As can be seen, both foams consist of an open network of interconnected macropores. Therefore, the addition of ZnCl₂ to the coal before the foaming step does not appear to affect the three-dimensional structure of the foams. When a larger amount of ZnCl₂ (i.e., mass ratio 1:2) was used for the activation, the precursor coal was unable to agglomerate during the foaming process and a powder was obtained instead of a one-piece foam.

The main macropore sizes in both samples ranged between 0.5 and 1.5 mm, but in the activated foam there was a larger proportion of voids in the walls of the main pores, as can be seen from Figs. 1b and 1d. Furthermore, magnification of these surfaces (Figs. 1e and 1f) reveals that the walls of the activated foam have a porous texture unlike those of the non-activated foam.

Furthermore, textural characterization of these foams (Table 3) shows that chemical activation increased the proportion of open porosity and the total pore volume. The activated foam therefore displays a lower apparent density. The pore size distributions obtained by mercury porosimetry are presented in Fig. 2. The activated foam PZ500 exhibits a wider range of macroporosity, with a significant macropore volume between 50 and 5 μm , which is absent in the case of the non-activated P500.

An increase in macroporosity is also observed in foam PZ, which has not yet been subjected to the 500 °C activation step, indicating that the presence of ZnCl₂ during the foaming process has a significant influence on its macroporous structure. There are two main factors responsible for the evolution of the pore structure in carbon foams: coal fluidity and the pressure generated inside the reactor during the foaming process. When the foam is prepared from the coal/ZnCl₂ mixture the pressure in the reactor increases from the 70 bar reached with the precursor coal to 94 bar. However, it should be taken into account that the blend, when loaded into the reactor, is not completely dry. Moreover, the ZnCl₂ has a melting point of 283 °C and the pressure increase might also be due to the release of the moisture associated with the solid phase of the ZnCl₂ (Ahmadpour and Do also observed an increase in the pressure at 300 °C).¹⁰ According to previous studies on coal foams,^{2,4} the increase in pressure may be the cause of the shift to a lower mean pore size. However, the non-activated foam (P500) presents a lower pore volume and this result is not consistent with the effects of the variation in pressure referred to above.^{2,4} In order to explain this inconsistency, it is necessary to take into account the other parameter which has a significant influence on foam properties, i.e., fluidity. The liquid phase of the ZnCl₂ may cause an increase in fluidity during the foaming process, and it is well known that this effect promotes the development of porosity. Swelling experiments on both Pondfork coal and the coal/ZnCl₂ blend carried out at 550 °C under a N₂ stream lend support to this hypothesis. Fig. 3 shows that the swelling of the coal is enhanced by the presence of ZnCl₂, which makes up 50% of the blend. The catalyst is molten at the temperature at which the foam is manufactured.

The development of macroporosity by chemical activation with ZnCl_2 has also been reported in peach stones by Caturla et al.¹⁶ They observed that when a high amount of ZnCl_2 was employed, a widening of the microporosity occurred in some parts of the foam, possibly due to the decomposition of organic matter, resulting in meso and macroporosity.

The results show that microporosity is not created before thermal treatment at 500 °C, as will be discussed below. As can be seen from Fig. 4, chemical activation results in significant changes in the capacity of the foam to adsorb N_2 . Whereas typical coal-derived foams are non-microporous materials, the activated foam PZ500 presents a Type I isotherm according to the IUPAC classification,¹⁷ which corresponds to a microporous material. The almost horizontal plateau in Fig. 4 indicates that the amount of N_2 adsorbed outside the micropores is very small.

Several textural parameters calculated from various analyses of the N_2 and CO_2 isotherms are listed in Table 4. As can be seen, the development of micropores is accompanied by an increase in specific BET surface area, S_{BET} . Thus, S_{BET} increases from 2 to more than 663 $\text{m}^2 \text{g}^{-1}$, while the micropore volume obtained by applying the Dubinin-Radushkevich method, $V_{\text{DR-N}_2}$ achieves values of 0.25 $\text{cm}^3 \text{g}^{-1}$. This value is very similar to that of the total pore volume, indicating that the porosity that has developed is almost exclusively microporosity. However, in the case of the foam PZ, S_{BET} barely changes (10 $\text{m}^2 \text{g}^{-1}$). These results suggest that, in the foaming process, ZnCl_2 only produces an increase in macroporosity, additional thermal treatment being necessary to develop microporosity.

The mechanism of pore formation promoted by ZnCl_2 has been extensively studied by several workers.^{10,12,16} In cellulosic materials, the reagent is incorporated into the interior of the particles, promoting a dehydration process^{16,18} that finally results in the formation of hydrated compounds, which make up the precursor structure. This prevents the contraction of particles during the heat treatment. It has been suggested, therefore, that ZnCl_2 acts as a template for the creation of microporosity.¹⁸ This chemical agent also inhibits the formation of tars, which could clog up the pores of the sample. However, in coals, ZnCl_2 seems to produce dehydrogenation of the aliphatic structures, while the aromatic hydrogen tends to increase.¹⁰ This process takes place during the early stages of pyrolysis (below 400 °C), delaying the escape of tar and the formation of cross-links. The results obtained with these foams indicate that, after the foaming process, the ZnCl_2 has not yet led to the creation of microporosity. The reason for this could be the low temperature and pressure inside the reactor. It has been previously demonstrated by Teng and Yeh¹² that temperatures below 500 °C lead to a reduction in porosity. They attributed this to the fact that the release of tar is not possible at low temperatures. An increase in pressure could also produce a similar result.

On the other hand, an increase in the activation temperature from 500 to 800 °C leads to a reduction in the capacity of the foam to adsorb N_2 (Fig. 4). This phenomenon has also been reported by other authors,^{10,16} who suggested that the presence of ZnCl_2 induces the formation of cross-links between the carbon aggregates during carbonization, favouring the development of microporosity. However, temperatures above 500 °C can cause these cross-links to break, resulting in a shrinkage of the carbon structure, with the

subsequent collapse of pores and the reduction of microporosity. Accordingly, the total volume of macropores increases (Table 3).

The variables studied in the following sections have been tested on foams activated at 500 °C, since this seems to be the most effective temperature for developing microporosity.

The PSD obtained for sample PZ500 by the NLDFT method (Fig. 5) shows two maxima at 0.7 and 1.2 nm, but it should be noted that the minimum at around 1 nm is only an artefact introduced by modelling assumptions.¹⁹

The micropore volume calculated from the CO₂ adsorption isotherm (V_{DR-CO_2}) only provides information about the volume of micropores smaller than 0.7 nm, as CO₂ cannot penetrate wider micropores at the relative pressure (0.03) attained at 0 °C.^{20,21} As Table 4 shows, the value obtained by CO₂ is lower to that achieved by N₂, which means that the microporosity developed in the activated foam has micropore sizes above and below 0.7 nm. Accordingly, the medium micropore sizes, calculated with the equation of Stoeckli and Ballerini¹⁵ for the foams activated at 500 °C, display values of 0.6 nm for the CO₂ adsorption isotherm and 1.1 nm for the N₂ one.

As pointed out in the Experimental section, all the foams prepared (including PZ and those heat-treated at 500 °C), were subjected to washing with HCl and water. This step plays an important role in the development of porosity, as the products originating from the decomposition of the chemical agent during activation tend to accumulate inside the generated pores, blocking the pore entrances to N₂ molecules. Insufficient washing would then lead to pore blockage and result in pore volume underestimations. Surface characterization of foam PZ500 was carried out by SEM-EDAX analysis to test the effect of

washing with room temperature water (using an ultrasonic bath) and with hot water (by Soxhlet) (in both cases, after washing with HCl). The results, presented in Fig. 6, clearly show that it is necessary to employ hot water to remove zinc salts completely. Moreover, after five days of Soxhlet washing, all chlorides are eliminated. Accordingly, S_{BET} increases from 290 to 663 $\text{m}^2 \text{g}^{-1}$.

3.2. Effect of different variables on the foaming step. Three different parameters involved in the foaming process (the precursor coal, heating rate and initial pressure) are evaluated in this section to determine their influence on the textural properties of the resultant carbon foams.

The results listed in Table 3 show that foam FZ500 has a higher total pore volume than foam PZ500. This finding is consistent with previous studies on coal foams,⁵ and it is related to the amount of volatile matter released. Fenxi coal is a low-volatile bituminous coal (Table 1), which explains why the pressure reached inside the reactor was lower (54 bar) than in the case of Pondfork coal (94 bar). Thus, in the case of foam FZ500 the release of volatile matter is easier and condensation reactions are less favoured. As a result, a better development of porosity is achieved.

Moreover, foam FZ500 displays a rather narrow macropore size distribution (determined by mercury porosimetry) and a smaller mean pore size in comparison with PZ500 (Fig. 7). These results could also be attributed to characteristics of the precursor coal (Table 1). The low fluidity of Fenxi coal inhibits the merging of adjacent pores, thereby preventing the formation of larger pores.

When other parameters, such as initial pressure in the case of PZ(10)500 and heating rate in the case of PZ(r)500, have been modified, the pressure

reached at the end of the foaming process does not differ much from that of foam PZ500 and the macroporosity texture remains unchanged.

The N₂ isotherms for these foams are presented in Fig. 8. The close similarity of shape and position reveals that modification of several variables in the foaming process has had practically no effect on the N₂ uptake. Consequently, the foams present similar micropore-related parameters (Table 3).

3.3. Effect of different variables on the activation step. The parameters evaluated in the activation process were the soaking time and Ar flow rate. As can be seen in Fig. 9, these parameters do not significantly affect the width of the macropore size distribution (as determined by mercury porosimetry). However, they do lead to an increase in pore volume. Whereas the Ar flow rate promotes the formation of low-sized macropores, a prolonged soaking time results in the formation of macropores over the whole size range.

From the results presented in Fig. 10, it can be inferred that, when the Ar flow rate in the activation step is raised from 100 ml min⁻¹ to 300 ml min⁻¹, a slight increase in N₂ uptake occurs. This is because both the surface area and the micropore volume increase (Table 4). When activating anthracite with KOH, Linares-Solano et al.²² observed an enhancement of N₂ adsorption capacity with increasing flow rate, which led them to conclude that a more rapid elimination of the gases favours the creation of micropores.

A longer soaking time also leads to a slight increase in the amount of N₂ adsorbed. This trend has also been reported by Teng et al., who state that a minimum amount of carbonization time must elapse for any significant development of porosity, even in conditions of high temperature.¹²

This would explain why foam PZ500[2][300], which was obtained by increasing both parameters, achieved the maximum specific surface area, S_{BET} , $762 \text{ m}^2 \text{ g}^{-1}$, and total pore volume, V_t , $0.32 \text{ cm}^3 \text{ g}^{-1}$.

3.4. Effect of combined activation with CO_2 . It was previously mentioned that temperatures above 600°C caused a severe reduction in porosity. However, physical activation at 800°C with CO_2 can be interesting as the main effect of this treatment is the formation of new pores and the widening of already existing pores.^{10,23,24} Our objective was to prevent a reduction in porosity resulting from the increase of temperature. It should also be pointed out that physical activation in the case of non-activated foam P500 did not produce any changes in textural properties.

The results listed in Table 4 and displayed in Fig. 11 show that physical activation is not enough to prevent a shrinkage of carbon pores, because, as well as gasification, carbonization also takes place. For this reason, foam PZ500-PA shows similar textural parameters to foam PZ800. However when physical activation is carried out at the same time as the ZnCl_2 activation step (foam PZ-PA), the reduction in porosity is lower and the mesopore volume increases slightly, until it reaches 22%. The levels of burn-off achieved were 40.4% in the case of PZ-PA and 22.6% for PZ500-PA. This difference can be attributed to the presence of ZnCl_2 during gasification. ZnCl_2 has a boiling point of $\sim 750^\circ\text{C}$. Therefore, in the case of foam PZ-PA, the ZnCl_2 present in the carbon structure is removed with the thermal treatment, resulting in the creation of new pores in the carbon structure, which are able to react more readily with CO_2 .

4. CONCLUSIONS

Carbon foams with combined macro- and microporous structures were obtained by carbonisation followed by chemical activation with ZnCl_2 . In the foam-producing carbonisation process, carried out at 450 or 475 °C, additional macroporosity was created compared to normal carbon foams, as a consequence of the presence of ZnCl_2 (previously blended with the precursor coal). The increase in the fluidity of the blend inside the reactor, due to ZnCl_2 being in a molten state at the foaming temperature, is thought to be responsible for the enhancement of macroporosity.

Using a coal with a lower volatile matter content as precursor favours the development of a higher porosity as a consequence of the lower pressure achieved in the reactor. Furthermore, a lower fluidity in the precursor coal hinders the merging of pores and results in lower pore sizes.

Microporosity and the specific BET surface area are created in the chemical activation step at 500 °C. Major micropore sizes are inside the 0.6-1.1 nm range and surface areas are above 600 m² g⁻¹ in most of the cases. A higher flow of inert gas produces an increase in micropore volume and surface area, probably due to a more rapid elimination of gases. An activation time of two hours is also recommended to achieve a better microporosity development.

Chemical activation at 800 °C is less effective for developing microporosity and surface area. However, simultaneous physical activation with CO_2 improves the textural properties, although they do not reach the values attained by chemical activation at 500 °C.

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TABLES

Table 1. Analytical data of the precursor coals.

<i>Giesler plasticity test</i>	Fenxi	Pondfork
Softening temperature (°C)	440	391
Solidification temperature (°C)	494	482
Maximum fluidity temperature (°C)	470	443
Fluidity (ddpm)	12	12401
<i>Proximate analysis</i>		
Volatile matter (% d.b.)	17.5	29.83
Ash (% d.b.)	10.0	6.46

ddpm: dial divisions per minute obtained in the Gieseler plasticity test (ASTM D2639-98).

Table 2. Experimental parameters and nomenclature of the carbon foams.

Carbon foam	Foaming			Activation		
	Rate (°C min ⁻¹)	Pressure (bar)	Temp. (°C)	Ar flow (ml min ⁻¹)	Time (h)	Temp. (°C)
P500	-	1	450	100	1	500
PZ	-	1	450	-	-	-
PZ500	-	1	450	100	1	500
FZ500	-	1	475	100	1	500
PZ(r)500	2	1	450	100	1	500
PZ(10)500	-	10	450	100	1	500
PZ500[300]	-	1	450	300	1	500
PZ500[2]	-	1	450	100	2	500
PZ500[2][300]	-	1	450	300	2	500
PZ600	-	1	450	100	1	600
PZ800	-	1	450	100	1	800
P500-PA	-	1	450	100	1	500
PZ500-PA	-	1	450	100	1	500
PZ-PA	-	1	450	100	-	800

Table 3. General properties of the carbon foams.

Carbon foam	True density (ρ_{He} , g cm ⁻³)	Apparent density (ρ_{Hg} , g cm ⁻³)	Open porosity (s, %)	Total pore volume (V_{Hg} , cm ³ g ⁻¹)
P500	1.59	0.92	42.1	0.46
PZ	1.46	0.51	65.0	1.27
PZ500	1.60	0.58	63.9	1.11
FZ500	1.51	0.43	71.6	1.67
PZ(r)500	1.50	0.53	64.7	1.22
PZ(10)500	1.58	0.52	67.2	1.30
PZ500[300]	1.51	0.49	67.2	1.36
PZ500[2]	1.52	0.44	62.7	1.59
PZ800	2.04	0.58	71.6	1.24
PZ600	1.66	0.42	74.8	1.79
PZ500-PA	1.88	0.54	71.0	1.30
PZ-PA	1.98	0.68	65.8	0.97

Table 4. Textural properties of carbon foams obtained from N₂ and CO₂ adsorption isotherms.

Carbon foam	S _{BET} (m ² g ⁻¹)	V _t (cm ³ g ⁻¹)	V _{DR-N2} (cm ³ g ⁻¹)	V _{mp} (cm ³ g ⁻¹)	V _{DR-CO2} (cm ³ g ⁻¹)
P500	2	-	-	-	-
PZ	10	-	-	-	-
PZ500	663	0.28	0.25	0.03	0.21
FZ500	655	0.26	0.24	0.02	0.21
PZ(r)500	615	0.28	0.26	0.02	0.21
PZ(10)500	598	0.27	0.25	0.02	0.21
PZ500[300]	700	0.30	0.29	0.01	0.22
PZ500[2]	672	0.29	0.27	0.02	0.22
PZ500[300][2]	762	0.32	0.30	0.02	0.23
PZ600	572	0.24	0.22	0.02	0.21
PZ800	252	0.12	0.10	0.02	0.13
P500-PA	3	-	-	-	-
PZ500-PA	240	0.12	0.10	0.02	0.10
PZ-PA	364	0.18	0.14	0.04	0.13

FIGURES

Fig. 1. SEM micrographs of the non-activated foam P500 (a-b), and the activated foam PZ500 (c-f).

Fig. 2. Pore size distribution obtained by mercury porosimetry for foams PZ500, PZ and P500.

Fig. 3. Residues of the swelling experiments carried out on Pondfork coal and on the Pondfork/ ZnCl_2 (1/1 weight) blend, in a tubular furnace, under the following conditions: heating rate, $5\text{ }^\circ\text{C min}^{-1}$; final temperature, $550\text{ }^\circ\text{C}$; soaking time, 1 h; flow of N_2 , 200 ml min^{-1} .

Fig. 4. N₂ adsorption isotherms at -196 °C of foams PZ500, PZ600, PZ800, P500 and PZ.

Fig. 5. PSD of PZ500 calculated by the NLDFT method from the N₂ adsorption isotherm at -196 °C.

Fig. 6. SEM-EDAX spectra of PZ500 after different washing procedures.

Fig. 7. Pore size distribution obtained by mercury porosimetry for foams PZ500, FZ500, PZ(10)500 and PZ(r)500.

Fig. 8. Nitrogen adsorption isotherms at -196 °C of foams PZ500, FZ500, PZ(10)500 and PZ(r)500.

Fig. 9. Pore size distribution obtained by mercury porosimetry for foams PZ500, PZ500[300] and PZ500[2].

Fig. 10. Nitrogen adsorption isotherms at -196 °C of foams PZ500, PZ500[300], PZ500[2] and PZ500[2][300].

Fig. 11. Nitrogen adsorption isotherms at -196 °C of foams PZ500, PZ800, PZ500-PA and PZ-PA.