

ANALYSIS OF SPENT ACTIVE COKE PROPERTIES BY SPOUTED BED TECHNIQUE

Bronislaw Buczek

AGH – University of Science and Technology, Faculty of Energy and Fuels, 30-059 Cracow, Poland

Samples of active coke, fresh and spent after cleaning flue gases from communal waste incinerators, were studied. The outer layers of both coke particles were separately removed by comminution mechanism in a spouted bed. Analyses included density, mercury porosimetry and adsorption. The remaining cores were examined to determine the degree of consumption of coke by adsorption of hazardous emissions (SO₂, HCl, heavy metals) through its bed. The differences in contamination levels within the porous structure of the particles were estimated. The study demonstrated the effectiveness of active coke in the cleaning of flue gases.

Keywords: active coke, spouted bed, waste incineration plant, WKV method

1. INTRODUCTION

Flue gases from waste incineration plants contain CO₂, CO, steam, NO_x, SO₂, HCl, HF, as well as toxic organic compounds, such as polychlorinated dibenzo-*p*-dioxins and dibenzophuranes despite the extreme conditions in which combustion is conducted (Jastrzab, 2012). Toxic heavy metals (e.g. Cd, Hg, Pb, As, and Tl) also occur in the volatile flue gas ash. Acceptable levels of pollutants in flue gases from the combustion of municipal waste are regulated by relevant provisions (Directive 2000/76/EC). Some pollutants are removed using technology commonly applied in power stations, such as gas dedusting with bag filters or electrostatic precipitators, desulphurisation and NO_x removal. The reduction of dioxin emissions poses a separate problem. The methods used are divided into primary (control of the conditions of the combustion process) and secondary (reducing the concentration of dioxins in the exhaust). The most prevalent in the latter group are flow-sorption, catalytic filter, and deposit methods.

Active coke is used in the secondary filter and deposit methods to adsorb dioxins, mercury vapour, and residues of SO₂ and HCl. Counter-current flow methods, for example WKV (Warme Kraftwerks - und Verfahrenstechnik), are applied in many countries (Witaliński, 1998). Usually the spent coke is incinerated and the bed refilled with fresh adsorbent. It is essential to assess how much of the removed coke has been spent, but the examination of its properties per unit mass is hindered by the deposition on the surface of the residual granules of volatile ash and corrosion products.

Various physical and chemical processes have been carried out in a spouted bed. Whether the phenomenon in a spouted bed is regarded as advantageous or not depends on the process in which it occurs (Mathur and Epstein, 1974; Passos et al., 1998; Zhu et al., 2005).

*Corresponding author, e-mail: bbuczek@agh.edu.pl

The aim of this study was to estimate the consumption of active coke by removing external particle layers using the gradual comminution in the spouted bed (Buczek, 1999).

2. EXPERIMENTAL

2.1. Materials

The commercial active coke AKP-5S produced by Gryfskand at Hajnówka (Poland) was used in the final stage of cleaning the flue gases generated in the incineration of municipal waste conducted by the municipal waste neutralisation plant in Warsaw (Poland).

A sample of applied coke was preliminary treated to remove powder produced by abrasion of coke particles during the operation of the adsorbent bed, and adhering vestiges of volatile powder and corrosion products abraded from the walls of the industrial apparatus.

2.2. Treatment of cokes in a spouted bed

Particles of spent, and for comparison, fresh active coke were subjected to comminution in a spouted bed. A diagram of the experimental equipment is shown in Fig. 1.

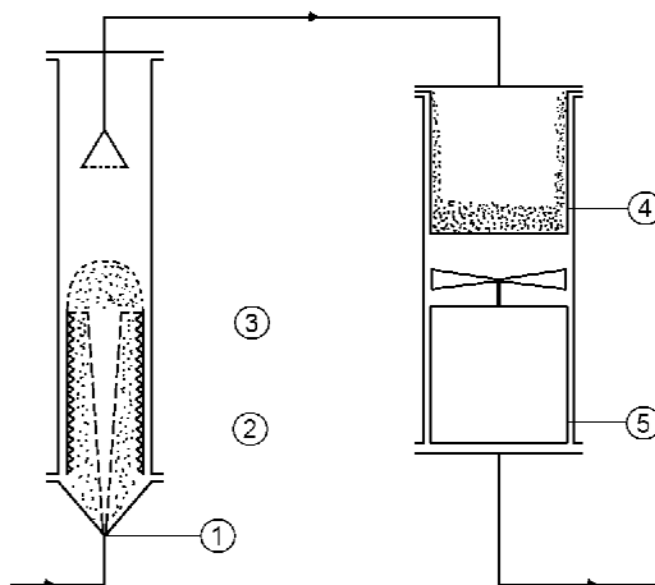


Fig. 1. Apparatus used for abrasion in a spouted bed.
1 - nozzle, 2 - abrasive lining, 3 - column, 4 - sack filter, 5 - fan

The time of the process was chosen so that the amount of material abraded from the external surface of the particles (dust) was removed to about 33 wt. %. The amount of this material was determined by weighing the dust and active coke remaining in the spouted column.

As a result of the attrition process, particles of fresh and spent active coke were obtained. They were designated: fresh AC0, fresh AC33 and spent ACS0, spent ACS33. As a result of the preparation process in the spouted bed, particles of active cokes change in shape and dimensions. These changes for granules removed to 33 wt. % are shown in Fig. 2.

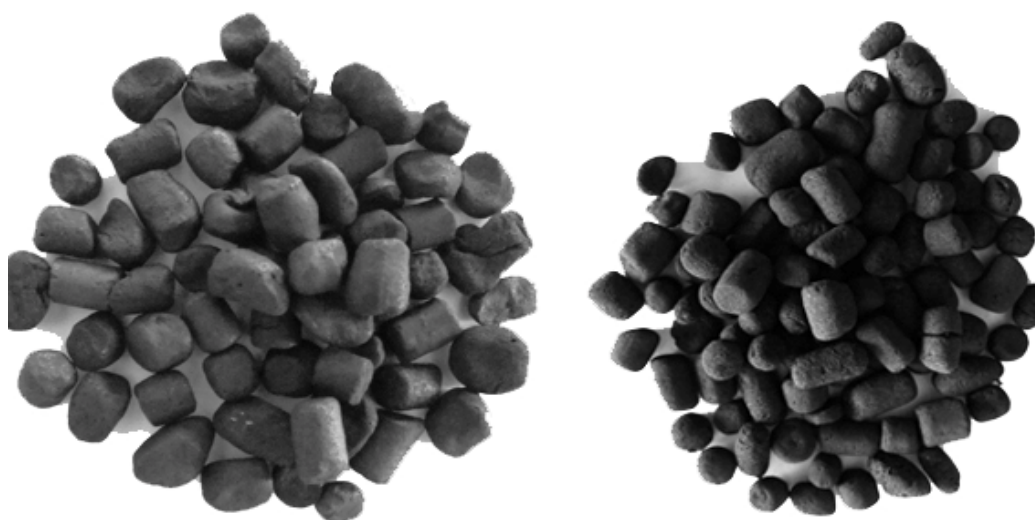


Fig. 2. Change in shape and dimensions of granules of active coke

3. RESULTS AND DISCUSSION

3.1. Densities

In order to characterise tentatively changes in the properties of the active cokes, density measurements were made and shape factors were evaluated. The results are given in Table 1.

Table 1. Densities and shape factors ($\phi = 1/\psi$, where ψ Wadell sphericity factor)

Active coke	AC0	AC33	ACS0	ACS33
True density [kg/m^3]	2380	2342	2314	2243
Apparent density [kg/m^3]	1661	1416	1396	1597
Bulk density [kg/m^3]	602	587	682	585
Shape factor, ϕ	1.25 - 1.32	1.10 - 1.22	1.22 - 1.30	1.09 - 1.20

Particles of all active cokes under investigations belong to group D according to the Geldart classification (Geldart, 1973).

3.2. Mercury porosimetry

The macropore volume for the cokes was obtained by the intrusion technique (Webb et al., 1997) at 293K using a Pascal 440 porosimeter - for pore radii from 5 to 7500 nm. Volumes of macropores in three radii ranges and total volume macropores are shown in Table 2.

Porosimetric investigations show a decrease in the total volume of macropores, depending on the degree of external layer removal (33 wt. %) for both active cokes. Differential dependence is observed for each macropore range. For fresh active cokes more macropores are in radius range 100–1000 nm, whereas in spent active cokes (ACS0, ACS33) maximum macropores were found in range 100-1000 and 1000 – 7500 nm. This indicates that heavy metals are deposited in the outer layer of particles, mainly in macropores with the greatest radii.

Table 2. Macroporosity of fresh and used active cokes

Active coke	AC0	AC33	ACS0	ACS33
Macropores	cm ³ /g	cm ³ /g	cm ³ /g	cm ³ /g
5 - 100 nm	0.023	0.014	0.101	0.017
100 - 1000 nm	0.093	0.076	0.118	0.042
1000 – 7500 nm	0.055	0.031	0.022	0.124
Total macropores	0.171	0.121	0.241	0.183

3.3. Pore structure analysis

Nitrogen adsorption was used to analyse the texture of active cokes. Each isotherm was determined by the volume method using a Sorptomatic 1900 apparatus. The measurements were performed at the temperature of 77.5K at the range of relative pressures $p/p_o = 0.00001 - 0.999$.

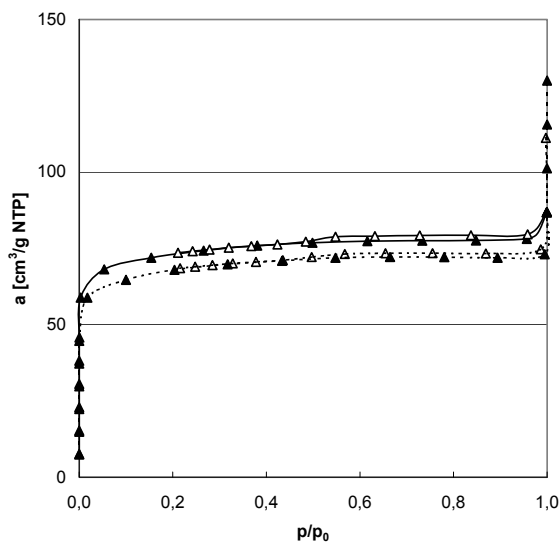


Fig. 3. Nitrogen adsorption-desorption isotherms for active cokes AC0 (solid) and AC33 (dashed line)

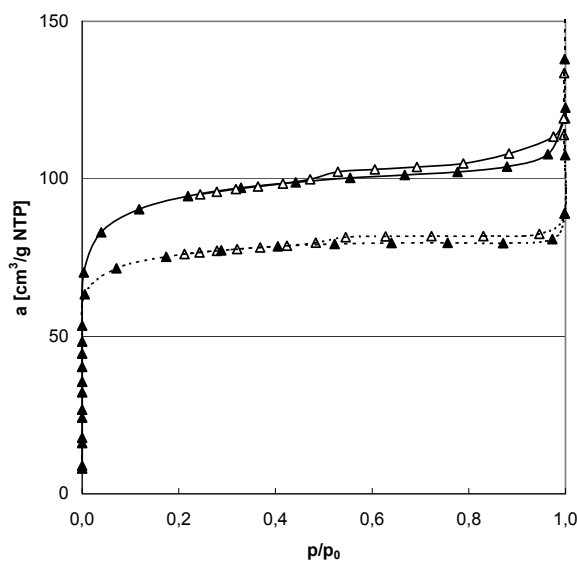


Fig. 4. Nitrogen adsorption-desorption isotherms for active cokes ACS0 (solid) and ACS33 (dashed line)

All the isotherms show the Langmuir behaviour of rising adsorption in the low pressure range and a hysteresis loop, which proves mainly microporous and to a small degree mesoporous structures for both kinds of active cokes.

From the obtained data, parameters characterising the microporous structure (W_0) and the characteristic energy (E_0) from the Dubinin-Radushkevich equation (Dubinin, 1987) were determined. Micropore volume and the amount of adsorbed nitrogen, the formal surface area of micropores (S_{DR}) were calculated. The surface area of mesopores (S_{me}) was calculated using the method proposed by Dollimore and Heal (Dollimore and Heal, 1964) and the specific surface area (S_{BET}) from the Brunauer, Emmet and Teller equation (Bansal and Goyal, 2005). Pore volume (V_p) was obtained from the amount of adsorbed nitrogen under pressure of $p/p_0 = 0.98$. The calculation and analyses of the results are summarised in Table 3. The pore volumes for all active cokes well correlate with the results of the total macroporosity obtained from mercury porosimetry.

Table 3. Analysis of pore structure, surface area of active cokes

Active Coke	W_0 [cm ³ ·g ⁻¹]	E_0 [kJ·mol ⁻¹]	S_{DR} [m ² ·g ⁻¹]	S_{me} [m ² ·g ⁻¹]	S_{BET} [m ² ·g ⁻¹]	V_p [cm ³ /g]
AC0	0.115	23.2	325	11	265	0.125
AC33	0.101	24.6	385	9	235	0.113
ACS0	0.132	24.4	370	21	325	0.172
ACS33	0.112	26.8	315	12	270	0.125

3.4. Content of heavy metals

Tests were carried out on full particles (AC0, ACS0) to determine the eleven heavy metals listed in the maximum emission limits (Hg, Cd, Tl, Sb, As, Pb, Cr, Co, Cu, Mn, and Ni). These measurements were made in the Central Chemical laboratory of Poland's National Geological Institute. Mercury content was determined using a WD-XRF P7 2400 X-ray fluorescence spectrometer by Philips (The Netherlands). 6g samples of the coke ground to a powder were mixed with 1.5 g of a special wax and pressed in a hydraulic press for subsequent spectroscopic determination. The remaining metals were determined in an ICP mass spectrometer, using an ELAN DRC II device by Perkin Elmer (USA). Coke samples were mineralised by microwave-supported concentrated HClO₄, HF, and HNO₃ acids, and the obtained solutions were examined in the spectrometer.

The values obtained in the determinations of content for the remaining heavy metals listed in provisions regulating maximum admissible concentrations for thermal waste disposal are presented in Table 4, and they show that activated coke has a fairly high efficiency for their removal.

Table 4. Contents of selected heavy metals in active coke samples

Active coke	Content of heavy metals										
	Cd	Tl	Sb	As	Pb	Cr	Co	Cu	Mn	Ni	V
Admissible daily level of concentr.	0.05 mg/m ³		Σ 0.05 mg/m ³								
AC0	0.09	0.05	0.74	2.0	4.01	13	6.68	26.1	131	14.4	33
ACS0	0.69	0.05	6.36	2.0	28.8	12	8.96	31.6	129	21.1	32

Nearly seven-fold increase in the content of Pb, Cd, and Sb in the coke was observed, which means that the coke layer absorbed a very substantial amount of these metals. The level of absorption for Cu, Co,

and Ni was lower, amounting only to 1.2-1.4 – fold. The content of Tl and As remained unchanged, while for Cr, Mn, and V there was even a slight decrease, which could be treated as insignificant - within the bounds of experimental error. The data presented in Table 2 relating to the last five metals are not necessarily evidence of the low absorptive efficiency of coke, but may be due to the absence of these metals in the volatile state in the flue gases.

4. CONCLUSIONS

AKP-SS active coke was found to be a good cleaning agent for flue gases generated in the incineration of municipal waste. This applies to its efficiency as a trap for SO₂ and HCl, as well as for the twelve heavy metals with limits to admissible levels of discharge designated under the relevant legal regulations. The properties of coke granules varied with respect to distance from the outer surface. It was observed that, close to the surface, the higher the activation level, the more developed the porous structure of the coke tended to be. A resulting differentiated distribution of trapped pollutants concentration was clearly observed for SO₂ and HCl, but not for Hg. The adsorptive properties for the coke within the working temperature range of the adsorber bed and at higher temperatures may be considered as stable.

The author is grateful to the AGH-University of Science and Technology (Project 11.11.210.244) for its financial support of this work.

I am also grateful to Professor A. S. Wronski from Bradford University UK for helpful suggestions and rewriting of the manuscript.

REFERENCES

- Bansal R.C., Goyal M., 2005. *Activated carbon adsorption*, CRC Press Taylor&Francis Group, Boca Raton, FL USA, 85-101.
- Buczek B., 1999. The influence of properties within particles of active carbons on selected adsorption processes. *Studies Surf. Sci. Catal.*, 120A, 507-530. DOI: 10.1016/S0167-2991(99)80563-1.
- Directive 2000/76/EC of the European Parliament and of the Council of 4 December 2000 on the incineration of waste, OJ L 332,28.12.2000, 91.
- Dollimore D., Heal G.R., 1964. An improved method for the calculation of pore size distribution from adsorption data. *J. Appl. Chem.*, 14, 109-116. DOI: 10.1002/jctb.5010140302.
- Dubin M.M., 1987. Adsorption properties and microporous structures of carbonaceous adsorbent. *Carbon*, 25, 593-598. DOI: 10.1016/0008-6223(87)90208-9.
- Geldart D., 1973. Types of gas fluidization. *Powder Technology*, 7, 285-292. DOI: 10.1016/0032-5910(73)80037-3.
- Jastrzab K., 2012. Properties of activated cokes used for flue gas treatment in industrial waste incineration plants. *Fuel Process. Technol.*, 101, 16-22. DOI: 10.1016/j.fuproc.2011.05.028.
- Mathur K.B., Epstein N., 1974. *Spouted Beds*. Academic Press.
- Passos M., Oliveira L., Franca A.S. Massarani G., 1998. Bixin powder production in conical spouted bed unit. *Drying Technology*, 16, 1855-1879. DOI: 10.1080/07373939808917500.
- Webb P., Orr C., 1997. *Analytical methods in fine particle technology*. Micromeritics Instrument Corporation, Norcross, GA USA, 168-171.
- Witalinski G., 1998. Przeciwwądowy system adsorpcyjnego oczyszczania spalin i przemysłowych gazów odlotowych metoda WKV z wykorzystaniem reaktorów ze złożem koksu/węgla aktywnego. *Przegląd Komunalny*, 3, 41-43.
- Zhu Q.Y., Lim C. J., Epstein N., Bi H.T., 2005. Hydrodynamic characteristics of a powder particle spouted bed with powder entrained in spouting gas. *Can. J. Chem. Eng.*, 83, 644-651. DOI: 10.1002/cjce.5450830404.

Received 11 April 2013

Received in revised form 17 July 2013

Accepted 24 July 2013