TEXTURAL PROPERTIES AND ORGANIC MATTER IN SEDIMENTS FROM A HARD COAL MINE LANDFILL

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Textural properties as micropore surfaces and sorption capacity, chemical and technological analyses of sediments collected in the Lazy coal mine landfill (Upper Silesian Coal basin) are presented. The adsorption capacities together with net calorific values (Q_i^d) and total organic carbon (TOC) decreased in the direction of flow while the ash content (A^d) increased. The samples with the highest TOC content have a relatively beneficial Q_i^d and for residual coal particles from coal mining, were comparable with the Q_i^d values of brown coal. The sorption capacity increased with increasing micropore content and correlated with higher levels of TOC. The sorption capacity decreased with distance from the saline water input. These materials play a significant role in the self-cleaning of mine water in-situ.

Keywords: adsorption, organic matter, coal sediments

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1. Introduction

Coal mining and coal processing is considered to be a significant source of contamination of environmental compartments on the Earth [1]. The storage of large amounts of coal mine waste and its disposal has been a widely discussed topic regarding environmental assessment [2]. The possibility of using coal mine waste as a partial substitute for brown coal has also been considered. To understand the processes that occur in the environment, mine waste must be analysed in detail, and, owing to its heterogeneity, monitored with respect to changes in its surroundings.

In the Lazy mine, hard coal has been intensively mined for more than 100 years. The study area is a part of the Ostrava-Karviná Coalfield, which is part of the Upper Silesian Coal basin stretching from the Czech Republic to Poland [3–5]. The local mining activities in the Lazy mine ceased in 2019. The former landscape in the surroundings have been completely changed due to intensive underground mining that resulted in cleaning (diluting) mine water in the cleaning tanks. Moreover, artificial streams with low flow-rate occur as the result of pumping mine water from the underground to the surface. The stream bed in the water bodies and streams is composed of fine to medium grained coal material with an admixture of mineral matter forming siltstone, sandstone and claystone.

Organic rich sediments are considered to be natural sorbents for taking up contaminants from water via adsorption processes. To evaluate these processes, detailed information about micropore characteristics is needed. The sorption potential of solid material depends on the distribution and size particles, organic content and mineral composition [6]. Classification and evaluation of organic matter must be performed because its composition is a key parameter for the sorption capacity of the sample, which contains both organic and inorganic matter [7].

Chemical (e.g. moisture and ash content, organic carbon content) and technological (e.g. calorific value, sulphur content) analyses are used to characterize materials that, in combination with textural analysis (surface of micropores and mesopores), provide valuable information about their composition and possible use. The properties of the coal materials studied were associated with texture and sorption capacity [8]. The knowledge of the sediments composition is the first point on the way to the maximum utilization of material [9]. Groups of organic matter according to their origin, type or degree of maturation in the sediments have recently been studied in the Bílina River [7,10]. In the case of the coal fraction, thermal maturation of organic matter is believed to be the key factor for increasing the micropore content and net calorific value of the coal [5,11].

The aim of this study is to provide an overview about textural parameters and the content of organic matter in sediments originating from activities in the coal mining industry.

2. Experimental part

2.1. Samples and methods

2.1.1 Study area

Four sediment samples of mine waste were taken from cleaning tanks and streams in the surrounding area of the Lazy Mine landfill; a plan of the site can be seen in Fig. 1. The study area was covered by isolated cleaning tanks, and artificial streams that serve as a recipient for saline mine discharges.

The sediment sample, marked as MW, was collected from a shallow artificial stream that was supplied by saline mine water discharges. The sample WP represents a location after freshwater infiltration through the coal mine heap. These two streams came together approximately 50 m from the inflow of saline mine water, near to sampling sites MW and WP.

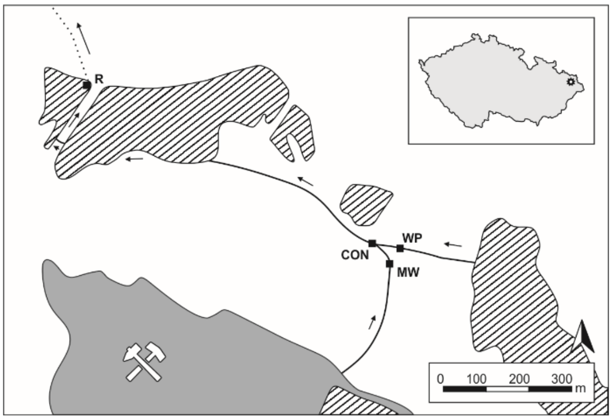

Fig. 1 Scheme of sampling points with marked mine, direction of water flow (arrow), cleaning tanks (hatched) and sampling points (square).

The flow of mixed water (sample CON) slowly passes into the cleaning tanks, represented by sample R, taken approximately 800 m from the confluence.

2.1.2 The main parameters

Samples were homogenized, dried, weighed, ground to a powder of the required grain size, less than 0.063 mm for analyses and less than 0.2 mm for the preparation of polished grain sections.

Prior to analysis, samples were air-dried at 105° until a constant mass. Chemical analyses as moisture content (W^a), ash content (A^d) and total organic carbon (TOC), technological analyses as net calorific value (Q_i^d) were determined according to the ISO 17246:2010; ISO 1928:2020; ISO 17247:2020 norms.

Specific surface area (S_{BET}) was evaluated from low pressure N_2 adsorption/desorption isotherms measured using a volumetric sorption analyser [12].

A gravimetric sorption analyser was used to measure the CO_2 sorption isotherms at a temperature of 25 °C and pressure up to 0.1 MPa in defined pressure steps.

The main micropore parameters, micropore surface area (S_{mic}) and total micropore volume (V_{mic}), were calculated according to the Dubinin equation [13], and the micropore size distribution by the Medek method [14]. Total CO_2 adsorption capacity (n_{tot}) was calculated from experimental data (n_{exp}) using Langmuir model, which assumes monolayer adsorption on a homogeneous surface [15].

Organic petrography analyses which included quantification of organic matter content and vitrinite reflectance measurements were carried out using an Olympus BX51 microscope equipped with an immersion objective (magnification 40 ×). The polished grain sections for microscopy were prepared according to ISO 7404-2 (2009) [ISO 7404-2. Methods for the Petrographic Analysis of Coal - part 2. Method of preparing coal samples. International Organization for Standardization, Geneva, Switzerland, 14p.] and the classification of organic matter was adapted from several publications [16–18]

3. Results and discussion

3.1. Chemical analyses

Samples of bottom sediments were heterogeneous materials differing in content of selected analysis groups. Variability of values depended on the area of sampling, as can be seen in Table 1. The ash content (A^d) increased with distance from the saline water input, whereas the TOC content decreased with distance from the source of saline mine water. The Q_i^d were significant only for the samples in the vicinity of the saline mine water outfall, see Tab. 1, samples WP and MW. Q_i^d of these two samples were comparable with the calorific values of Czech brown energetic coal e.g. from Bílina mine [19]. The direct correlation of Q_i^d and TOC content for all studied sediments were the same, with a correlation factor R^2, comparable with brown and hard coal mined in the Czech Republic [11]. The relation between Q_i^d and TOC is illustrated in Fig. 2

The TOC content was partly affected by the presence of pores, and the textural parameters are reported in Tab. 1, as well as the sorption capacity of samples; this will be discussed in section 3.3.

Tab. 1 Selected parameters of sediments

Parameter	MW	WP	CON	R
W^a (%)	1.95	3.48	1.01	0.79
A^d (%)	31.56	43.62	77.15	90.53
Q_i^d (MJ.kg^{-1})	21.18	15.97	5.76	1.49
R_r (%)	0.833	0.747	0.788	0.853
TOC (%)	52.99	41.59	16.37	3.16
n_{tot} (mmol.g^{-1})	0.39	0.42	0.12	0.07
S_{BET} (m^2.g^{-1})	11.0	6.7	5.6	12.0
S_{mic} (m^2.g^{-1})	88.4	96.4	28.3	17.5

W^a – moisture content, A^d - ash content, R_r - random reflectance, TOC - total organic carbon content, Q_i^d – net calorific value, n_{tot} - total adsorption capacity, S_{BET} - specific surface area, S_{mic} - surface of micropores.

3.2. Organic petrography

Organic matter (OM) present in samples was divided into three main groups: fossil, recent and carbonized. The most dominant group was fossil OM, which correspondents with hard coal that is being mined in the area being studied. Its further division and representation are illustrated in Tab. 2. Coal particles of the fossil OM group were dominant in most samples and were observed either as single large or fine-grained particles or as aggregates that were caused by recent mineralization at the site of their new deposition. However, in sample R, the fossil OM was mainly represented by organic-rich rocks. Recent and carbonized OM group were still present, but in much lower quantity. Carbonized OM was observed mainly in the form of porous to dense chars and recent OM in the form of preserved remains of plants, spores, algae, and fungi. The random reflectance

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(R_r = 0.75-0.86 %) was measured on fossil OM in the form of vitrinite and the measurements matched the coal extracted in the Lazy mine and in the same basin in Poland [20]. The highest content of coal particles was measured in the WP and CON samples. Organic particles contained in the samples are shown in Fig. 3 A-D.

A connection between R_r and adsorption / TOC content was not observed. On the other hand, the net calorific value strongly depended on the TOC content for the samples studied (R^2 = 0.9971), and corresponds with studies of different kinds of Czech coals [11].

Tab. 2 Volumes of fossil OM group in the monitored samples (vol.%, mmf.).

Parameter	MW	WP	CON	R
Coal	98.2	91.1	92.7	25.0
Claystone with OM	0.0	3.4	5.6	75.0

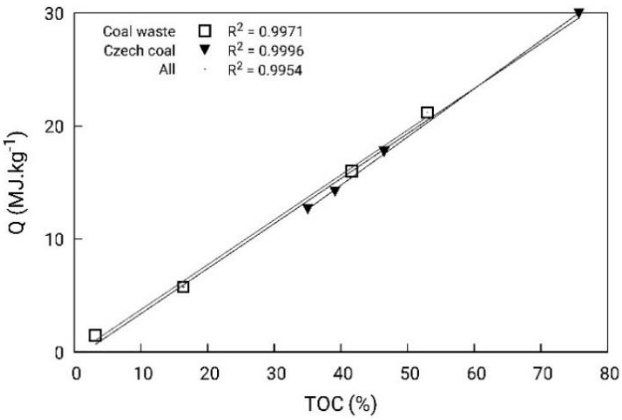

Fig. 2 Correlation of the TOC content and net calorific value of samples from this study with Czech brown and hard coals

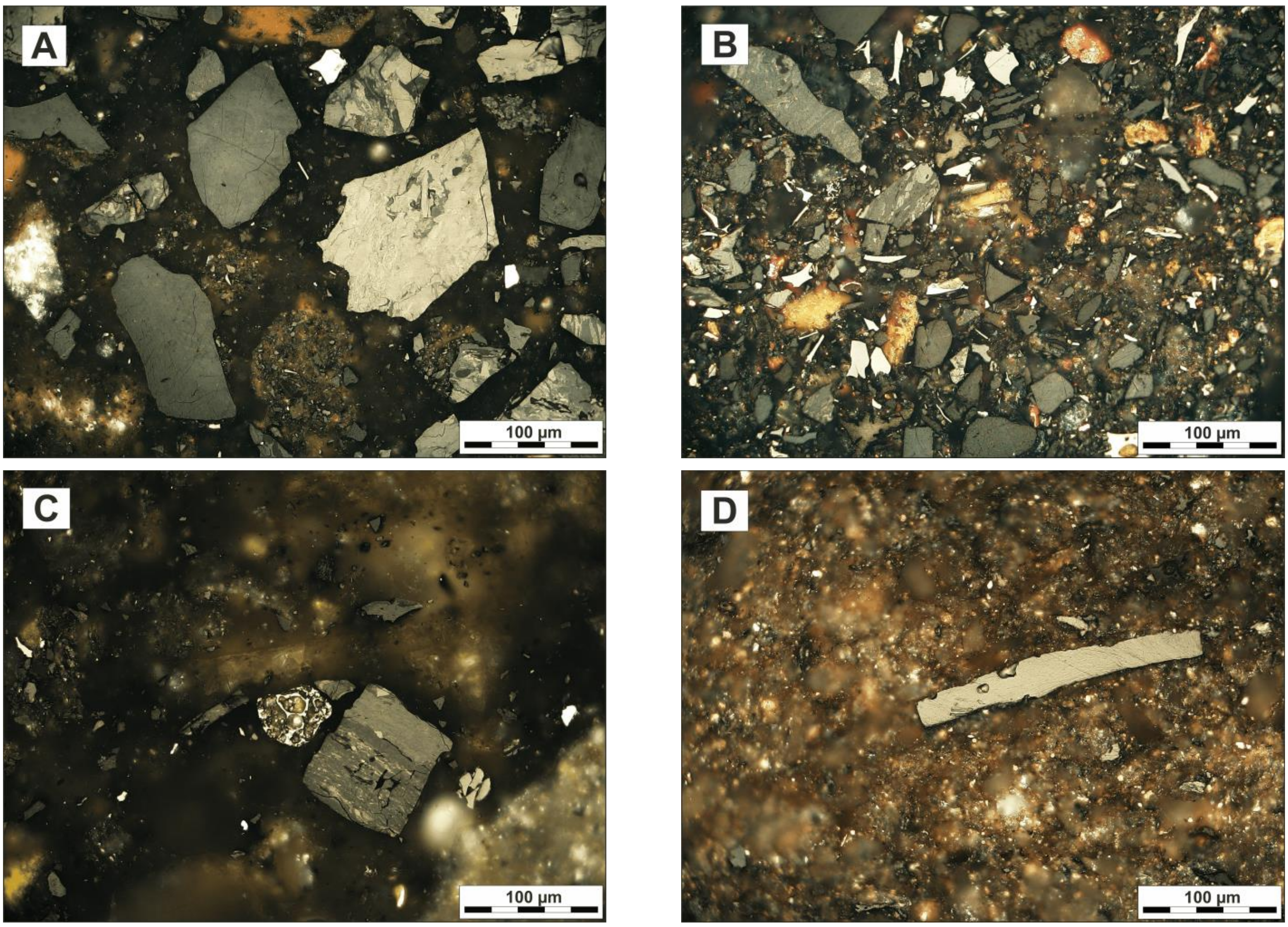

Fig. 3 A) Sample MW - Various sizes of coal particles formed by vitrinite (dark grey colour) or inertinite (light grey colour). On the bottom in the middle aggregates of coal created by the recent mineralization. B) Sample WP - Recent mineralization of coal particles at their new site of deposition forming a large, mineralized aggregate of coal waste. C) Sample CON - Porous char with light colour in the middle. To the right is coal comprised of all maceral groups: vitrinite, inertinite and liptinite. D) Samples R - Fossil OM represented by original claystone with OM, which was deposited at the time of hard coal deposition

3.3. Microporous texture and sorption ability

CO_2 sorption capacity is positively or negatively influenced by many factors. The influence of organic matter and the presence of pores was considered. The total CO_2 sorption capacities of samples obtained using Langmuir model are shown in Table 1 and the experimental sorption isotherms are demonstrated in Fig. 4. Calculated values of total sorption capacity (n_{tot}) were from 0.07 mmol.g^{-1} for sample R to 0.42 mmol.g^{-1} for sample WP, see Fig. 4 and Table 1. The values determined for the CO_2 sorption capacities were the highest in samples MW and WP. These two values were comparable to the sorption capacities of hard coal mined in the same basin in Poland [20].

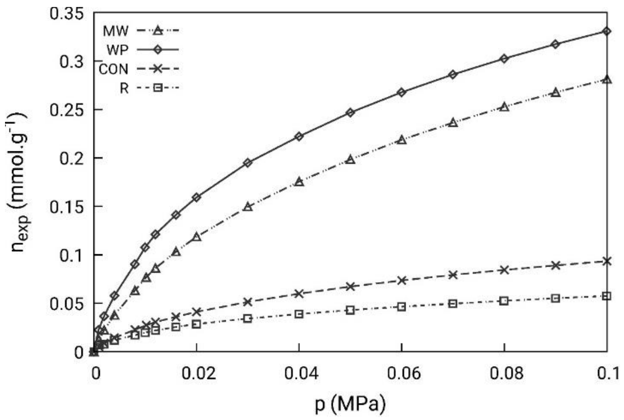

Fig. 4 The low-pressure CO_2 sorption isotherms of sediments at 25 °C and pressure up to 0.1 MPa

The connection between textural parameters and sorption ability (Table 1) was demonstrated and the positive effect of micropore content and TOC content (R^2 = 0.831) on sorption capacity was clear.

Monitored sediments are heterogeneous porous materials with relatively low sorption surface when compared to commercial activated carbon sorbents, but they play an important role in direct self-cleaning processes of water in the environment. This is due to the not negligible micropore content. S_{BET} values of all four samples were between 5.6 m^2.g^{-1} and 12.0 m^2.g^{-1} and S_{mic} values ranged from 17.5 m^2.g^{-1} to 95.5 m^2.g^{-1}. The highest content of micropores were in samples WP and MW, also the highest content of TOC. The CO_2 adsorption was closely connected with S_{mic} (R^2 = 0.9944). The CO_2 sorption capacity increased with micropore content and the S_{mic} sequence was of the same order as n_{tot} WP > MW > CON > R. The micropore size distributions expressed as the differential pore volume (dV/dr) vs. pore radius are shown in Fig. 5.

The micropore content is one of the contributing factors enhancing sorption processes. Micropores are present in the organic matter, and in the inorganic component particularly in feldspar. In coal, a similar positive correlation between CO_2 sorption and TOC was observed [5]. The inorganic matter present at higher levels in sample WP also enhanced the CO_2 sorption capacity.

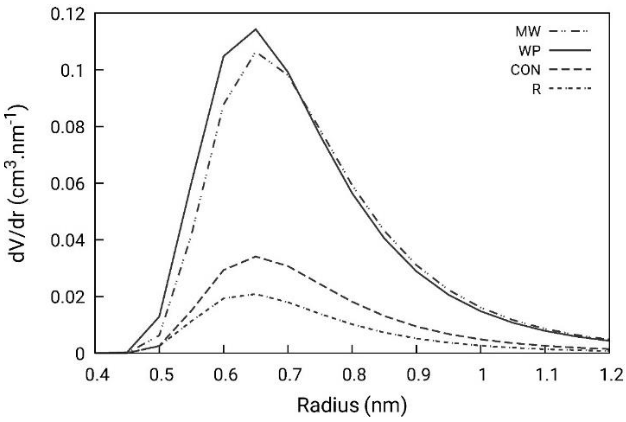

Fig. 5 Micropore size distribution of sediments

4. Conclusions

Sediments from cleaning tanks and streams were analysed. The materials were rich in carbon particles from coal mined in the area and had comparable Q_i^d values as brown energetic coal. The TOC content corresponded with the Q_i^d values. Chemical and technological analyses usually performed on this type of material are not sufficient. Therefore, a different view and more detailed material specifications have been incorporated using special methods such as optical microscopy, textural analysis and sorption tests. This material plays a significant role in self-cleaning processes in-situ, particularly for their sorption capacity and not negligible micropore content. A higher content of TOC in samples enhanced the CO_2 adsorption capacity and is directly connected with increasing micropore content.

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