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Supplementary material

SUPPLEMENTARY MATERIAL TO

Geochemistry of neutral mine drainage at sulfide deposits – Example of the „Grot" Pb–Zn mine, south-eastern Serbia

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STUDY AREA

The Grot Mine is located in the southeastern part of Serbia, within the municipalities of Bosilegrad and Vranje. The mining area is characterized by mountainous terrain. In the central part of the mining field, there is the ridge of Besna Kobila, which is also the highest point in the relief (1923 m). Besna Kobila represents the watershed divide between the Black Sea basin (South Morava River basin) and Aegean Sea basin.[1] The river streams are characterized by a snow-rain regime, with peak flows occurring during snowmelt and spring rains. The area has a moderate continental climate with mountainous influences. The average annual air temperature ranges from 5 to 6 °C, with an average annual precipitation exceeding 1000 mm.[2] In geological terms, the ore field comprises older Paleozoic crystalline schists that are intruded by older granitoids, younger Tertiary granitoids, and the youngest volcanic rocks (quartz latites) (Fig. S-1). The ore deposit is hosted in the schists of the Lisina Series, accompanied by quartz-latite, calcschists, and marbles.[1,2] The formation of the mineral paragenesis is associated with several stages. The most important stage that led to mineralization (mesothermal phase) is characterized by the minerals such as galena, sphalerite, pyrite, chalcopyrite, arsenopyrite, molybdenite, tennantite, quartz, stibnite, rhodochrosite, calcite, manganese siderite, chalcedony, and aragonite.[3] During the supergene stage, minerals such as cerussite, smithsonite, pyrolusite, and limonite were formed through transformations.[3] From a hydrogeological perspective, the fractured aquifer has a predominant distribution in the exploration area. It is formed within the granitoid and quartzlatite rocks and crystalline schists (Lisina and Jerešnica Series).[2] The fracturing of the crystalline schist complex is significant. Groundwater accumulation is related to the fracture and fault systems of crystalline schists, marble, and quartz latite. The permeability of the rocks depends on the type of crystalline schist, with the Jerešnica-age crystalline schists being less permeable than the Lisina-age schists, representing a hydrogeological barrier for groundwater movement.[1] The mining works were carried out from 1290 m to 1720 m. Completing the main export adit (MEA) at the lowest mining horizon involved advancing through the entire massif of Besna Kobila, reducing the inflow of water into the mining works at higher elevations.[1] The drainage of mining operations is entirely gravity-based. All the water from the mine is discharged at

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three levels: VI, VIII and IX horizons. In places where mine waters are discharged, sedimentation ponds have been installed at the outlets of mining horizons.[1] The majority of mine waters are drained through the MEA at the IX horizon, where the water flows in three directions (towards the flotation plant, towards the Hajdučki Osoj adit, and the outlet of the IX horizon at the Crna Reka site).[1]

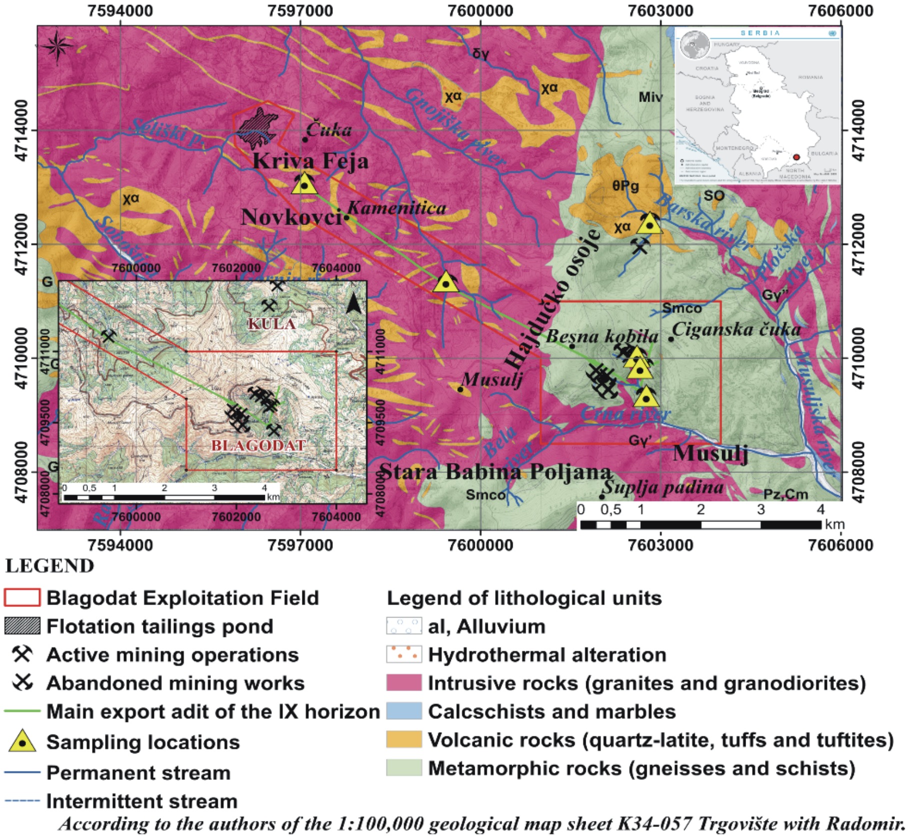

Fig. S-1. Geological map of the study area (modified) with locations of mine water sampling points.[3-5]

Table S-I. Results of chemical analyses for the examined mine water samples relative to the USEPA standards for drinking water and emission limit values according to the Regulation on emission limit values for water pollutants and deadlines for their achievement (Official Gazeta RS 67/2011, 48/2012 and 1/2016)

Parameter	Unit	Sample											USEPA	Criteria for Wastewater
		1	2	3	4	5	6	7	8	9	10	11		
t	°C	7.1	7.5	7.2	14.5	14	10	9	9	10	10.5	9.5	/	/
TDS	mg L^{-1}	719	442	353	183	187	166	163	385	375	167	482	500	/
EC	μS cm^{-1}	610	608	569	249	262	197	180	431	433	225	632	/	<3000
pH	/	7.53	7.52	7.43	7.6	7.4	7.39	7.5	7.35	7.52	7.04	7.5	6.5-8.5	6-9
Dissolved O_2	mg O_2 L^{-1}	5.4	6	9.3	7	6.2	10	10.4	10.7	10.9	10.3	9	/	>0.4
Dissolved H_2S	mg L^{-1}	0.351	0.329	0.052	0.048	0.329	0.006	0.008	0.009	0.006	0.063	0.026	/	≤1.0
Ca^{2+}	mg L^{-1}	/	/	/	/	/	25.6	25.6	56.8	52.8	40.8	40	/	/
Mg^{2+}	mg L^{-1}	/	/	/	/	/	1.5	1.2	4.2	4.2	3.2	4.1	/	/
Na^{+}	mg L^{-1}	/	/	/	/	/	6.6	4.25	4.65	4.62	3.5	4.7	30-60	/
K^{+}	mg L^{-1}	/	/	/	/	/	1	1	1	1	1	1.1	/	/
HCO_3^{-}	mg L^{-1}	/	/	/	/	/	61	61	91.5	91.5	85.4	91.5	/	/
SO_4^{2-}	mg L^{-1}	177.7	116.1	93.2	90.5	41.7	44.4	37.4	153.4	152.8	53.8	154.4	250	<300
Cl^{-}	mg L^{-1}	18	12	8	10	8	4	4	6	6	5	6	250	<250
NO_3^{-}	mg L^{-1}	1	1	1.7	12.09	11.83	1.5	0.9	2.6	2.8	0.83	3.7	10	<15
NO_2^{-}	mg L^{-1}	0.333	0.298	0.197	0.041	0.035	0.005	0.009	0.06	0.03	0.006	0.061	1	/
NH_4^{+}	mg L^{-1}	0.93	0.86	0.91	0.86	1.5	0.18	0.33	0.43	0.39	0.033	0.54	/	<1.5
Fe total	mg L^{-1}	2.37	0.64	0.8	1.6	1.6	0.55	0.26	0.15	1.24	0.11	0.23	0.3	≤5
Cr total	mg L^{-1}	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	0.1	≤0.25
Cu total	mg L^{-1}	<0.03	<0.03	<0.03	<0.03	<0.03	<0.03	<0.03	<0.03	<0.03	<0.03	<0.03	1.3	≤0.25
Zn total	mg L^{-1}	0.366	0.221	0.188	0.7	0.56	0.07	0.05	0.09	0.39	0.054	0.35	5	≤1
Pb total	mg L^{-1}	0.17	0.11	0.08	0.47	0.3	0.02	0.02	0.02	0.25	0.02	0.045	0.015	≤0.25

As total	mg L^{-1}	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	0.01	≤0.05
Ba total	mg L^{-1}	<0.5	<0.5	<0.5	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	2	<1
Mn total	mg L^{-1}	0.6	0.25	0.29	0.34	0.36	0.05	0.05	0.08	0.22	0.08	0.12	0.05	<1

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