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Secondary mineralisation processes in coal pit heaps and its impact on the environment in NE Hungary

Szénmeddők másodlagos mineralizációs folyamatai és környezeti hatásuk Északkelet-Magyarországon

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Abstract – Ottnangian-Karpatian brown coal seams were exploited from the late 19th century producing numerous pit heaps accumulated between 1920 and 1970 in the hilly foreground of the Bükk Mountains, northern Hungary. The aim of this paper was the observation of the processes in the pit heaps and its environmental impacts.

The five coal seams were formed in paralic transgressional-progradational swamps. The oxihydration of the pyrite and marcasite content of the coal heap resulted in the production of sulphuric acids that exposed the components of the embedding sediments. Furthermore, the self-combustion of the partly siliceous and fragmented coal material in the pit heap was frequent. In this partly open system with varying temperature, hydrothermal, low-pressure and high-temperature pneumatolitic and thermo-contact micro-environments occurred simultaneously. In remobilising the original elements of the organic and the heap material, the migration of the adsorbed water and the gravitational free water equally played an important role. According to the microscopic, micromorphological electron microscopic, microprobe and X-ray analyses, primarily, sulphates occur in the heaps and the formation of rhombic native sulphur is frequent.

The environmental impact of the re-mineralisation processes was studied. The results showed that only a few soluble components had moderately damaging effects on natural fresh water and groundwater and only a few caused the increase of As-, Sr-, Fe-, Mn-, SO_4 contents. Due to local dilution, these were only occasionally increased above the tolerance limit.

Micro-climatic and ecological measurements were made on the surface of the heaps. These observations prove that the temperature of the soil developing on the top of the heap is higher than in the surroundings of the heaps. At places sulphur exhalation and transitionally slightly toxic element concentrations can be detected. As a result a moderately deteriorated pioneer vegetation appeared on the pit heaps.

Összefoglalás – A 19. század második felétől a Bükk hegység dombsági előterében ottnangi-kárpáti korú barnakőszén telepek kitermelése folyt számos meddőhányó létrejöttét eredményezve különösen 1920 és 1970 között. A közleményben a meddőhányókban lezajló folyamatok megfigyelésének eredményeit, valamint azok környezeti hatásait mutatjuk be.

Az említett rétegsorban megtalálható öt széntelep paralikus, transzgressziós-progradációs lápövezetekben képződött. A szénmeddő pirit és markazit tartalmának oxihidratációjából hőfejlődés mellett keletkező kénessavak a meddő képződményeivel reagálva feltárták azok szerkezetét. A meddőre került kovás szén, valamint a diszperz és töredékes széntörmelék anyagában gyakran következett be öngyulladás. Az így kialakuló, változó hőmérsékletű, félig nyitott rendszerben egyidejűleg alakultak ki hidrotermás, valamint kis nyomású, nagy hőmérsékletű pneumatolitos és termokontakt mikrokörnyezetek. Az öngyulladásban és a szerves, illetve meddő anyagok elemeinek mobilizációjában az agyagos üledékek szerkezetileg lazán kötött vizei, valamint a csapadék eredetű gravitációs szabad vizek egyaránt fontos szerepet játszottak. A kiégett meddő anyagában végzett mikroszkópi, mikromorfológiai, elektonmikoszkópi, mikroszonda és röntgen elemzések segítségével azonosított másodlagos ásványtársulásokban elsősorban szulfátok fordulnak elő, rombos terméskén gyakori megjelenésével kísérve.

A meddő szétesett és újraásványosodott anyagának környezeti hatását vizsgálva elmondható, hogy mindössze néhány vízoldékony összetevő okozott enyhe-közepes szennyeződést a természetes élővizekben és a talajvízben. Néhány esetben észleltük az As, Sr, Fe, Mn, SO_4 növekedését, de ezek is csupán helyenként haladták meg a kritikus határértéket.

A meddők felszínén folytatott mikroklima és ökológiai vizsgálatok során tapasztaltuk, hogy a meddőn képződő talajkezdemény hőmérséklete nagyobb, mint a tágabb környezet talajaiban, s több helyütt figyelhető meg foltszerűen kén kigőzölés, illetve átmenetileg enyhén toxikus elemkoncentrálódás, ami miatt a hányók felszínén csupán közepesen leromlott pionír növénytársulások jelentek meg.

Key words – coal pit heaps, self-combustion, mineralization, water contamination, environmental impact
Tárgyszavak – szénmeddők, öngyulladás, mineralizáció, vízszennyezés, környezeti hatás

Introduction

To the NE of Miskolc city in the hilly foreground (East-Borsod coal basin) of the Bükk-mountains made up mainly by Miocene molasse sediments, Ottnangian-Karpatian brown coal deposits have been under exploitation for almost 200 years. Mining production in the area reached its peak in the 1960s (5 million tons/year), but today only one field is in operation. Most of the pit heaps accumulated between the 1920s and 1970s.

The barren material of the coal beds is mainly of fine sand and clayey siltstone, with tuffaceous clays (smectite, mixed structures etc.), brown ironstone condensations, and fossils containing carbonate (KOZÁK & PÜSPÖKI 1995; PÜSPÖKI 2002; VICZIÁN et al. 1998).

In the course of the research the mechanism of self combustion of the pit heaps, the characteristics and results of subsequent mineralisation processes were studied. The determination of the chemical elements accumulated due to the secondary mineralisation processes induced by self combustion was attempted. It is also important to know the effect of these processes on the surface waters and also on the subsurface geological environment of the immediate surroundings of the pit heaps.

Materials and methods

The minerals produced by secondary mineralisation have been studied by polarisation microscope, SEM, microprobe, and X-ray analyses.

Burning experiments with temperatures between 250°C – 1200°C have been carried out on the barren material of the outcropping coal seams, to determine the burning temperature of the heaps. The DTA investigation results of our burnt out samples with those of the self-burnt heap material were compared.

To examine the possible emission effect of the re-mineralisation processes, dissolutions by distilled water with varying time scales (1 hour, 1 day, 1 week, 1 year) were carried out. For this, 10kg of heap material was ground and mixed to avoid non-representativity. Water samples were also taken from streams and wells (from a depth of 2-5m) in the direction of possible pollution moving away from the bottom of the heaps. The element content of the samples was determined by ICP-MS (*Table 1*), while accredited laboratories according to the relating Hungarian standards made the chemical water qualification (*Table 1*).

element (ppm)	**1.**	**2.**	**3.**	**4.**	**5.**	**I.**	**II.**	**III.**	**IV.**	**V.**	**B.grnd**
Al	0.171	0.215	0.029	0.029	0.063	0.02	0.05	0.20	0.50	>0.50	
As	0.017	0.008	0.007	0.007	0.009	0.01	0.02	0.05	0.10	>0.10	
B	0.176	0.061	0.039	0.053	0.137	0.10	0.20	0.50	1.00	>1.0	
Ca	91.5	241	256	237	297						133
Cd	<0.00022	0.0005	0.0003	<0.00024	<0.0003	0.0005	0.001	0.002	0.005	>0.005	
Cr	0.0007	0.0009	0.0028	0.0009	0.0010	0.01	0.02	0.05	0.10	>0.10	
Cu	0.0051	0.0020	0.0060	0.0018	0.0026	0.005	0.01	0.05	0.10	>0.10	
Fe	0.090	0.848	0.589	0.067	0.207	0.10	0.20	0.50	1.00	>1.0	0.5
Mg	294.7	67.3	73	54.9	100						40.4
Ni	0.018	0.013	0.010	0.011	0.014	0.015	0.03	0.05	0.20	>0.20	
Pb	<0.00148	0.005	0.006	0.005	0.006	0.005	0.02	0.05	0.10	>0.10	
S	451	148	238	159	346						
Zn	0.012	0.014	0.496	0.231	0.015	0.05	0.075	0.10	0.30	>0.30	
pH	8.5	6.9	7.1	7.4	7.8						7.1
Conductivity (µS/cm)	6970	1440	1830	1430	2430	500	700	1000	2000	>2000	
HCO_3^- *(mg/l)*	512	592	501	483	607						416
Cl^- *(mg/l)*	39	7.1	15	15	26						14.6
SO_4^{2-} *(mg/l)*	4112	446	710	487	975						163
NO_2^- *(mg/l)*	0.244	0.019	0.013	0.05	0.029	0.01	0.03	0.1	0.3	>0.3	0 – 0.1
NO_3^- *(mg/l)*	31	12	47	16	2.6	1	5	10	25	>25	1.1
NH_4^+ *(mg/l)*	0.08	0.08	0.11	0.02	0.11	0.2	0.5	1.0	2.0	>2.0	0.49
Total dissolved material (mg/l)	7400	1350	1850	1320	2570						

Table 1 Element content and chemical qualification of the water samples from the surroundings of a pit heap situated in the Ádám valley (samples analysed by ICP-MS)

1. táblázat Az Ádám-völgyi meddőhányó vízmintáinak elemtartalma és kémiai minősítése (a mintákat ICP-MS készülékkel elemeztük)

Legend: 1: Spring at pit heap foot / forrás a meddőhányó lábánál; 2: Spring 100m from the heap / forrás a hányótól 100m-re; 3: well 500 m from the heap / kút a hányótól 500m-re; 4: well 1000 m from the heap / kút a hányótól 1000m-re; 5: Tardona stream / Tardona-patak
Water qualification classes / Vízminőségi osztályok: I excellent / kitűnő; II good / jó; III reasonable / megfelelő; IV polluted / szennyezett; V strongly polluted / erősen szennyezett (MSZ 12749, 1993); B.grnd: Background concentrations from the groundwater of the region / a háttér koncentrációk a környék talajvizéből származnak

The ecological parameters of the vegetation types to be found on the examined pit heaps were observed on the different surfaces.

Because of the air and dust pollution the gas exhalation and wind conditions of pit deposits in the valley head were examined together with micro-climatic measurements.

Results and discussion

Burning and mineralisation

The migration and transvaporisation effects of the adsorbed waters and the gravitational free waters both played a part in re-mobilising the original mineral and element content of the pit heaps. In the reductive depositional environment of the coal seams significant amount of bacterial sulphide minerals (brassel, cellular pyrite) were formed. The sulphuric acid and sulphurous acid, produced by the oxy-hydration of these minerals destructed the structure of the pelitic sediments and damaged the different materials of the coal-seam bearing sediments (in the same way as in the case of sample preparation by acids).

Self-combustion and long-term burning of the petrified coal fragments and black metals frequently occurred in the coarsely dumped heaps. Hydrothermal, low pressure, pneumatolytic and thermo-contact micro-environments occurred at the same time in the open and partly open system of varying temperature. Domination of native sulphur and sulphates and also the occurrence of ammonium and organic material in the studied East-Borsod coal basin and in other European sites in the literature, reflect the interaction between the volatiles and the heap rocks (SCHERBAKOVA 2000).

The pieces of pelitic barren rock of varying clay mineral content (0-15 weight% based on X-ray analysis), were burnt to a light brown and red colour. Fissures were formed corresponding to the original bedding due to compaction. The partly re-melted internal parts are reminiscent of toadstone volcanic cinders (*Fig. 1/1-2*) and iron and/or sulphur rich melts were formed on their surface (SÜTŐ 2000). At the high temperature points (above 1000°C according to DTA control) isolated mullite and wollastonite, in the medium temperature zones *hematite* and *fluorite*, in the hydrothermal phase primarily sulphates (*barite, szomolnokite, thaumasite, jarosite, hexahydrite, antlerite*) and often *rhombic native sulphur* are formed, while in the presence of carbonates *calcite*, *aragonite* and *huntite* occur (*Fig. 1/5-6*). In some places progressive corrosive dissolving and re-crystallisation of the carbonate fossil structures could be observed. In the course of burning, the silicified coal pieces lost most of their organic material but retained their specific texture (*Fig. 1/3*). In their light grey and especially in the white versions dominantly *cristobalite* (80-95%) (*Fig. 1/4*), a little *silica gel* and in their inner pores in subordinate quantity *anhydrite*, *gypsum*, *sulphur* and *aragonite* can be found.

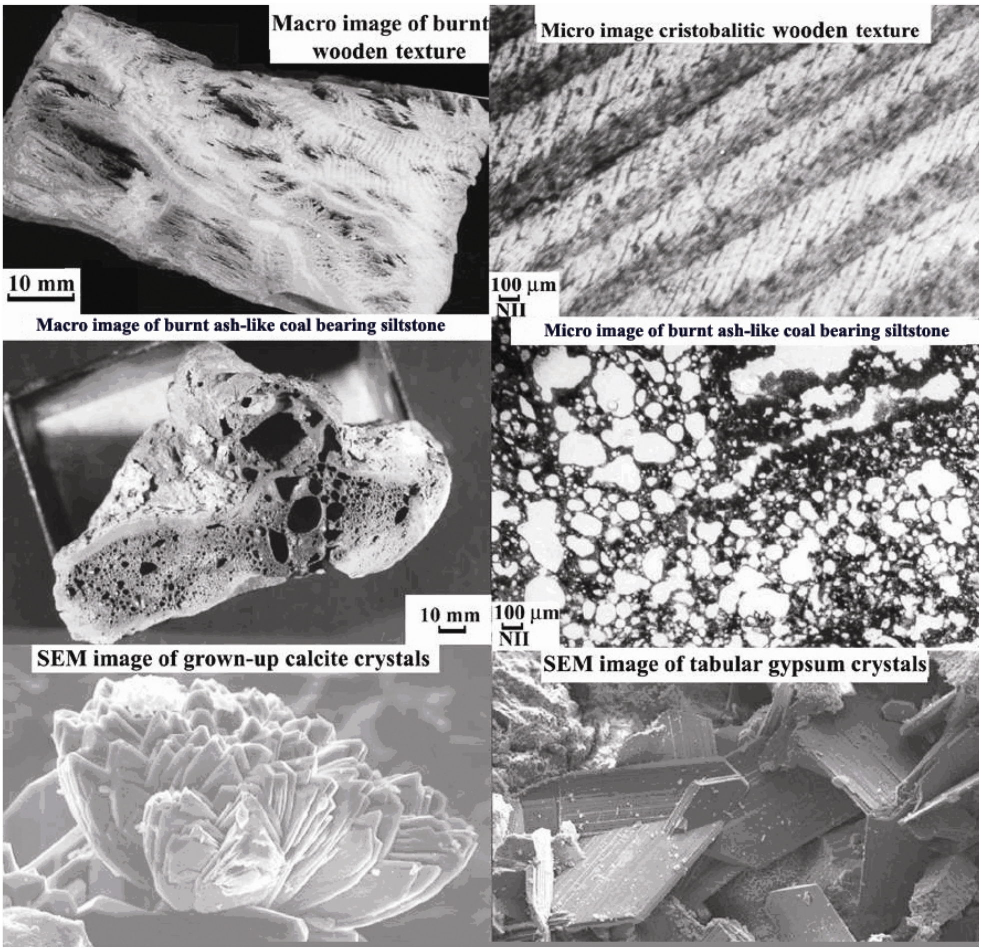

Figure 1 Products of secondary mineralisation in the pit heap
1. ábra A meddőhányó másodlagos mineralizációs ásványai

Water contamination

Due to the mineralisation processes in the pit heaps water pollution is detectable in the surroundings of the heaps. The dissolubly element content exceeded moderate harmful effect on the natural surface and groundwater only in the case of a few components and indicated increase in dissolved As, B, Ca, S, Sr, and SO_4 contents. The latter already reached the possible maximum (1100-1400mg/l) at the 1 hour dissolution, and scarcely changed after this (1 hour, 1 day). Ca also displayed a short period of dissolution, and reached the maximum solution within 1 week. As opposed to this B appeared first after 1 week dissoluion, and reached a slight contamination after 1 year.

All of the samples collected in the surroundings of the pit heaps showed higher concentrations than the euroconform Hungarian Drinking Water Quality Standard (MSZ 12749). Due to the dilution taking place in the given local environment these concentrations only increase above the tolerance threshold value in exceptional cases and temporarily. The surface water and groundwater around the pit heaps which have diminishing activity, fall into the tolerable-good classification category (Hungarian standard) regarding Al content. Considering As, B, Cd, Cr, Ni, Pb, Cu content they are classified as excellent-good, while in the case of Fe, Mn and Zn they are found as polluted (*Table 1*). As for conductivity the waters are classified as polluted and strongly polluted due to their high cation content at the foot of the heaps. The samples from springs near the foot of the heaps display higher pH than the background resulting from higher HCO_3^- and CO_3^-, SO_4^{2-} (*Table 1*).

In the region's artesian waters around 160mg/l SO_4 content can be displayed while the SO_4 content of the springs at the foot of the pit heaps moved around 4000mg/l, and the total quantity of dissolved material was 7400mg/l (*Table 1*). Both the SO_4 and dissolved material contents were reduced exponentially moving away from the pit heap. Ca, Cl, Fe and Mg values showed slight positive anomaly compared to natural conditions. At the foot of the pit heaps NO_2 and NO_3 values exceed the tolerance limit, however, again strongly decreasing concentrations can be observed away from the heaps (*Table 1*).

The spreading of this contamination is significantly influenced by the geological formations at or near the surface. The construction of our pollution-sensitivity map was based on the porosity of formations creating the surface and the depth of the groundwater table (*Fig. 2*). Accordingly we separated good conducting (10^{-6}-10^{-5}m/s) and less good/poor conducting (10^{-6}-10^{-8}m/s) beds, and unsaturated and water saturated or periodically saturating bed groups. The specific pollution-sensitivity relating to acidic loading and the magnitude of natural buffer capacity are increased by the natural carbonate content of the sandy sediments of the coal bearing sequence (5-10%) and the siltstone horizons (often exceeds 10%).

Although varying stratification and increasing water conduction capacity in some places impede the localisation of the chemical pollution, overall the natural basement of the pit heaps is favourable for trapping the pollution. In determining the direction of further spreading, besides surface drainage conditions, the regional flow relations of shallow artesian waters also play a role. In our case the beds dipping opposite to the surface runoff conditions are responsible for subsurface spreading of contaminants, the tracing and measurements of which, however, can only be carried out outside our examination area (*Fig. 2*).

Other environmental impacts

The surface temperature of the pit heaps of decreasing activity at Kazincbarcika, according to micro-climatic measurements in summer during the day, appears as an environmental loading which obstructs the vegetation from gaining ground. The surface (to a depth of 5cm) soil temperature values of the still active heap sections proved to still be above 50°C. Where the excess heat effect caused by internal burning is no longer realised, there values of 25-30°C are measured. While in the tip surroundings the soil temperature is 15-20°C (HOMOKI et al. 2000).

On the active and the partly already stabilised tips, as a result of the extreme water balance and temperature, and the low supply of nutrition, a moderately deteriorated - impaired association appears. When making the cenological observations we found a dominance of less demanding weeds and cosmopolitan species, among which, however, indications reflecting toxic effects do not appear.

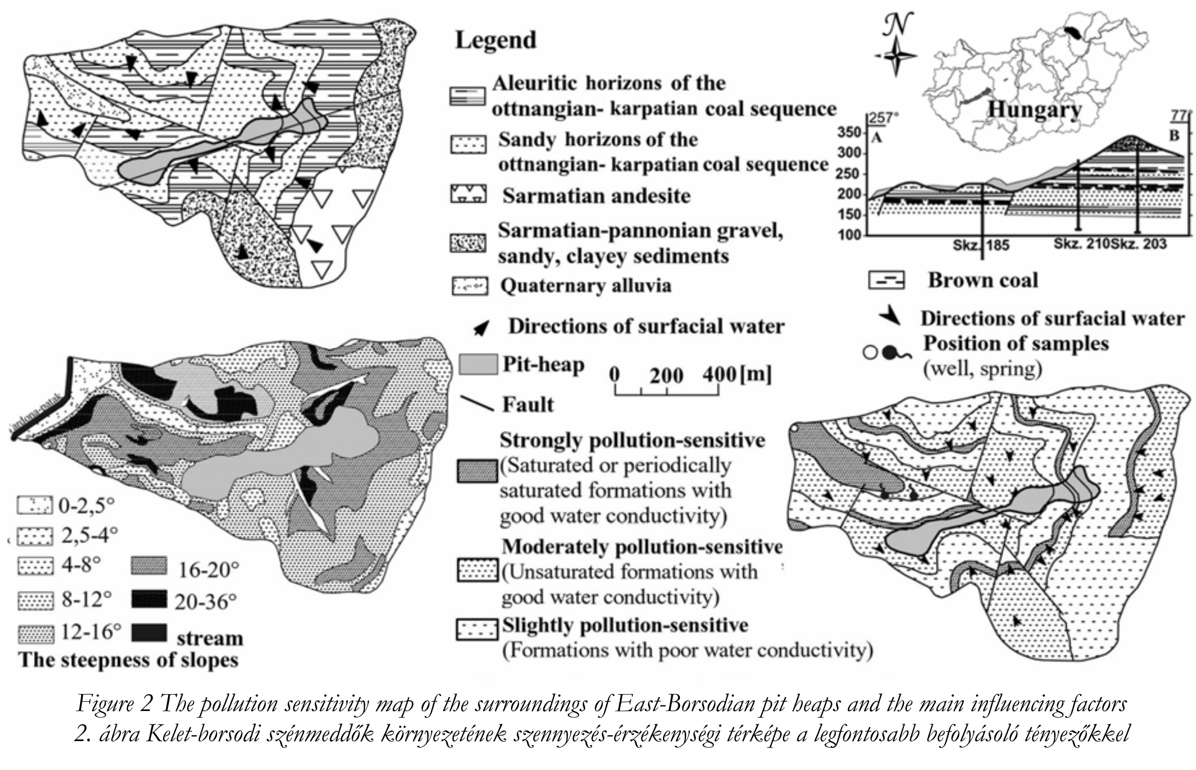

Figure 2 The pollution sensitivity map of the surroundings of East-Borsodian pit heaps and the main influencing factors
2. ábra Kelet-borsodi szénmeddők környezetének szennyezés-érzékenységi térképe a legfontosabb befolyásoló tényezőkkel

On the basis of our micro-climatic wind measurements, it could be established that the „mountain winds" developing in the evening and night-time period, blowing from the pit heap towards the valley are responsible for the spread of pollution to the inhabited areas. Among the gases released in the course of the burning, an environmental problem is caused by the strong odour effect of hydrogen sulphide.

Conclusions

The re-mineralisation of the pit heaps produced the accumulation of Al, Ba, Ca, Fe, Mn, S, SO_4^{2-}in the form of certain rare minerals, presenting, therefore, a possible source of pollution for the surrounding environment. However, we found that, despite the chemical emission of the pit heaps contamination appeared as not significant due to the geological characteristics of the area. The concentrations of certain elements increased in the groundwater comparing to the background and to the Hungarian Standards but this fact does not endanger human life yet**.** On the other hand, we think that the careful re-cultivation of these pit heaps is absolutely necessary.

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