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SORPTIVE PROPERTIES OF BLACK COAL ASH FROM MELTING BOILERS

WŁAŚCIWOŚCI SORPCYJNE POPIOŁU ZE SPALANIA WĘGLA W TOPIELNIKU

Abstract

The article presents properties of black coal ash and underlines their utilization as absorbents. During coal combustion in melting boilers, mineral novelties (aluminosilicates of Fe, Ca, K, Na and others) akin to zeolites (phillipsite, klinoptilolite and others) are created. The study of mineralogical composition of fly ash zeolites and results of laboratory research confirmed their selective sorptive properties to Pb, Cu, Cd, NH_4^+. The adsorption isotherms of Pb were measured in fly ash samples with a high content of loss on ignition (LOI) in particular grain classes (22–84.8% LOI). According to the results, the adsorption of Pb^{2+} depending on a surface area size of particular fly ash samples does not show considerable deviation within sorptive strength.

Keywords: black coal ash, sorptive properties, fly ash zeolites

Streszczenie

W artykule przedstawiono właściwości popiołu ze spalania węgla pod kątem jego utylizacji jako absorbentu. Podczas spalania węgla w topielniku tworzą się nowe minerały (glinokrzemiany Fe, Ca, K, Na i innych) podobne do zeolitów (filipsyt, klinoptilolit i in.). Analiza składu mineralogicznego popiołów oraz wyniki badań laboratoryjnych potwierdziły ich selektywną zdolności sorpcji Pb, Cu, Cd, NH_4^+. Wyznaczono izotermy adsorpcji Pb na popiołach o wysokich stratach prażenia (LOI), w szczególności w przedziale 22–84,8% w poszczególnych klasach uziarnienia. Stwierdzono, że adsorpcja Pb^{2+} zależy od wielkości powierzchni popiołu. Nie stwierdzono różnic zdolności sorpcyjnej pomiędzy różnymi próbkami popiołów.

Słowa kluczowe: popiół ze spalania węgla, właściwości sorpcyjne, zeolity

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1. Introduction

The object of the research is fly ash from combustion of black coal in melting boilers of EVO Vojany power plant with combustion temperature in the range of 1400–1600°C. The particle shape of inorganic part of fly ashes is spherical (see Fig. 1); particles of organic part – unburned coal residues - have a ragged irregular shape (see Fig. 2).

The ability of zeolites to absorb some ions is well-known and it is used for removal of some contaminants. The fly ash has also good sorptive properties on the basis of the following:

- the size of surface area – provides active centres for adsorption of cations. The surface area of unburned particles is in the range of about 10 $m^2 \cdot g^{-1}$, the surface area of inorganic part of fly ash is about 1 to 3 $m^2 \cdot g^{-1}$.
- fly ash particles contain residues of unburned particles with a ragged surface. An inorganic part of fly ashes has a lower surface area depending on a type of combustion mechanism. During combustion of the same type of coal in different combustion devices (melting, fluidized-bed and dry bottom boilers), ashes with different morphology are created.

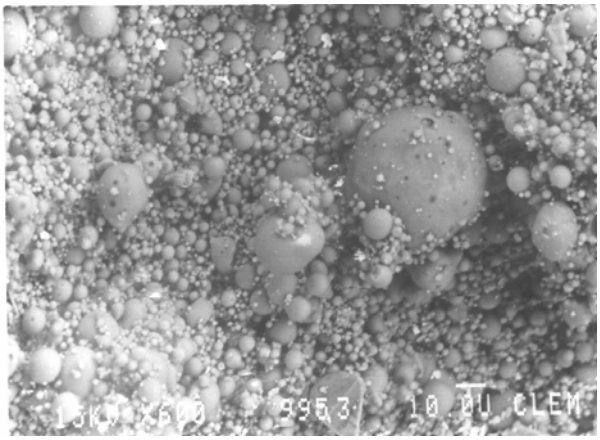

Fig. 1. Morphology of black coal ash particles from melting boiler of EVO Vojany power plant

Rys. 1. Morfologia popiołu ze spalania węgla w topielniku w elektrowni EVO Vojany

In Figure 2 there is acomposition of unburned coal particles. A flotation concentrate contains 82.18% of LOI. From the morphology of particles it is evident that the surface area of unburned coal particles is larger in comparison with the surface area of an inorganic part. The surface of unburned coal is markedly porous.

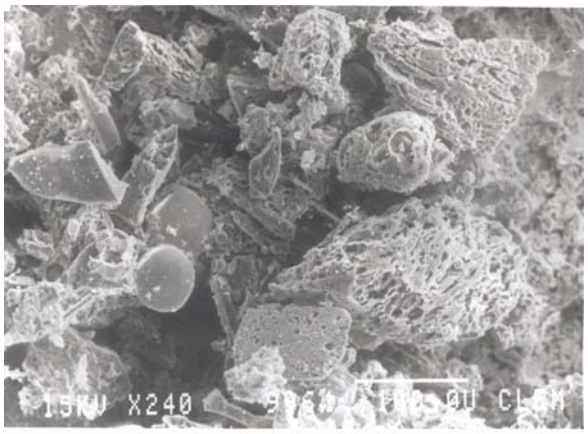

Fig. 2. Morphology of unburned coal particles from melting boiler from EVO Vojany power plant obtained by flotation (flotation concentrate)

Rys. 2. Morfologia niespalonego węgla z topielnika w EVO Vojany uzyskanego na drodze flotacji (koncentrat)

Fig. 3 presents a detail of the particle from the flotation concentrate showed in Fig. 2, enlarged 2000 times. In pores of partly burned coal particles, spherical inorganic particles of fly ash – microspheres – are visibly wedged.

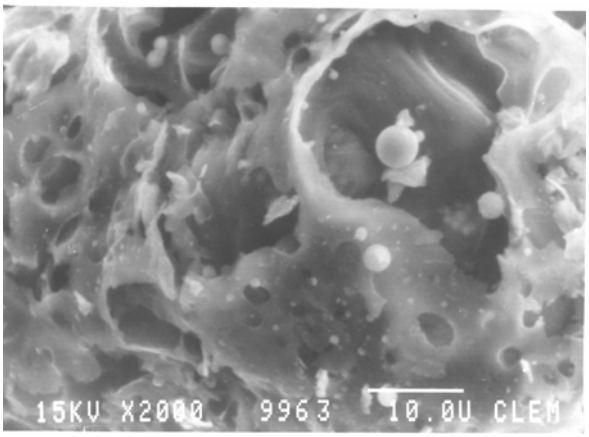

Fig. 3. A detail of the particle from flotation concentrate in Fig. 2 (enlargement: 2000x)

Rys. 3. Szczegół ziarna koncentratu poflotacyjnego prezentowanego na rys. 2 (powiększenie 2000x)

Figure 4 shows particles of unburned coal, enlarged 480 times. The porous structure is visible in a detail of an unburned coal particle. The size of the particle is about 0.18 mm. The porosity of particles in the flotation concentrate (Fig. 4) confirms that a large surface area of an organic component is an explanation of the relatively high consumption of flotation reagent (Flotalex and their modifications – Flotalex bio, Flotalex economy), severalfold higher than the consumption of flotation reagent during the flotation of primary coal.

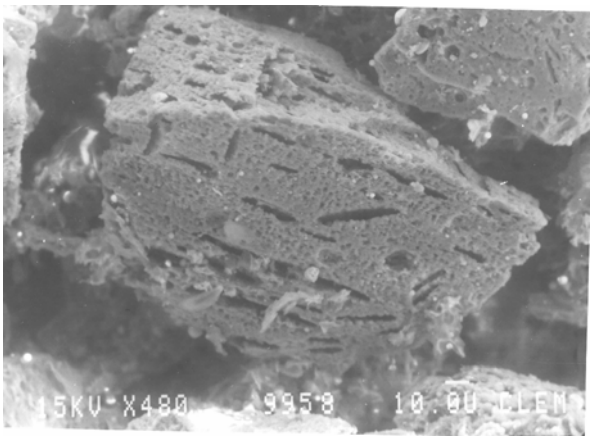

Fig. 4. Particles of unburned coal (enlargement: 480x)

Rys. 4. Ziarna niespalonego węgla (powiększenie 480x)

2. Theoretical presumption of the assessment of fly ash suitability as absorbent of some cations

2.1. Mineralogical composition of silicates and aluminosilicates in tested fly ash

The contents of the most frequent chemical elements in fly ashes are the following: SiO_2 40–65%, Al_2O_3 10–35%, Fe 3–11%. Properties of some fly ashes (most commonly brown coal ashes) after their modification can be used as an alternative to natural zeolites. Kolousek (1993), Kusnierova (1997) and Kovanda (1993) were concerned with the problem.

Black coal ashes contain mineral novelties which can be classed as natural zeolites (most of all phillipsite, klinoptilolite and others) according to their useful properties.

The properties of brown coal ash, the most similar to the properties of natural mineral phillipsite, were described by Libersky (1991) and Kolousek (1993).

Natural zeolites are hydro-aluminosilicates, created by virtue of volcanic activity during cooling under natural conditions. The zeolite novelties were created at "volcanic temperatures" in combustion boilers of thermal power plants. The existence of pores, micropores, and cavities in all zeolites is substantive and their volume is measurable.

Nowadays, natural sorptive properties of fly ashes are used in waste water treatment. Kolousek et al. (1993) dealed with zeolite synthesis from black coal ashes from Detmarovice. They prepared certain preparations by hydrothermal alternation under pilot conditions on the principle of hydrothermal contact of fly ash with hydroxide solutions – NaOH and KOH, whereby the contact was realized for 3–5 hours at 130°C. The fly ash from Detmarovice was highly selective towards Pb^{2+}. By sorption of Pb^{2+} on fly ashes, their concentration decreased from 212 $mg \cdot l^{-1}$ to 0.5 $mg \cdot l^{-1}$. Subsequently, the desorption was made by KOH solution.

It was confirmed experimentally that synthetic zeolite has a substantial selectivity towards Cu, Pb, Cd. The elements like Ca, Mg, Mn and Zn are not seized by zeolites, they pass through a sorptive filler without change. Experiments (Kolousek et al., 1993) proved that synthetic zeolite can be a perspective sorbent for an effective fixation of heavy metals, whereby it has a significant higher sorptive capacity than natural zeolites.

Synthetic zeolite from Detmarovice (phillipsite) was also used for the disposal of ammonium ions from waste waters. The sorption efficiency of synthetic zeolite was higher in comparison with operationally used natural zeolite – klinoptilolite.

Kusnierova et al. (1997) investigated zeolitization of fly ashes from brown coal from the Sokolovce area. They tested an exchange capacity of individual grain classes of fly ash samples. In term of zeolitization, the amorphous phase is considered a utility component. The highest values of exchange capacities were measured in a sample with grain size of 0–0.04 mm. The exchange capacity of natural zeolites is 1.88 $mol \cdot kg^{-1}$ and of the tested fly ash is 2.44 $mol \cdot kg^{-1}$.

Notes:

The subject is monitored for more detail, because utilization of zeolites has a rising trend. A lot of disposal sites of natural zeolites ensued from volcanic ash – an amorphous, vitrified material, rejected to water environment during the process of diagenesis. The exact conditions are simulated during the preparation of synthetic zeolites. On the basis of knowledge about environmental modifications of natural ashes – vitrified phases from which deposits of natural zeolites were created – we can presume that what is interesting for the process of zeolitization is an amorphous phase which should be transformed to zeolite by hydrothermal alternation.

The aim of the research by Bacinsky, Kurnierova and Vaskova was a verification of the possibility of zeolite preparation by hydrothermal alternation of fly ashes depending on the qualitative composition of a batch which changed with the application of beneficiation methods (Bacinsky et al., 1997, 1998).

Water is used to transport fly ashes to a decanting plant. During the contact of fly ash (the temperature in a hopper is in the range of 100–140°C or more) with water, the zeolitization is realized. This process caused the decreasing of leachability of fly ashes, e.g. the leachability of dry black coal ash from a batch is in the pH range of 8.5–9.1. The leachability of the same fly ash which was transported to the decanting plant is markedly lower – within the pH range of 7.2–8.0 (Michalikova, Nagyova, Belanska).

2.2. Adsorption isotherms

Isotherm models provide an adequate description of metal adsorption equilibria on a wide range of adsorbent materials.

Equilibrium data, used for designing adsorption isotherms, are used for the estimation of an adsorption system. Three adsorption models were used to describe the equilibrium between adsorbed metal ions (Pb^{2+}) on the adsorbent zeolite (q_{eq}) and metal ions in a solution (c_{eq}) at a constant temperature and pH.

The Langmuir equation that is valid for monolayer sorption onto a surface is given by the equation

$$q_{eq} = q_{\max} \frac{b_L c_{eq}}{1 + b_L c_{eq}} \tag{1}$$

The Freundlich expression is an exponential equation and therefore it assumes that as the adsorbate concentration increases, the concentration of adsorbate on the adsorbent surface also increases.

The empirical Freundlich equation based on sorption onto a heterogeneous surface is given by the equation

$$q_{eq} = k_F C_{eq}^{\frac{1}{n}} \tag{2}$$

The Redlich-Peterson isotherm (R-P) contains three parameters unlike the Langmuir and the Freundlich isotherms that contain two parameters. The form of R-P equation includes features of the Langmuir and Freundlich isotherms and is given by the equation

$$q_{eq} = \frac{k_R c_{eq}}{1 + b_R c_{eq}^{\beta}} \tag{3}$$

This equation can be converted to a linear form by taking logarithms of both sides. The linear form is

$$\ln\left(k_R \frac{c_{eq}}{q_{eq}}\right) = \ln b_R + \beta \ln c_{eq} \tag{4}$$

Plotting the left-side of the equation against ln c_{eq} to obtain the isotherm constants is not possible because of the three unknown quantities b_R, k_R and β. Hence, the isotherm constants can be determined by minimizing the error between the experimental data and the calculation of values of q_{eq} by the R-P equation. The isotherms were determined using the solver add-in for Microsoft Excel.

2.3. Adsorption experiments

A series of flasks containing 200 ml of lead solutions of different concentrations prepared from lead nitrate and a fixed dosage of fly ash (1 kg·m^{-3}) were agitated for 3 hours in a rotary shaker at 200 rpm, with a temperature control at 25ºC, which was sufficient for the lead adsorption to reach an equilibrium. After the equilibration and sedimentation of suspensions the samples of aqueous phases were analysed for lead content. The amounts of lead adsorbed q_{eq} in each flask were determined from the difference between the initial metal concentration c_0 and metal concentration at equilibrium c_{eq} in the solution.

2.4. Analysis of concentration

The concentrations of unadsorbed lead were measured by the atomic absorption spectrometer (AAS) Perkin Elmer 3100 with deuterium correction background. Atomic absorption spectroscopy is an optical method based on absorption of electromagnetic radiation in the range of wavelengths 190 to 850 nm.

3. Experimental results

The experimental equilibrium data for lead adsorption on fly ash were fitted by the Freundlich, Langmuir and Redlich-Peterson isotherms using nonlinear regression analysis. The experimental data are presented by dots, isotherms are presented in the form of lines.

Table 1

Coefficients of isotherms correlation for individual grain classes of fly ash obtained by sieve analysis

Adsorbent	Freundlich Isotherm	Langmuir isotherm	Redlich--Peterson isotherm	Loss on ignition (LOI)
Fly ash from DC (0.040 – 0.050 mm)	0.8803	**0.9905**	0.9591	50.40
Fly ash from DC (0.050 – 0.071 mm)	**0.9178**	0.7539	0.8279	58.17
Fly ash from DC (+ 0.180 mm)	0.9301	**0.9423**	0.9339	50.32
Fly ash from WC (0 - 0.050 mm)	0.9256	0.8445	**0.9624**	22.47
Fly ash from WC (+ 0.050 mm)	0.8618	0.4023	**0.9946**	48.85

Measurements were performed on the following samples of black coal ash:

- fly ash sample of grain class 0.040–0.050 mm from dry classification (DC) contains 50.40% of LOI,
- fly ash sample of grain class 0.050–0.071 mm from dry classification (DC) contains 58.17% of LOI,
- fly ash sample of grain class +0.180 mm from dry classification (DC) contains 50.32% of LOI,

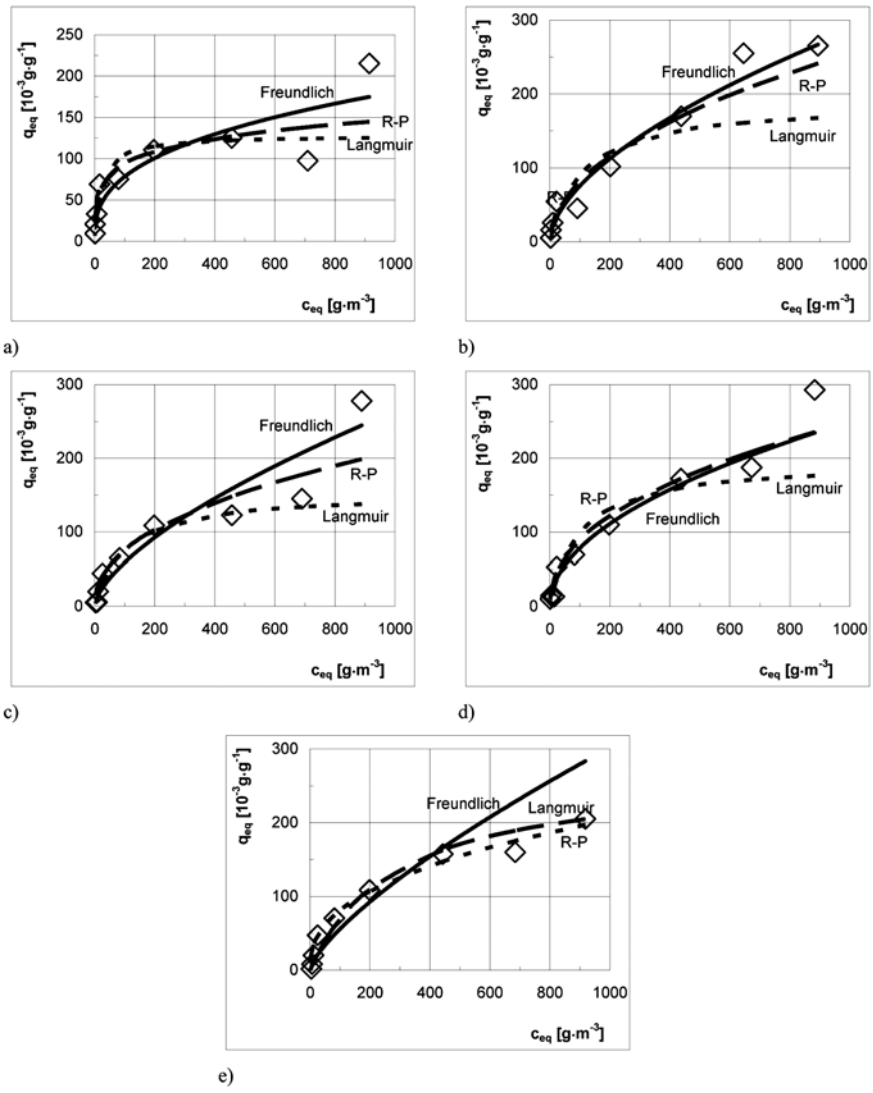

Fig. 5. Adsorption isotherm of Pb to fly ash From a dry sieve analysis with a grain size of: **a).** 0.040–0.050 mm (50.40% LOI), **b)** 0.050–0.071 mm (58.17% LOI), **c)** +0.180 mm (50.32% LOI), From a wet sieve analysis with a grain size of: **d)** –0.050 mm (22.47% LOI), **e)** +0.050 mm (84.85% LOI)

Rys. 5. Izotermy absorpcji Pb na popiołach lotnych: O uziarnieniu oznaczonym metodą suchą: **a)** 0,040–0,050 mm (50,40% LOI), **b)** 0,050-0,071 mm (58,17% LOI), **c)** +0,180 mm (50,32% LOI), O uziarnieniu oznaczonym metodą mokrą: **d)** –0,050 mm (22,47% LOI), **e)** +0,050 mm (84,85% LOI)

– fly ash sample of grain class 0–0.050 mm from wet classification (WC) contains 22.47% of LOI,
– fly ash sample of grain class +0.050 mm from wet classification (WC) contains 48.85% of LOI.

According to the data presented in Table. 1 for different fractions of fly ash the adsorption is described by different adsorption isotherms depending on a separation method.

From the comparison of isotherm correlation (Tab. 1) of lead adsorption as well as from the comparison of individual pictures, it is possible to say that the best adsorption of lead (Pb^{2+}) was achieved with fly ash samples with a grain size of +0.050 mm (84.85% LOI) obtained from wet sieve analysis.

4. Conclusion

The results of adsorption measurements confirm that fly ash from black coal combustion in melting boilers is a suitable adsorbent for Pb^{2+} removal. On the basis of Fig. 5, the maximum sorption capacity of fly ashes for bivalent ions of Pb is in the range of 200–300 $mg \cdot l^{-1}$.

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