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Effects of waste rocks on the properties of the natural waters in the abandoned mining site Krumovo, Southeast Bulgaria

Влияние на отпадната скална маса върху качествата на природните води в изоставения минен обект Крумово, Югоизточна България

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Introduction

Krumovo iron ore deposit is located in Southeast Bulgaria, about 25 km south of Yambol. The main ore mineral is magnetite but it contains also irregularly distributed sulfides, mostly chalcopyrite and pyrite, pyrrhotite and marcasite. The mineralization is contact-metasomatic, as both magnesium and calcium skarns are common. These skarns were formed, where intermediate to basic magmas intruded Triassic marbles in the contact aureole of the gabbroic Upper Cretaceous Monastir pluton. The Monastir pluton forms the core of the forested Monastir Heights. This deposit is exceptionally rich in iron, because of its compact magnetite bodies and was known from ancient times. In modern time mining started in 1906 and continued till 1986 (Kanurkov, 1988) as it was performed by both open pits and underground workings. In 1986 the mining was stopped not because of ore depletion, but because of numerous fatal accidents due to collapse of mine working above unmarked underground caverns.

The mine landscape is dominated by underground galleries and overground pits and waste rock piles stored in topographic depressions. A small seasonal stream drains the galleries and discharges waters in the river Kalnitsa, located about 2.7 km to northeast of the mine area. The heavily disturbed area of the deposit is about 3 km^2 but pits and galleries can be found outside this perimeter. Since 1990 secondary mining of the mine waste began for use as a road construction stone. Practically all larger waste piles were removed and now at the bottom of the depressions small seasonal lakes are formed. A study, with the purpose to evaluate the regeneration potential of the environment in this landscape commenced in the early 2020. Its main subject is the water, which drains pits, waste piles and galleries. To this moment data about the water chemistry from Krumovo have not been published.

Methods, materials and purpose of this study

In the study course, three water sampling initiatives were undertaken. In March and June, two small lakes at the bottoms of mine pits were studied in situ, for integral water parameters, and in lab condition for micro- and macro-components. These samplings represent the waters in normally saturated (March) and dry conditions (June). The results are accepted for publication in the Ecology and Environment volume of the SGEM 2020 Conference in Varna, as the exact bibliography of the article is still not known. During the summer months, a severe drought affected the region. This allowed the effects of the drought to be studied, by sampling isolated puddles in the stream that passes through the mine area. However, only four small puddles were found and sampled in the middle of September. The results of this sampling ($K_1 – K_4$) are presented in this paper. Since all samplings, to this moment, showed practically clean waters, usable for domestic purposes from legal point of view, it appears that explanation is needed.

The main question that arises is why after so severe damage, caused by mining, the waters are little affected by pollution. It seems that the geochemical properties of the rock medium itself (e.g. Drever, 1088) do not favor significant pollution, or the buffering potential of the environment is significant (Panayotova, Dimitrov, 2014). In order to clarify that, experiments of controlled leaching with acidified water (resembling acid mine drainage) and distilled water (resembling rainwater) were undertaken and the results are shown in this paper. For the leaching experiments, about 40 kg of waste rock, containing fragments of diorite, skarn, magnetite ore and altered rock with sulfides were excavated close to the points, where samples K_1 and K_2 were taken. After that, about 20 kg of waste rocks were put into contact with 10 l of water for each sample K_1 and K_2 and acidified correspondingly with 55 ml 20% sulfuric acid (p.a.) for K_1 and 25 ml sulfuric acid for K_2. These were marked as K_1-a and K_2-a. In addition, the same amount of material excavated from the point where K_1 was taken was placed in contact with 10 l of distilled water (sample K_1-d was obtained). The contact time was 3 days, after which measurements were carried out. Portable multifunctional system 340i WTW was used to measure temperature (T), acidity index (pH), oxidation-reduction potential (Eh), conductivity (c), and dissolved O_2. Classical analytical methods were applied to determine water macro-components. ICP-OES was used for the analysis of micro-components.

Results and discussion

The analyses carried out in March and June showed that depending on the material they are contacting with, the waters can be classified in 2 main groups – hydrogen-carbonate-calcium type, "soft" and hydrogen-carbonate-sulfate-magnesium-calcium type, "hard" waters. Most important thing was that all water samples met the requirements with respect to macro-components' concentrations in water, intended for drinking and household purposes (*Regulation № H-4; Regulation № 9*). The studied waters met the legal requirements with respect to heavy metals, except of that for Mn, which naturally exists in elevated concentrations in the ores in the region. It probably comes with manganese oxide from the ore. The elevated concentration of phosphorus probably reflects the presence of the mineral apatite in the host rocks and mine waste.

The results of the in situ measured integral parameters during the September sampling are shown in Table 1. The data on water macro-components are shown in Table 2. Integral parameters of water samples after artificial material leaching with acidified or distilled water are presented in Table 3, while data on macro-components of the same samples are shown in Table 4. Considering the information presented in Tables 1–4 and our previous findings (from March and June studies) we have decided that it is useless to carry out determination of water micro-components for non-acidified water samples, since at the measured pH and Eh values, they are not expected to present in dangerous concentrations. The data on micro-components measured in acidified samples are given in Table 5.

As it can be seen in from Tables 1 and 2 the studied water meets the legal requirements with respect to integral parameters and macro-components. Sulfates and chlorides are practically absent. It can be seen that only the extreme leaching conditions (pH 2.2) can lead to unacceptable conductivity of 5860 mS/cm (Table 3). This leaching that was intended to simulate long term and exceptionally harsh conditions did not prove to supply large amounts of pollutants in the water.

The pollution is restricted to the heavy metals, which exist in the mineral composition of the ore itself. Since most of heavy metals, except iron, are found in the ore in small amounts, they do not have

Table 1. Integral parameters of studied water – September sampling

Water sample	T, °C	pH	Eh, mV	χ, μS/cm	Diss. O_2, mg/l
K_1	24.4	7.30	459	171	5.5
K_2	24.1	7.34	458	177	5.5
K_3	24.0	7.63	444	173	4.8
K_4	23.9	7.63	446	191	4.4
Legal requirements*		6.5–9.5		2000	<6

**Regulation 9, 2001; Regulation H-4, 2012*

Table 2. Water macro-components (in mg/l) – September sampling

Water sample	Ca^{2+}	Mg^{2+}	$Na^{+}+K^{+}$	Cl^{-}	SO_4^{2}	HCO_3^{-}
K_1	25	5.2	9.2	3	4	114
K_2	29	2.9	11.5	3	3	130
K_3	25	1.1	15.1	2	7	117
K_4	33	2.3	10.8	2	3	140
Legal requirement*	150	80	200	250	250	–

* *Regulation 9, 2001*

Table 3. Integral parameters of water samples after an artificial material leaching with acidified or distilled water

Water sample	T, °C	pH	Eh, mV	χ, mS/cm	Diss.O_2, mg/l
K_1-a	26.2	2.2	674	5860	5.74
K_2-a	23.3	2.75	694	1904	6.49
K_1-d	24.5	7.3	454	81	6.68
Legal requirements*		6.5–9.5		2000	<6

**Regulation 9, 2001; Regulation H-4, 2012*

Table 4. Water macro-components of water samples (in mg/l), after an artificial material leaching with acidified or distilled water

Water sample	Ca^{2+}	Mg^{2+}	$Na^{+}+K^{+}$	Cl^{-}	SO_4^{2-}	HCO_3^{-}
K_1	548.2	26.40	19.0	3	1450	–
K_2	271.5	12.71	12.3	3	720	–
K_3	16.3	1.1	12.1	2	2	62
Legal requirement	150	80	200	250	250	–

Table 5. Water micro-components of water samples (in mg/l), after an artificial material leaching with acidified or distilled water

Sample	Co	Cu	Fe	Mn	Ni	Al	Cd	Cr	Pb	Zn	PO_4^{3-}
K_1-a	0.117	9.66	2.70	4.63	0.08	4.98	<0.005	<0.005	<0.01	0.389	4
K_2-a	0.032	3.80	0.353	1.69	<0.01	1.49	<0.005	<0.005	<0.01	0.114	5
Legal demand*	0.02	2.0	0.2	0.05	0.02	0.2	0.005	0.05	0.01	4.0	0.5

**Regulation 9, 2001; Regulation 12, 2002*

the quantity to pollute the surface and underground waters. Even the iron is not very mobile in absence of sulfur or chlorine. The host rock, being nearly neutral in environmental sense, is interpreted not to supply pollutants with the exception of phosphorous, which probably comes with the host rocks and the skarns. It cannot be attributed to fertilizers since the Monastir heights are located above the level of arable lands and are not fertilized. The ore comprises mainly oxide minerals, providing iron and manganese, and negligible amount of copper from the chalcopyrite. The extreme leaching shown in this paper is highly unlikely in nature.

Conclusion

The main fact, found in this study, is that the waters in Krumovo deposit area are predominantly pure in all weather conditions. They comply with the legal requirements for domestic purposes for these parameters that are tested in the work. This can be explained with the neutral nature of the host rocks, which are mainly diorites and with the limited amount of sulfide in the ore, which contains predominantly iron oxide. This suggests that the different metal deposits should not be treated under equal terms. Exploitation of oxide deposits like Krumovo shows much less negative environmental impact compared with sulfide deposits, able to be a source of acid mine drainage, and this must be reflected in the environmental legislation, as well as explained to the communities impacted by the mining activity.

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