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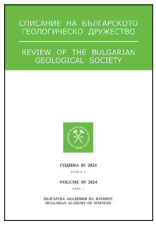

Petrographic and geochemical features of weathered and pyrolytic altered organic matter of dump samples from Troyanovo-3 Mine (Mini Maritsa Iztok EAD, Bulgaria) – a comparison

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Петрографски и геохимични особености на изветряло и пиролитично променено органично вещество в насипищни материали от рудник „Трояново-3“ („Мини Марица-изток“ ЕАД, България) – сравнение

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Резюме. Експлоатацията на лигнитните въглища от Източномаришкия басейн чрез открит добив е свързана с образуването на отпадъчни седиментни скали с ниско съдържание на органично вещество, които се депонират във вътрешни насипища. Веднага след отлагането насипищните материали претърпяват процеси на изветряне, вкл. окисление на органичното вещество, което в някои случаи води до самозапалване. Целите на изследването са проследяване влиянието на тези процеси върху мацералите, органичните съединения и техните разпределения. Събраните 27 проби от рудник „Трояново-3“ се различават по степен на промяна. Първата група съдържа непроменени мацерали и показва нормално разпределение на *n*-алкани, феноли не са установени и T_{max}, определена с Rock-Eval пиролиз, варира от 420 до 430 °C. Втората група съдържа мацерали с неравномерни пукнатини, с по-бледи, окислени ръбове, по-висока отражателна способност, близко до гаусовото разпределение на *n*-алканите, висока концентрация на феноли и полиарометни въглеводороди и понижени стойности на T_{max} (под 400 °C). Пробите съдържат повишено количество пирит, чието окисление допринася за развиване на процесите на самозапалване.

Ключови думи: насипищно органично вещество, окисление, самозапалване, рудник „Трояново-3“, Източномаришки лигнитен басейн, България.

Abstract. The open-pit exploitation of the Maritsa Iztok lignite field (Bulgaria) generated sedimentary waste rocks of low organic matter content that were deposited in internal dumps. Immediately after deposition the re-deposited sediments underwent weathering, including organic matter oxidation leading in some cases to self-heating. The aims of the research were to study the impact of weathering and self-heating on the maceral alterations in the dump site associated with the sediment re-deposition, and organic compounds identification and distribution. The 27 samples collected from Troyanovo-3 Mine internal dump differed in degree of alteration. The first group

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contained unaltered macerals and showed normal distribution of *n*-alkanes, phenols were absent and Rock-Eval T_{max} ranged from 420 to 430 °C. The second group contained macerals with irregular cracks, paler oxidation rims, higher reflectance, Gaussian distribution of *n*-alkanes, high concentration of phenols and PAHs, and lowered T_{max} values (below 400 °C). The samples contained elevated amount of pyrite which oxidation might contribute to self-hating.

Keywords: dump organic matter, oxidation, self-heating, Troyanovo-3 Mine, Maritsa Iztok lignite field, Bulgaria.

Introduction

Internal and external dump areas are a part of mining activities in open cast mining of Maritsa Iztok lignite deposit. Carbonaceous sediments of low organic matter (OM) content blended in different proportions by lignite fragments were stored by free heaping in internal dumps forming a mixture of high porosity and water content. In the dump areas the re-deposited sediments undergo several secondary processes. These include oxidation of organic and inorganic fragments by atmospheric oxygen, microbial degradation of organic matter, dissolution of minerals, and the most significant from the environmental point of view, the spontaneous increase in temperature within a dump leading to heating, smoldering and at the end – combustion (Stracher, Taylor, 2004; Ribeiro et al., 2010; Misz-Kennan, Fabiańska, 2011; Fabiańska et al., 2024). These processes affect the petrographic, mineralogical, and geochemical signatures of the dump materials and may lead to the migration of hazardous elements and compounds to the surrounding environment, including the atmosphere, water reservoirs, soil, and plants growing on the dumps and in their nearby.

The occurrence and extent of self-heating within a dump depend on several issues. Three factors should be met for the process to take place, i.e. key component presence: (i) organic matter and/or sulphides that exothermically oxidize; (ii) oxygen access into the dump interior; (iii) heat accumulation (Kaymakçi, Didari, 2002; Pone et al., 2007). The last two are related to the dump structure, whereas the first one – to the re-deposited sediment composition.

The research presents a petrographic and geochemical study on dump samples from Troyanovo-3 Mine (Maritsa Iztok EAD, Bulgaria). The aims of the research are: (1) study of the impact of weathering and self-heating on the alterations of macerals in the dump site associated with the sediments re-deposition; (2) identification and distribution of organic compounds generated during self-heating of the coal wastes.

Basic characteristics of Maritsa Iztok lignite field and internal dump site

Maritsa Iztok lignite field (240 km^2) has been exploited by Mini Maritsa Iztok EAD. Three open-cast mines operate in the coalfield: Troyanovo-1, Troyanovo-North and Troyanovo-3. The lignite-bearing sequence comprises coal basement of grey-black mudstone and sand; three lignite seams separated by black clay with lignite inclusions, coaly shale and carbonaceous mudstone. Coal Seams II and III have economic value and are exploited. The upper, Seam I, is thin (0.5–1 m) and has no economic value. The coal is very immature (0.2% R_o), lignite (Rock Eval T_{max} ~380 °C); total organic carbon content, dry basis (TOC_{db}) = 21.3–56.7 wt%; ash, dry basis (A_{db}) = 16–45 wt%; total moisture (M_t) 50–60 wt%; Sulphur, dry basis (S_{db}) = 3–6 wt%; net calorific value = 6.5–7.3 MJ/kg (Nedjalkov, 1979, https://www.marica-iztok.com/).

The mining works in the basin have generated an enormous volume of dump materials (4,278,655,232 m^3) due to long opencast exploitation. External and inner dumps were constructed in Maritsa Iztok Basin because of the huge volumes of overburden material excavated. The carbonaceous mudstone intercalating and separating the lignite seams and the sediments of Seam I were excavated and re-deposited in internal dump sites. The free-heaping techniques form a dump site of a truncated pyramid view with a wide base and hilly relief on the top and sloping walls. Important features of the dump environment are the vast territories without trees and with bare grass and bushes (Fig. 1) which promotes disintegration and degradation, and washout and evaporation processes.

Materials and methods

Two main groups of samples were collected from different areas of Troyanovo-3 Mine internal dump: (I) 13 naturally weathered samples (Sm. 1–13 in Fig. 1), including samples which primary OM was of elevated maturity; (II) 14 *in-situ* smoldered/self-

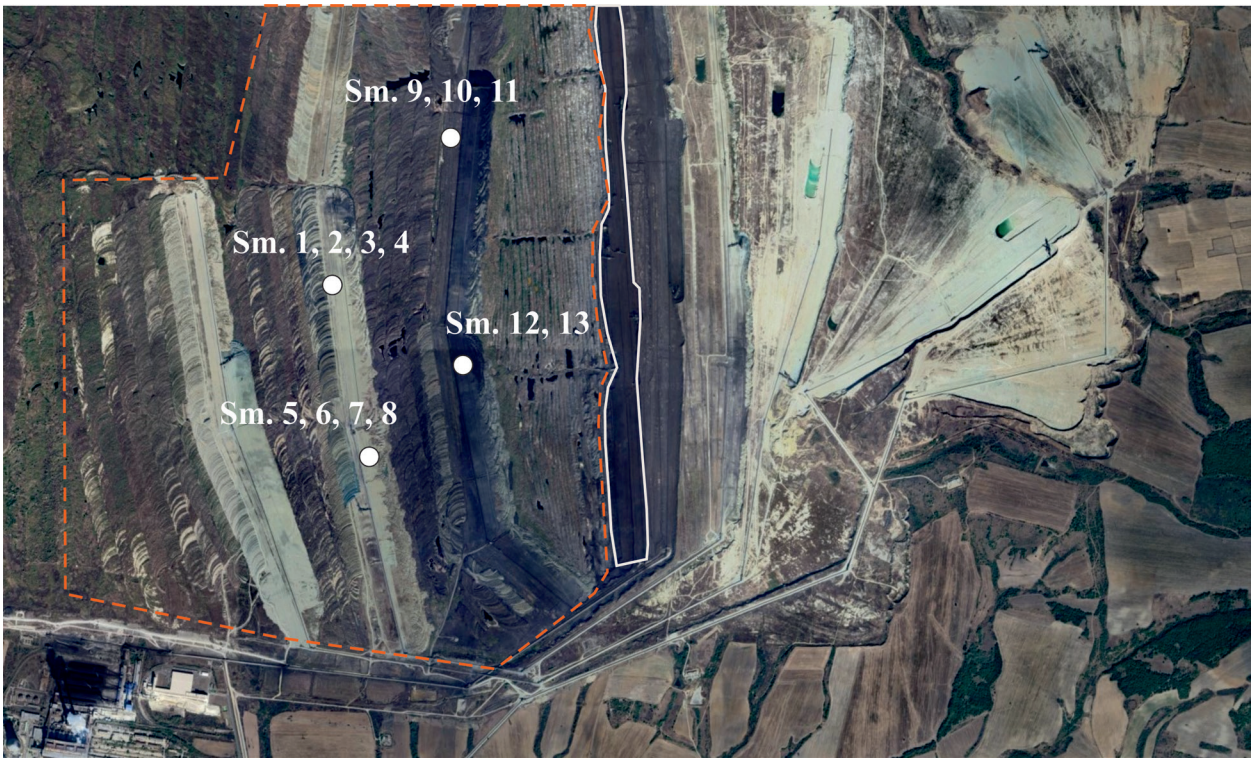

Fig. 1. Google map (https://earth.google.com/web) of Troyanovo-3 Mine internal dump (orange contour) and exploitation (white contour) area (Mini Maritsa Iztok, EAD) with first sample set position.

Фиг. 1. Карта (https://earth.google.com/web) на вътрешно насипище (оранжев контур) и добивния участък (бял контур) в рудник „Трояново-3“ („Мини Марица-изток“ ЕАД) и местоположение на пробите от първата група.

heated samples (SN 1–14) spread over the dump area. Naturally weathered carbonaceous mudstone are presented by: grey laminated mudstone initially deposited between Seam I and Seam II, and sediments of Seam I and black mudstone covering Seam I collected a year after re-deposition (Sm. 1-4 and 5-8); black mudstone covering Seam II collected up to 8–9 years after re-deposition (Sm. 6–7, 9–11 and 12–13). At each sample point 1–1.5 kg of surface dump material was collected. The smoldered/self-heated areas were first surveyed and sampled when the processes have been finished. The samples were air-dried and crushed to <1 mm for petrographic analyses and to <0.2 mm for geochemical analyses. After crushing, samples were embedded in epoxy resin, and polished blocks for microscopic studies were prepared.

The polished blocks were examined using reflected white light and fluorescence with a Zeiss Axioplan2 microscope at 500× magnification. The content of maceral groups and mineral matter was determined at 500 points evenly distributed over the sample surface. To determine the OM rank, huminite reflectance measurements (R_r) were taken at 15–100 points in each sample, depending on the availability of particles suitable for reflectance measurements.

Samples powdered to <0.2 mm were extracted with dichloromethane in Dionex rapid extractor. Extracts composition was analysed with GC-MS (Agilent gas chromatograph 7890A with a DB-5 column, a mass spectrometer 5975C XL MDS). Compounds were identified from mass spectra and by comparison with standard retention times. All petrographic and geochemical analyses were carried out in the Institute of Earth Sciences at the University of Silesia in Katowice, Poland.

The screening pyrolytical analysis was conducted using Rock-Eval 6 Turbo apparatus in the Faculty of Geology, Geophysics, and Environmental Protection at AGH University of Krakow applying the Basic cycle of the Bulk Rock method. The analysis consisted of two steps: firstly, pulverised rock sample (ca. 50 mg) was heated in a pyrolytic

oven under nitrogen flow (100 ml/min) at temperatures from 300 °C (1 min. isothermal) to 650 °C (at rate 25 °C/min) resulting in OM pyrolysis. The pyrolyzed sample was then transferred to an oxidation oven, where, in the air (100 ml/min) and temperature form 300 °C (1 min isothermal) to 850 °C (at rate 20 °C/min, 5 min final isothermal), the remaining organic material was burned.

Results and discussion

Organic matter content in the investigated samples ranges from 1.4–94.2%, 20.7% on average. However, the OM content differs in the two sample sets. In the first set (samples 1-13) OM content is from 7.4 to 94.2% (on average 30.6%), while in the second set – OM content is much lower and in the range 0.2–50.0% (on average 14.2%). All three maceral groups are present in the samples. Organic matter is dominated by huminite macerals represented mostly by textinite, ulminite, attrinite, densinite, and corpohuminite. The content of these macerals ranges from 0 to 92.6% and is higher in the first sample set (7.4–92.6%, usually 15–25%; average 26%) than in the second sample set (0–42.0%, usually <10%; average 11.6%). Commonly these macerals occur as unaltered, not showing any temperature impact (Fig. 2. A, B). The oxidized or self-heated samples show paler colour and higher reflectance. Their typical feature is irregular crack presence within the particles but in rare cases cracks occur also at the particle edges. Paler oxidation rims are rare feature of the dump samples indicating higher temperature processes. Such rims occur around the external edges of particles and also around cracks (Fig. 2. C, D, E). They are mostly seen in one sample (Sm. 2) while in the other samples undergone self-heating sometimes only a few particles with oxidation rims occur. Some particles have rounded edges that indicate higher heating rate, causing the plasticity of that particle. Rarely small devolatilisation pores can be seen. Oxidized or mildly thermally affected samples have higher reflectance in the range 0.25–0.53%, 0.33% on average.

Inertinite macerals are present mostly as fusinite, inertodetrinite, macrinite, and funginite. The content of inertinite macerals is generally low, on average < 1.6%. Only one sample had outstanding amount of inertinite, mostly represented by fusinite, and the content of inertinite was 14.8% while in the remaining samples did not exceed 5%. Liptinite is presented by sporinite, resinite, liptodetrinite, suberinite, sometimes also cutinite and alginite. The content of liptinite was <2.2%, on average 0.5%.

Minerals are present in greater amount in the second sample set than in the first one (on average 85.8% and 69.4%, respectively) and are mostly represented by clay minerals and pyrite. In many samples, pyrite commonly occurs in the form of framboidal pyrite that forms larger balls and agglomerations of balls. In addition, many samples contain altered pyrite that has a reddish colour. Commonly framboidal pyrite occurs in ball-like accumulations with a rim of the width of few μm, indicating its alteration (Fig. 2F). The content of pyrite is higher in the first sample set than in the second one (4.0% and 0.9%, respectively). It might be related to the fact that in the second set pyrite was altered and different new mineral phases were formed.

As it is common in the case of low maturity OM presence, the dump extracts contained a wide range of compounds of various chemical characteristics, including aliphatic saturated and unsaturated hydrocarbons, aromatic hydrocarbons and polar compounds, with oxygen functional groups predominating. The abundance of compound types is increased by secondary processes affecting dump samples. Two population of them can be distinguished: (1) dump samples of low level of OM thermal maturity (i.e. early geochemical diagenesis), and (2) dump samples exposed to self-heating that correspond to the early catagenesis. The first group of samples contained very low concentration of *n*-alkanes, with distribution typical for immature kerogen Type III, showing high predominance of odd-over-even carbon atom *n*-alkanes (CPI values *ca*. 5–6; Fig. 3A). These samples contained relatively high concentrations of diterpenoids such as 16_{α}(H)-phyllocladane, kauren-15-ene, and abietane, such as abietene, abietadiene and abietic acid. Pentacyclic triterpanes, lighter phenols, and aromatic hydrocarbons, both substituted and unsubstituted, were mostly absent. Among polar compounds ferruginol, benzoic aldehyde derivatives, and fatty acids predominate. Higher phenolic compounds derived from lignin weathering such as guiacol were found in this sample set. Comparing to the first group, the second group (samples SN1, SN2, SN7, SN8, SN9, SN14, and possibly also SN6) showed the signs of thermal changes. The significant sign of a thermal impact is the Gaussian outline of peaks

caused by rapid increase of temperature and expulsion of pyrolytical *n*-alkanes from the macromolecule (Fig. 3B). The maximum of the profile is at *n*-C_{20}, i.e. for much lighter compounds than in the case of samples not affected by fire. This kind of distribution does not conform with low maturity of organic matter but is common in dump samples subjected to self-heating. The another important feature of these samples is the presence of alkyl aromatic hydrocarbons including C_1-C_5 naphthalenes and

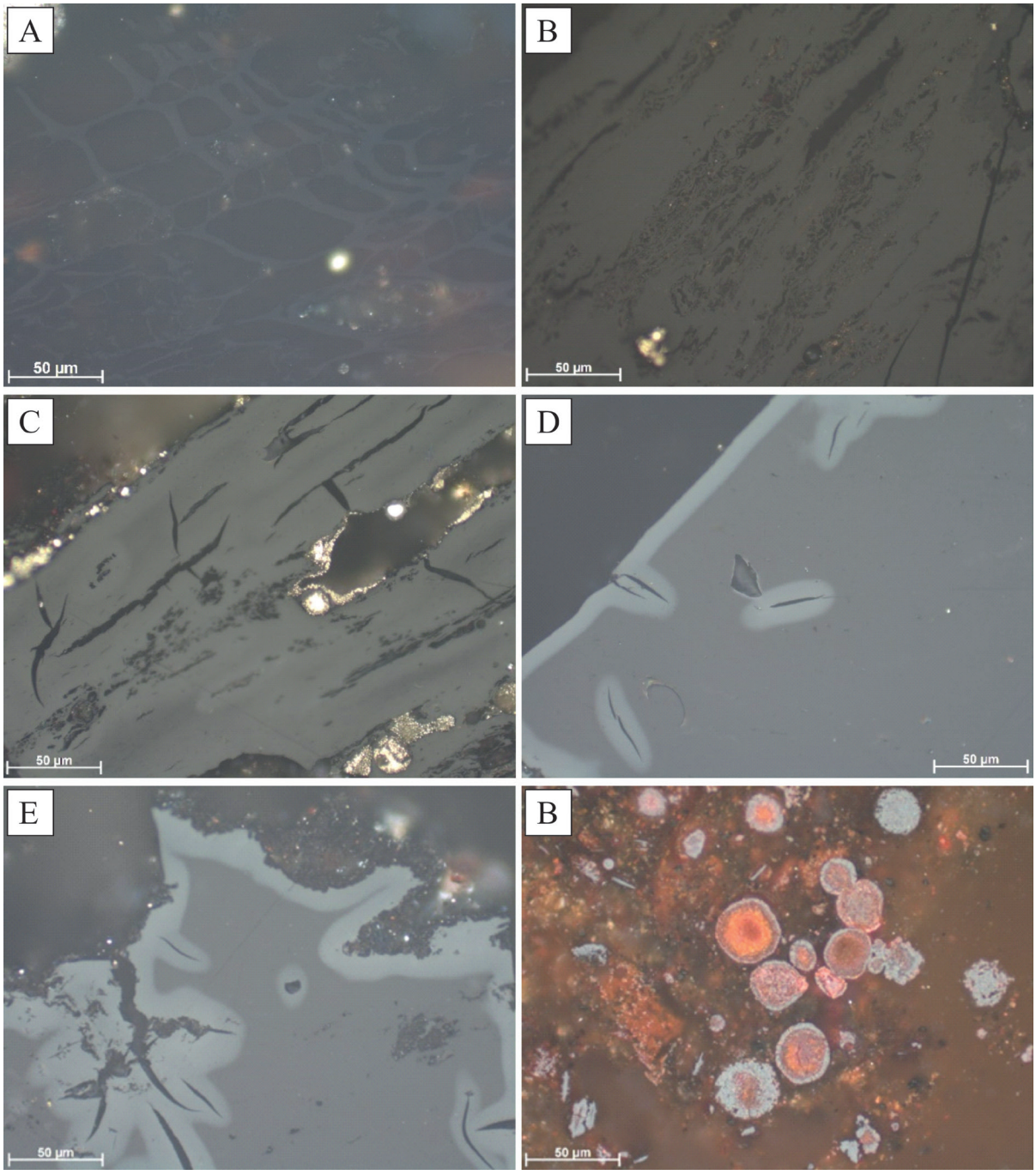

Fig. 2. Microphotographs of dump samples of re-deposited lignite and carbonaceous sediments collected from Troyanovo-3 Mine internal dump. A, B, unaltered huminite macerals; C, D, E, huminite with cracks and paler oxidation rims; F, altered pyrite. Reflected white light, immersion oil.

Фиг. 2. Микрофотографии на насипищни проби от преотложени лигнити и седименти с органично вещество от вътрешно насипище на рудник „Трояново-3“. A, B – непроменени хуминитови мацерали; C, D, E – хуминит с пукнатини и по-бледи окислени ръбове; F – променен пирит. Отразена бяла светлина, маслена имерсия.

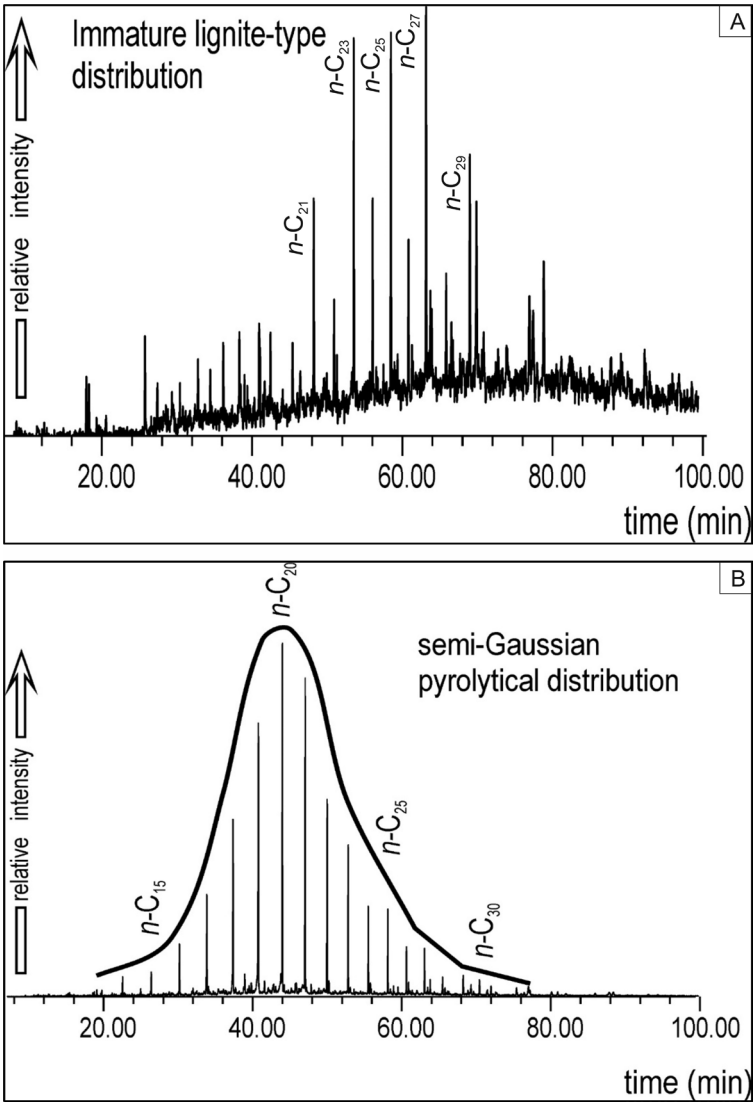

Fig. 3. Distribution of *n*-alkanes in dump samples collected from Troyanovo-3 Mine internal dump. A, immature organic matter distribution; B, semi-Gaussian pyrolytical distribution.

Фиг. 3. Разпеделение на *n*-алкани в проби от вътрешно насипище на рудник „Трояново-3“. А – разпределение, характерно за незряло органично вещество; В – разпределение близко до Гаусово пиролитично разпределение.

C_1-C_2 phenanthrenes, absent in the first set. Their distribution is mature – an artifical change caused by the thermal stress during self-heating. Alkyl naphthalene distributions do not show signs of weathering or leaching testifying the recent origin of these compounds generated during self-heating. The same concerns polycyclic aromatic hydrocarbons (PAHs). Whereas they are practically absent in the first sample set, their wide range has been identified in the affected by self- heating, second set. However, there are no 5-ring PAHs (possibly due to too short time of heating or too low temperature). Lighter phenolic compounds that comprised phenol, cresols, and xylenols were present only in the second sample set. These are pyrolytical products, with phenol predominating. This feature once again indicates relative fresh phenol production during pyrolysis since this compound is both well water soluble and also easily evaporates from dump surface. During heating in pyrolytical conditions the lignin structure was thermally destroyed producing various phenolic derivatives, with sinapyl, coniferyl, and syringyl units. The sinapyl structure is typical for herbaceous lignin (mostly grasses), the coniferyl structure – for conifer tree lignins, whereas the syringyl structure – for lignin of deciduous trees.

Results of the Rock-Eval analysis indicate changeable TOC concentrations in both sample sets, from 1.9 to 63.8 wt% (median 8.8 wt%) and from 1.06 to 12.6 wt% (median 6 wt%), respectively. The TOC values correlate well with the petrographically determined OM content. The mineral carbon content varies from 0.5 to 2.0 wt% for both sets. The values of hydrogen (HI) and oxygen (OI) indices suggest occurrence in all analysed samples of the gas-prone Type-III kerogen: HI and OI medians equal 156 mg HC/g TOC and 63 mg CO_2/g TOC for the first set of samples and 64 mg HC/g TOC and 109 mg CO_2/g TOC for the second set, respectively. These data are in good agreement with results of the petrographic analysis. The lowered HI and elevated OI values of the second sample set simultaneously may indicate the higher range of OM oxidation. This picture may be a result of the self-heating or weathering processes. The on-going secondary processes in sampled sites (or in the close proximity) of both sets are evidenced by usually abnormally elevated production index (PI) values: from 0.05 to 0.33 (median 0.18) and from 0.15 to 0.71 (median 0.47), for the first and second sets, respectively; the share of the light (migrating) hydrocarbons (HC) in the total amount of pyrolysable HC is significantly higher in the second sample set, suggesting they were taken from an area where self-heating processes have a significant range. The PI values are well inversely correlated with maximal temperature (T_{max}) values: from 342 to 430 °C (median 408 °C) and from 342 to 413 °C (median 373 °C), for the frist and second sets, respectively. The highest T_{max} values (420–430 °C) correlate well with R_r measurements (immature OM) and were determined for samples with lowest PI values. The low T_{max} values indicate the presence of short-chain HC, being the products of the secondary transformation.

Conclusions

Petrographic and geochemical investigations showed different degree of alteration of the collected dump material. All the samples can be divided into two groups: (1) unaltered samples with low reflectance in the range 0.19–0.25%, Rock-Eval T_{max} from 420 to 430 °C and HI from 200 to 300 mg HC/g TOC, showing normal distribution of *n*-alkanes and absence of phenols; (2) mildly altered OM with higher reflectance in the range 0.33–0.52% containing irregular cracks, paler in colour oxidation rims, sometimes paler colour particles related to longer heating time, and sometimes devolatilisation pores and plasticised edges. They characterize elevated values of Rock-Eval production index (up to 0.47) and lowered T_{max} values (below 400 °C). These particles also contain high concentration of phenolic compounds, alkyl aromatic hydrocarbons, polycyclic aromatic hydrocarbons, and Gaussian distribution of *n*-alkanes. Elevated content of pyrite might have contributed to the self-heating processes as oxidation of pyrite is exothermic reaction.

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References

Fabiańska, M. J., J. Ciesielczuk, M. Szczerba, M. Misz-Kennan, D. Więcław, E. Szram, Á. Ńadudvari, Z. Ciesielska. 2024. Weathering alterations of coal mining wastes geochemistry, petrography, and mineralogy, a case study from the Janina and Marcel Coal Mines, Upper Silesian Coal Basin (Poland). – *Int. J. Coal Geol.*, *281*, 104407; https://doi.org/10.1016/j.coal.2023.104407.

Kaymakçi, E., V. Didari. 2002. Relations between coal properties and spontaneous combustion parameters. – *Turk. J. Eng. Environ. Sci.*, *26*, 59–64; https://online-journals.tubitak.gov.tr/engineering/issue.htm?id=392.

Misz-Kennan, M., M. J. Fabiańska. 2011. Application of organic petrology and geochemistry to coal waste studies. – *Int. J. Coal Geol.*, *88*, 1–23; https://doi.org/10.1016/j.coal.2011.07.001.

Nedjalkov, N. 1979. Maritsa Iztok lignite Basin – mining-geological environment, quality characteristics, and special features of the deposit. – *Coal*, *9*, 8–12 (in Bulgarian with English abstract).

Pone, J. D. N., K. A. A. Hein, G. B. Stracher, H. J. Annegarn, R. B. Finkelman, D. R. Blake, J. K. McCormack, P. Schroeder. 2007. The spontaneous combustion of coal and its by-products in the Witbank and Sasolburg coalfields of South Africa. – *Int. J. Coal Geol.*, *72*, 124–140; https://doi.org/10.1016/j.coal.2007.01.001.

Ribeiro, J., E. Ferreira da Silva, D. Flores. 2010. Burning of coal waste piles from Douro Coalfield (Portugal): petrological, geochemical and mineralogical characterisation. – *Int. J. Coal Geol.*, *81*, 359–372; https://doi.org/10.1016/j.coal.2009.10.005.

Stracher, G. B., T. P. Taylor. 2004. Coal fires burning out of control around the world: thermodynamic recipe for environmental catastrophe. – *Int. J. Coal Geol.*, *59*, 1–2, 7–17; https://doi.org/10.1016/j.coal.2003.03.002.

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