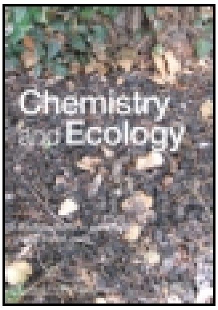

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Z. O. Stevanovic [a] , M. M. Antonijevic [b] , G. D. Bogdanovic [b] , V. K. Trujic [a] & M. M. Bugarin [a]

[a] Mining and Metallurgy Institute Bor, Bor, Serbia

[b] University of Belgrade, Technical Faculty Bor, Bor, Serbia

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Influence of the chemical and mineralogical composition on the acidity of an abandoned copper mine in the Bor river valley (eastern Serbia)

Z.O. Stevanovic[a]*, M.M. Antonijevic[b], G.D. Bogdanovic[b], V.K. Trujic[a] and M.M. Bugarin[a]

[a] *Mining and Metallurgy Institute Bor, Bor, Serbia;* [b] *University of Belgrade, Technical Faculty Bor, Bor, Serbia*

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Since the end of operations in 1987, the flotation tailing pond in the area of the former Bor River valley has been left without any type of remediation, leading to a great environmental impact on the wider surrounding area. Because the relative abundance of minerals is critical in determining the quality of the water draining from such materials, research to define the influence of the chemical and mineralogical characteristics on the acidity of the Bor flotation tailing was performed. With this aim in mind, core sampling from eight, 20-m deep drilling holes was undertaken, followed by mineralogical analysis of the composites from each drilling hole and chemical analysis of the composites of the holes and samples taken every 5 m. In addition, the tailing acidity was measured on samples from all drilling holes taken every 1 m from the surface to the base of the tailing using distilled water and 1 M KCl. The average tailing acidity was very high, with a pH value between 2.2 and 4.0 along the depth of the holes, indicating that pyrite, as the dominant sulphide mineral, was oxidised even in the deepest layers of flotation tailing.

Keywords: flotation tailing; copper; pyrite; acidity; environmental impact

1. Introduction

The flotation concentration of raw materials, as is case in the Mining and Smelting Combine Bor, is the origin of large quantities of finely ground flotation tailing, the mass participation of which is usually ~98% in comparison with flotation feeds. The particle sizes of these waste materials are mostly <0.1 mm because of the requirements of the flotation process. The tailings consist of gangue minerals and a certain amount of oxide and sulphide minerals which are not valorised through flotation concentration. However, the physical and chemical characteristics of these minerals are changed significantly by the numerous electrochemical reactions occurring through the flotation process.

The flotation tailing ponds formed in sulphide metal mines, when abandoned without any type of remediation, are usually characterised by increased acidity and content of toxic elements [1]. The described phenomena are the result of the chemical and biochemical oxidation of pyrite and

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*Corresponding author. Email: zoran.stevanovic@irmbor.co.rs

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other sulphide minerals by atmospheric precipitations [2,3] and in the presence of oxygen from the air [4–6]. The oxidation of pyrite and other sulphide minerals further induces the generation of contaminated acid mine drainages (AMD) [7] of low pH (2.5–4.5) and an increased content of SO_4, metals ions, metalloids, etc. [8–14].

A typical example of an abandoned flotation tailing is that within the scope of the Mining and Smelting Combine Bor, one of the main copper producers on the Balkan Peninsula, with a mining and ore processing history of over 100 years.

The Bor region, in the geological sense, consists of complex tectonic structures in which a various types of sedimentary, volcanic and metamorphic rocks appear. The existing surface of the Bor Municipality was once under sea, lakes and swamps. During this period, sedimentary rocks were formed, which were subsequently hydrothermally altered by pressure and heat from movements of the earth’s crust into igneous and eruptive rocks, rich in copper, silver, platinum, gold and other metals. The Bor deposits are defined as an outbreak of a massive sulphide ore deposit above the transitional layer lying over the porphyritic copper mineralisation at depth. They are located in the porphyritic hornblende–biotite andesites with a little dacites and their equivalent pyroclastic rocks, and they are limited in the west by the Bor fault. The geology of the Bor copper deposit area is mainly characterised by an ore deposit at an altitude from 360 to 5 m in the hydrothermally altered timocite. There are massive conglomerate and timocite zones to the northeast, and in the southwest, there are andesite zones with basaltic bodies which are at higher altitudes. The mineralogy of the deposit is characterised by chalcopyrite, pyrite, pyrrhotite, magnetite, rare molybdenite and traces of enargite, galena and sphalerite. In the underground mine, the massive sulphide deposit with chlorite, kaolin, silica and gypsum–anhydrite alteration, is mined. Mineralisation consists of pyrite, chalcopyrite, enargite, bornite, chalcocite and covellite [15].

The Bor area is mainly characterised by a hornblende–andesite agglomerate and conglomerates having low permeability. Surface outbreaking of the hydrothermally altered timocite has created low permeable surfaces. The only primary zone of higher permeability was in the alluvial deposits of the Bor River. The original terrain was characterised by a variety of relief and numerous tributaries of the Bor River, most of the waterfall type, and which together with the Bor River drains and dewaters the terrain. Drainage and dewatering of the whole zone are significantly changed in comparison with the original hydrogeological order, which is the result of gravitational depletion due to a depression formed by the open ore pits that intersect the aquifers. Based on the geological structure, the presence of rock masses of different porosity, conditions of formation and renewal of underground water reserves over a wider area of the Bor copper deposit, aquifers of a compact, fracture and karst type have been distinguished. Drainage of aquifers is done mostly by springs of minor abundance ($<0.1\ L \cdot s^{-1}$). Many of these springs exist only in rainy periods. Under natural and inviolate conditions, the groundwaters are mostly a low mineralised hydrocarbon class of complex cationic composition. Beside these waters, the groundwaters in the Mesozoic clastics are formed of slightly mineralised water of a hydrocarbonate class of the calcium group and, at greater depth, the hydrocarbonate water of the sodium group [16,17].

From a hydrology point of view, Bor Municipality has no significant hydro potentials. Most streams and rivers belong to the Timok River basin. The terrains in the northwest belong to the Mlava River basin, those in the north to the Pek River basin, and those in the northeast to the Velik Timok River basin. Mountain massive Crni Vrh (1027 m) presents a watershed for these river basins. The natural distribution of the hydrological network is determined by geological ranking and the tectonics of the region. Most of the streams and major rivers are situated in a north–northeast and south–southeast direction, in accordance with the directions of the main tectonic dislocations (faults) in the Timok eruptive zone. Water flows are low with varying water levels. The most important rivers are the Zlot River, Bor River, Krivelj River, Ravna River and Timok River. The hydrological situation in the Bor mining region is complex because of many areas of wastewater discharge from three mines and a metallurgical complex, along with sanitary

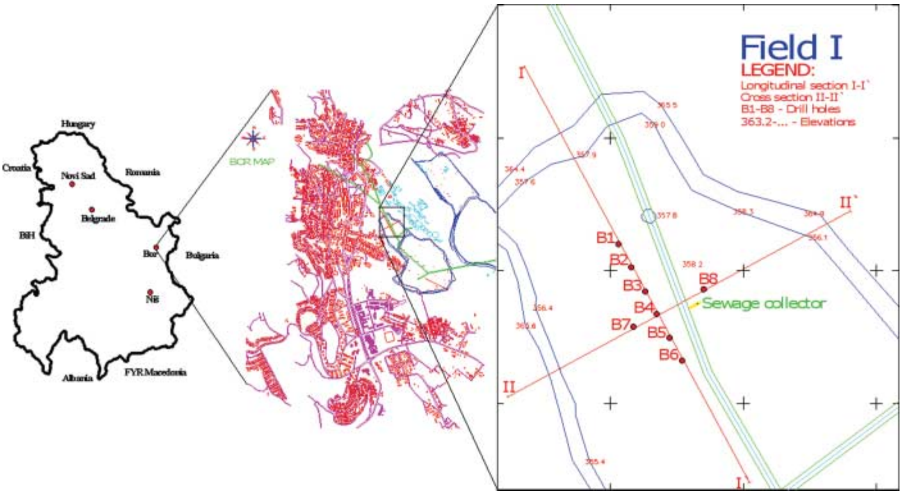

Figure 1. Location of the flotation tailing pond with routes of drilling cross-sections.

wastewater from the town of Bor and many surrounding villages. The whole complex has an extremely negative impact on waterways because wastewater treatment has not been conducted in the past. The Bor River and Krivelj River are the final destinations for mine drainage water, wastewater from the smelter and refinery and untreated municipal wastewater. Therefore, the surface water is highly polluted and degraded in relation to pH, dissolved solids, copper and iron. The water in the Bor River is acidic, with high content of Fe, Cu and Zn even at a distance of 10 km from the RTB complex [18].

The locality of the Bor Municipality, because of the latitude at which it is situated, has a moderate continental climate. Because of the influence of the hilly to the mountainous relief, the transition from summer to winter is sudden, and the transition periods, spring and autumn, are relatively short. One important difference from a typical continental climate is that air humidity is rather high. There is rainfall throughout the year, with higher rainfall in spring and autumn (spring has more rainfall than autumn). Winters are cold with lots of snow and ice, and last for several months, whereas summers are dry with high temperatures. The lowest average temperature (0 °C to -1.5 °C) is in January and the maximum average temperature (20.5 °C to 22.4 °C) is in July. According to data from 2009, in January, the average monthly temperature was -3.6 °C, mean humidity was 81%, and average monthly rainfall was 53.1 $\mathrm{L{\cdot}m^{-2}}$; in July, the average monthly temperature was 21.6 °C, mean humidity was 64%, and average monthly rainfall was 82.8 $\mathrm{L{\cdot}m^{-2}}$; the average annual temperature in 2009 was $+10.8$ °C [19].

The old flotation tailing pond was formed in the period from 1933 to 1987, during which time, the Bor flotation plant disposed of process tailing into the Bor River valley; the municipal sewage collector is located underneath (Figure 1).

Because it has an average copper content of ~0.2% [20], the old flotation tailing has been the subject of numerous studies since the termination of operations, mostly aimed at defining the possibilities for copper revalorisation. This research has confirmed that the flotation tailing represents a very viable resource for copper revalorisation [21] with achieved recoveries of ~60% on a laboratory scale. However, this waste material remains unprotected, without a precise date for the implementation of revalorisation, and as such it is still causing a lot of environmental problems. Because it has been abandoned for over 20 years, this tailings pond is the greatest source of mineral dust, and has also become the source of acid mine drainage waters containing heavy metals, which pollute nearby soil and plants, as well as surface and underground water systems. Therefore, the aim of this study was to make a modest contribution to our understanding of the hazardous impact of the abandoned flotation tailing, in its current state and condition, on the environment.

According to the proposed aim, chemical and mineralogical analyses of cores samples from eight, 20-m drilling holes were performed, followed by acidity measurements of samples taken every 1 m from all holes from the surface to the base of the tailing. The intention was to determine the influence of the chemical and mineralogical composition on the surface and deep acidity of the unprotected flotation tailing in Bor. Special attention was given to the presence of minerals that could be defined as main sources of pollution for copper, zinc and arsenic ions. The basis of this approach was that the oxidation of pyrite and the accompanying sulphides will lead to large environmental problems because the spontaneous leaching of heavy metal could continue for tens, even hundreds, of years. By determining the main sulphide minerals as sources of released heavy metals ions, one might roughly predict the period and extent of environmental pollution. In addition, the high acidity of the flotation tailing will indicate the achieved reactivity of pyrite and other sulphide minerals under current conditions.

The results of this study should determine the direction of further steps for resolving this issue and aid in determining the economic and/or ecological priorities for this waste and hazardous material.

2. Experimental procedures

2.1. *Bor flotation tailing pond characteristics*

Disposal of flotation tailing from the Bor plant began in 1933 in the Bor River valley, where dams for tailing disposal were initially constructed from earth and timber in the northern part of the brook. After construction of the municipality sewage collector in the lower part of the Bor River valley during 1940, systematic disposal of the tailing was started, using cyclone separation of the coarse particles for the construction of dams over the entire area of valley along the Bor flotation plant. Disposal of flotation tailing in the Bor River valley continued in the same manner until the end of 1987 when the final height of the dams was attained. The annual processing capacity of the Bor flotation plant together with the quantities of concentrates and tailings produced during the operational period of the flotation tailing pond are illustrated in Figure 2 [22].

At the end of tailing disposal in 1987, the whole Bor River valley was filled with flotation tailings and the terrain was roughly flattened and levelled at an approximate elevation of 356 m in the central part of Field I and 369 m in Field II of the flotation tailings pond. The depth of the tailings pond is ~20 m in Field I and 30 m in Field II. The ultimate height of the upstream dam next to the flotation plants was 372 m, while the downstream dam was completed at an elevation of 373 m. Total quantity of the discharged tailings in old Bor flotation tailing amount to 27 Mt.

The colour of the tailings, range from yellow–grey to dark grey, depending on the initial raw materials and/or various agents used. The copper content in the old flotation tailings is on average ~0.2%, gold content is between 0.3 and 0.6 $g\cdot t^{-1}$, silver content is 2.5 $g\cdot t^{-1}$ and sulphur content is 10.5% [23].

2.2. *Drilling and sampling procedure*

Drilling and sampling of Field I of the Bor flotation tailing was realised during the second half of 2007. The length of the tailing dump up to the dam in the south is 380 m with an average width of 208 m; thus the total area of Field I is ~79,000 m^2 with an average depth of ~20 m. Drilling was carried out per set of cross-sections, as shown in Figure 1.

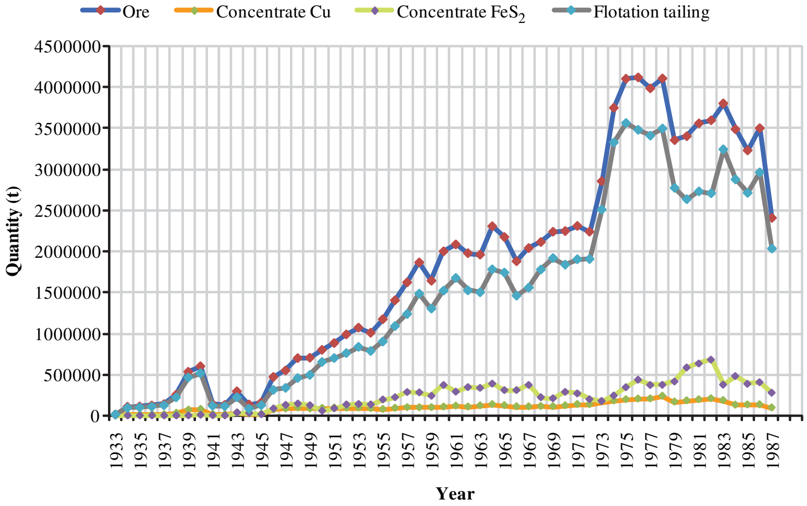

Figure 2. Processing capacity in the Bor flotation plant (1933–1987).

Altogether, eight holes were drilled (B1–B8), of which six (B1–B6) were situated along the longitudinal section (I–I') at 20-m intervals, whereas B7 and B8 were situated along the cross-section (II–II'), which crossed drilling hole B4. The distance between B7 and B4 was 20 m and the distance between B8 and B4 was increased to 40 m in order to avoid the municipal sewage collector. Drilling was performed using depth prospecting drill set S.K.B-5, by rotary drilling with a simple core tube without the introduction of flush (i.e. dry). The bore holes diameter was 101 mm.

During drilling, sampling was performed at 1 m intervals. The core samples were sorted according to the depth of the boreholes and marked as deep samples. In order to obtain representative samples, composite samples of 5 kg total mass for each drilling hole (drilling hole composites) and one composite sample of 40 kg total mass for all drilling holes (cumulative composite sample), which represents all the prospected area of the flotation tailing pond, were prepared.

2.3. *Analysis*

2.3.1. *Chemical analysis*

Quantitative chemical analyses were performed on the cumulative composite sample, all drilling hole composites and the deep samples taken at 5m intervals from the surface of all drilling holes. All chemical analyses were performed using the AES method and an atomic emission spectrometer with induced coupled plasma (ICPAES). The tailing samples were first homogenised using a standard mixing procedure and subsequently, smaller samples of mass 20 g were taken using the 'chess board' method. These smaller samples were again homogenised and 0.5g samples were then taken for the respective chemical analyses. The samples for chemical analysis were dissolved in 10 mL *aqua regia* ($HCl:HNO_3 = 3:1$). The dissolved samples were transferred to 25 mL volumetric flasks and made up to the mark with redistilled water. The prepared solutions were introduced into the induced coupled plasma flame ($T = 7000K$) of ICP using a peristaltic pump, where atomisation and ionisation of elements were realised. Finally, the concentrations of the elements were determined through the CCD detector of ICP. The percentage concentrations of the elements were calculated based on the registered concentrations and the mass of the used samples. Before the beginning of the research, testing for the validation of results from analysing solid and liquid tailing samples was performed. Owing to precision and accuracy of chemical

Table 1. Precision and accuracy of data with uncertainty of measurement.

Element	Sample state	Linear range ($mg \cdot L^{-1}$)	Detection limit ($mg \cdot L^{-1}$)	Precision and accuracy (%) Min recovery	Max recovery	Average value	Uncertainty of measurement on 95% confidence (%)
Copper	solid	0–5	0.07	96	110	103	7.50
	liquid	0–5	0.08	97	106	101	5.00
Iron	solid	0–5	0.3	98	105	101	6.82
	liquid	0–5	0.4	85	115	100	4.33
Zinc	solid	0–1	0.015	94	105	99	5.90
	liquid	0–1	0.02	81	116	98	5.06
Lead	solid	2–8	1.81	98	101	99	6.41
	liquid	2–8	1.90	81	119	100	5.12
Arsenic	solid	0–20	0.17	88	105	97	5.16
	liquid	0–20	0.18	85	115	100	5.00
Manganese	solid	1–3	0.81	95	107	101	7.30
	liquid	0.5–1	0.91	97	115	106	4.68

analyses and uncertainty of applied measurement techniques determination, achieved results were statistically arranged. Values are presented in Table 1.

2.3.2. *Mineralogical analysis*

Qualitative and quantitative mineralogical analysis of each drilling hole composite was performed using prepared mine briquette samples in acrylic glass. The qualitative mineralogical analysis, which included identification of including ore and gangue minerals, was performed using a polarisation microscope (JENAPOL-U, Carl Zeiss-Jena) under reflected light in air. The quantitative mineralogical analysis was performed using the parallel profiles method at a distance of 1 mm. Aggregate surfaces were determined using the software package OZARIA v. 2.5 and the Pinnacle System for microphotography. Further surface correction was realised via the specific density of the minerals (automatically) and through chemical analysis of a sample on a reference elements. All corrections were performed using KVAMAS v. 3.0 software.

2.3.3. *Tailing acidity determination*

The active acidity of the flotation tailing was measured in samples taken every 1 m from the surface of the tailing pond to the ultimate depth of all drilling holes. A suspension for measuring the acidity was prepared by mixing 10 g of a flotation tailing sample and 10 mL of distilled water for 25 min at room temperature. Subsequently, the suspension was left standing for 5 min without mixing to allow the solids to settle. The active acidity was measured for 30 s after exactly 30 min from the beginning of mixing using an INOLAB 720 – WTW Series pH meter. These pH values were marked as pH_{H_2O}. The pH values of a suspension of the tailing in 1 M KCl were also measured. The procedure was the same as for the measurements of pH_{H_2O} except that a 1 M KCl solution was used instead of distilled water. These pH values were marked as pH_{KCl}.

3. Results and discussion

3.1. *Particle size distribution*

The particle size distribution was determined for only the cumulative composite sample from all drilling holes. This method was used because flotation tailing represents a material with a very

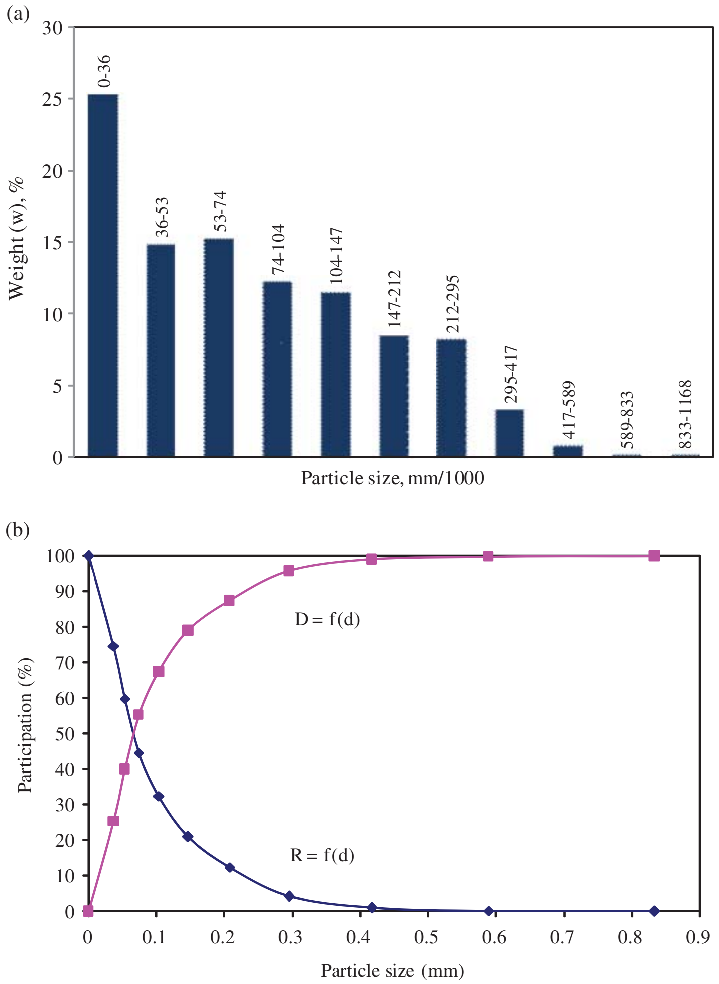

Figure 3. Particle-size distribution of the cumulative composite sample of the flotation tailing. (a). Particle-size distribution. (b) Grain-size distribution curves.

uniform particle size distribution, due to the standard requirements for the liberation of sulphide copper minerals in the flotation processes. The results of the determination are given in Figure 3.

As can be seen from Figure 3, the flotation tailing consisted mostly of very fine particles; >55% of the particles were <0.074 mm. Knowing that the reactivity of sulphide minerals increases with decreasing particle size [24,25], the real predisposition of flotation tailing for higher acidity and AMD generation could be accentuated.

3.2. *Chemical composition*

Quantitative chemical analyses were performed on the cumulative composite sample and the obtained results are given in Table 2.

The objective of comparison of the detected concentrations of the elements with the maximum allowable content (MAC) values for soils and waters (Table 2) was to obtain indications of the elements which, under acidic conditions, might release ions that would later give rise to toxic concentrations in the AMDs [26,27]. MAC are limits defined by state regulations to provide a

Table 2. Chemical composition of the cumulative composite sample.

Element	Unit	MAC*	Flotation tailing
Copper	mg·kg^{-1}	100	3000
Zinc	mg·kg^{-1}	30	250
Arsenic	mg·kg^{-1}	25	130
Lead	mg·kg^{-1}	100	50
Iron	mg·kg^{-1}	–	83,000
Mercury	mg·kg^{-1}	2	0.7
Nickel	mg·kg^{-1}	50	10

Note: *MAC, Maximum allowable content.

Table 3. Chemical composition of the drilling holes composites.

		Drilling hole composite							
Element	Unit	B1	B2	B3	B4	B5	B6	B7	B8
Copper	mg·kg^{-1}	3100	3100	3200	3100	2900	2400	2400	3000
Zinc	mg·kg^{-1}	100	390	390	250	150	120	180	150
Arsenic	mg·kg^{-1}	150	160	170	160	160	130	120	160
Iron	mg·kg^{-1}	83800	79200	80500	87300	84400	78200	80100	75400
Lead	mg·kg^{-1}	60	40	40	30	30	30	30	30

legal framework for the protection of water and soil from pollution by dangerous and harmful substances. The values in Table 2 show the times increase in the concentrations of detected dangerous elements in the tailing in comparison with MAC. Element concentrations values above the MAC and iron concentrations in each of the drilling hole composites and in the 5 m interval deep samples from the surface of all drilling holes are given in Tables 3 and 4, respectively.

Increased concentrations of heavy metals above and/or close to the MAC values in the drilling hole composites were detected for copper, zinc and arsenic, whereas the concentrations of lead were mostly significantly below the allowed limit. Significantly increased concentrations of copper and iron were found in the deep samples from 10 m below the surface to the base of the tailing pond. Possible reasons for this copper content distribution might be the dissolution of copper in the upper layers and/or different copper contents in the flotation tailing during the disposal period. This assumption is based on the fact that the bottom layers originated long ago during a period when there was lower recovery during the flotation processes. The concentrations of zinc, arsenic and lead were very small in the surface layer and highest at a depth of 10 m, whereas at greater depth there was a slight decrease in the concentrations. Possible reasons for these content distributions might be the same as those suggested for copper. However, regarding the decreasing concentrations in the deepest layers, it is most likely that there were significant variations the Zn, As and Pb contents in the treated ore during the initial operation period. Finally, the trace concentrations found in the surface layers were probably a consequence of the dissolution processes [24,26].

3.3. *Mineralogical composition*

Using qualitative mineralogical analyses, a similar mineralogical composition was found in all composite samples from the drilling holes, including pyrite as the dominant sulphide mineral and others as follows: covellite, enargite, chalcopyrite, chalcocite, bornite, tetrahedrite, rutile, limonite, magnetite, leucocsen, sphalerite, sylvanite, arsenopyrite, molybdenite and malachite; and gangue minerals, which were mostly present as quartz, silicates and carbonates.

Table 4. Chemical composition of deep samples.

Element	Depth (m)	Deep samples							
		B1	B2	B3	B4	B5	B6	B7	B8
Copper (mg·kg^{-1})	0	22	28	33	26	35	11	65	70
	1	260	970	620	130	260	190	430	250
	5	3200	3300	2900	2500	3100	1700	2200	1800
	10	4100	5100	4100	4700	4000	3100	2700	4400
	15	3500	3300	6700	3500	4600	4100	4100	4700
	20	3700	3800	4300	3800	3800	2200	3500	2600
Zinc (mg·kg^{-1})	0	8	10	6	7	7	4	6	6
	1	16	470	160	180	120	19	110	170
	5	26	23	120	120	59	130	110	42
	10	64	550	280	240	79	110	160	260
	15	41	400	150	320	140	150	150	180
	20	27	160	100	140	170	110	190	200
Arsenic (mg·kg^{-1})	0	16	61	39	11	30	10	18	25
	1	36	78	60	12	40	20	25	29
	5	240	150	190	120	170	110	110	130
	10	190	160	140	320	180	170	150	180
	15	150	190	260	200	230	290	150	230
	20	150	190	200	190	150	110	150	130
Iron (mg·kg^{-1})	0	44,600	41,900	41,800	42,400	41,800	39,000	41,200	38,800
	1	45,100	39,800	40,400	39,200	42,500	41,800	42,800	39,200
	5	72,300	71,200	73,200	74,500	74,500	72,800	74,100	71,100
	10	83,100	80,200	82,300	85,800	84,000	81,500	80,900	79,800
	15	139,200	138,500	140,100	145,100	143,800	141,100	143,200	132,600
	20	140,200	141,100	142,000	142,100	139,800	141,100	140,200	139,800
Lead (mg·kg^{-1})	0	ND	ND	93	ND	ND	ND	ND	20
	1	60	90	110	50	60	40	0	30
	5	80	80	80	70	80	50	40	40
	10	230	130	80	100	60	80	60	60
	15	60	100	110	90	70	50	60	70
	20	70	80	100	100	80	40	50	50

Note: ND, Not determined.

The sulphide mineralisation content in the drilling holes composites fluctuated from 17.8% to 25.7%, with an average value for all samples of 22.2%. Liberation of sulphide minerals varied from 84% to 97%, with an average value for all samples of 89% (Figure 4). The average oxide and gangue mineral contents were 0.8% and 77%, respectively.

The structural characteristics of pyrite and aggregates of copper minerals are illustrated in Figures 5 and 6.

The calculated average participation of covellite, chalcopyrite and enargite is illustrated in Figure 7.

Covellite appeared mostly as impregnations, simple and complex intergrowths (please see Figure S1 (available online only) for current present sulphide minerals). Chalcopyrite was detected to a lesser degree as free grains, but was mostly in the shape of impregnations and accretes, whereas enargite was only found as complex accretes.

That pyrite was the dominant sulphide mineral and was significantly present as free grains, 90.9% (Figure 5), indicates the huge predisposition for pyrite to react in the presence of water and oxygen [5,7,10], resulting in increased acidity of the tailing and the production of iron(III). Furthermore, iron(III) is a strong oxidant for boosting the release of other heavy metal ions from sulphide minerals into solution by the acid medium [11,12,14,28]. Therefore, mobilisation and the release of copper ions into acidic solutions could be expected, mostly from covellite and enargite,

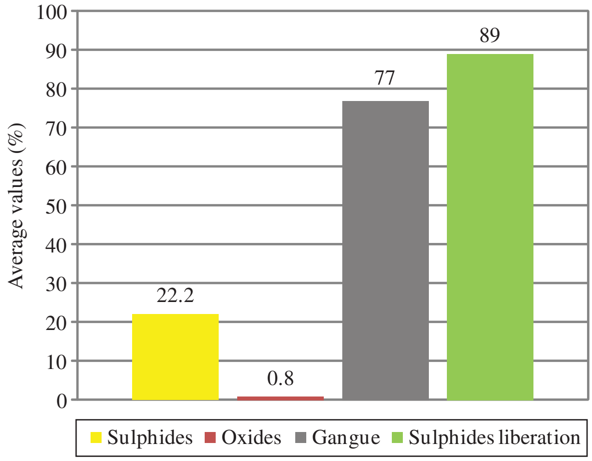

Figure 4. Content of sulphide, oxide and gangue minerals (average values).

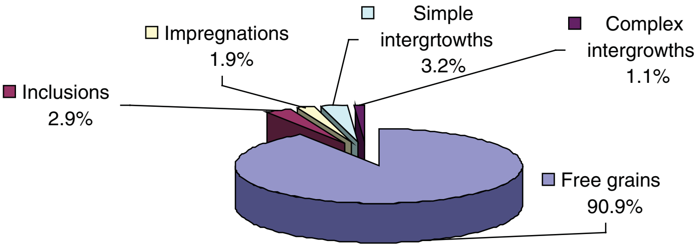

Figure 5. Structural characteristics of the pyrite aggregates (average values).

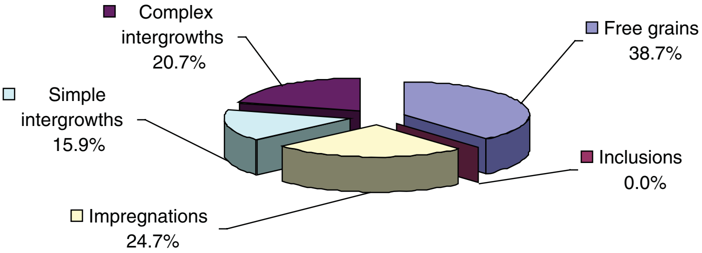

Figure 6. Structural characteristics of the aggregates of copper minerals (average values).

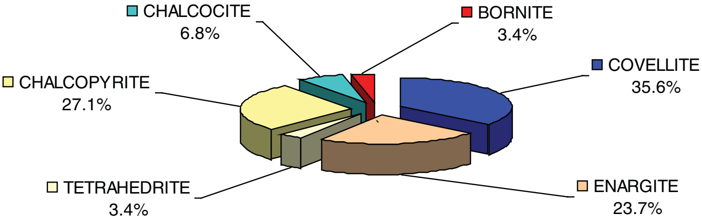

Figure 7. Copper minerals participation (average values).

Table 5. Acidity of the flotation tailing along the depth of the tailing pond.

Depth	Flotation tailing acidity by drilling holes															
	B1		B2		B3		B4		B5		B6		B7		B8	
(m)	H_2O*	KCl**	H_2O	KCl	H_2O	KCl	H_2O	KCl	H_2O	KCl	H_2O	KCl	H_2O	KCl	H_2O	KCl
1	3.29	3.38	2.81	2.72	2.27	2.25	2.95	3.15	3.00	2.96	2.61	2.57	3.00	2.88	2.68	2.66
2	3.61	3.71	2.58	2.59	2.24	2.27	2.74	2.79	2.89	2.95	2.56	2.50	2.78	2.65	2.75	2.71
3	2.70	2.63	2.94	2.89	2.27	2.31	3.04	3.14	3.31	3.53	2.90	2.83	2.89	2.76	2.60	2.57
4	2.97	2.92	3.78	3.81	2.76	2.61	3.96	4.10	3.85	3.97	3.48	3.64	3.80	3.93	2.74	2.65
5	3.62	3.64	3.55	3.57	3.53	3.64	3.89	4.07	4.09	4.22	3.64	3.76	3.80	3.93	2.81	2.66
6	3.71	3.80	3.22	3.20	3.75	3.85	3.68	3.84	3.99	4.04	3.83	3.95	3.87	3.87	2.94	2.87
7	3.62	3.65	3.23	3.20	3.66	3.71	3.47	3.70	3.84	3.95	3.69	3.79	3.79	3.84	3.53	3.73
8	3.42	3.37	3.69	3.75	3.83	3.92	3.50	3.78	3.68	3.79	3.12	3.16	2.95	2.92	3.72	3.88
9	3.91	4.01	3.19	3.19	3.76	3.84	3.21	3.38	3.42	3.55	2.96	3.00	3.65	3.75	3.68	3.78
10	3.74	3.86	3.46	3.45	3.53	3.56	3.28	3.44	3.41	3.55	3.14	3.33	3.29	3.37	3.80	3.91
11	3.62	3.71	3.35	3.41	3.76	3.83	3.53	3.65	3.51	3.62	3.56	3.66	3.72	3.66	3.78	3.91
12	4.06	3.93	3.41	3.48	3.46	3.54	3.67	3.78	3.56	3.64	3.57	3.76	3.50	3.54	3.77	3.87
13	3.69	3.60	3.58	3.65	2.68	2.66	3.01	3.15	3.47	3.56	3.55	3.71	3.28	3.34	3.75	3.87
14	3.42	3.43	3.52	3.57	3.66	3.78	3.31	3.37	2.87	2.88	3.50	3.65	3.54	3.68	3.71	3.85
15	3.00	3.00	3.00	3.03	3.86	3.92	2.85	2.80	3.05	3.02	3.32	3.48	3.62	3.78	3.80	3.92
16	2.96	2.94	2.87	2.82	3.80	3.93	3.12	3.14	3.04	3.17	3.61	3.63	3.42	3.43	3.90	3.90
17	2.93	2.85	2.93	2.94	3.55	3.74	3.08	3.19	3.10	3.24	3.47	3.58	3.50	3.53	3.92	3.91
18	3.47	3.57	3.34	3.43	3.35	3.50	3.01	3.12	3.07	3.22	3.63	3.71	2.81	2.75	3.65	3.71
19	2.93	2.87	3.14	3.21	2.96	3.10	2.78	2.79	2.83	2.86	3.33	3.39	2.80	2.76	2.85	2.78
20	2.89	2.73	2.85	2.86	2.86	2.93	2.72	2.70	2.81	2.84	3.10	3.17	2.76	2.70	2.88	2.83

Notes: *Acidity measured with distilled water (pH H_2O); **Acidity measured with 1M KCl solution (pH KCl).

which are often closely intergrown with pyrite. Moreover, the release of copper ions could be expected and from chalcopyrite, but to a lesser degree owing to its more complex dissolution characteristics [29]. The main minerals of zinc and arsenic detected were sphalerite, enargite and arsenopyrite with trace concentrations of luzonite. Because sphalerite, enargite and arsenopyrite carry the majority of the Zn and As concentrations, they also represent the main sources for further mobilisation and release of Zn and As ions into solution under acidic conditions.

3.4. *Flotation tailing acidity*

Measurements of the flotation tailing showed increased acidity along the depth of the tailing pond with pH values varying between 2.25 and 4.22 (Table 5), which is indicative of the high reactivity achieved by the pyrite.

The results presented in Table 5 also show that the pH_{H_2O} values did not have a constant trend along the tailing pond depth, but increased erratically and then decreased. There are a few factors that have an effect on the considered phenomenon. First, there is variability in the amount available atmospheric oxygen, which enters into the solutions by dissolution and diffusion, and represents the main oxidising agent for pyrite oxidation and H^+ ion generation. Second, during the disposal period, the flotation tailing was a highly alkaline waste material, with a pH value in the range 10–12, owing to the requirements for copper concentration, which determines the quantity of H^+ ions required for neutralisation and transition into the acid range. Hence, it follows that a higher alkalinity tailing will have higher pH values in comparison with a tailing that had a lower alkalinity during the disposal period. The third factor is probably the variable distribution of the main sulphide mineral pyrite along the tailing depth.

Similar observations were registered for the pH_{KCl} values, which followed same trend as that observed for pH_{H_2O}. The differences between pH_{H_2O} and pH_{KCl} along the depth of all drilling holes were generally small. However, variations in the pH_{H_2O} to pH_{KCl} ratio were found.

In some cases, the measured pH_{KCl} values were higher than the measured pH_{H_2O} values and in some cases lower. In the first case, in addition to the above-mentioned factors that influence the inequality of the acidity along the depth of the tailing pond, larger replacements of OH^- ions adsorbed on the tailing minerals with Cl^- ions probably occurred. This might induce decreases in the concentration of H^+ ions due to the neutralisation process. In the second case, desorption of Fe^{3+} and Al^{3+} ions from the surface of tailing minerals caused by K^+ ions occurred, which resulted in their hydrolysis ($Fe^{3+} + H_2O = Fe(OH)^{2+} + H^+$; $Al^{3+} + H_2O = Al(OH)^{2+} + H^+$). Consequentially the pH_{KCl} value decreased relative to pH_{H_2O}. The decrease in pH_{KCl} might also be the result of the desorption of other cations and their subsequent hydrolysis. Pyrite oxidation and dissolution of the aluminates present might be the origin of the Fe^{3+} and Al^{3+} ions, whereas dissolution of other minerals present, such as CuS, Cu_2S, ZnS and $CuFeS_2$, might be the origin of Cu^{2+}, Zn^{2+}, Fe^{2+} and other ions. Taking into account the very low values of pH_{H_2O} and pH_{KCl}, an increased mobility of the heavy metal ions could be expected, which could cause serious pollution by toxic ions by their transfer into the surrounding soil and underground water system.

Based on the chemical and mineralogical characterisation, copper and iron ions are present at the highest concentrations, causing serious pollution. But, the tailing also contained a certain amount of arsenic from enargite and arsenopyrite, which could be mobilised and released, causing heavy contamination of the environment.

Finally, it should be emphasised that further potential activity related to flotation tailing should be observed from two aspects and in accordance with basic sustainable development principles [30]. The first is the economic aspect, because of the confirmed potential of the flotation tailing for copper revalorisation [21]. Taking into account the new RTB Bor Copper Smelter Modernisation/Reconstruction Project [31], possible copper revalorisation could be considered by tailing treatment through provided hydrometallurgical system for copper smelter wastewaters. The second, but very important aspect, is ecological, in that tailing retreatment means a reduction in uncontrolled environmental contamination by the toxic ions released from the tailing. The significance of the ecological aspect is based on fact that abandoned tailings represent one of the main AMD sources in RTB Bor, especially owing to determined high permeability. However, in cases where tailing is not so permeable, possible stability problems could be expected due to the accumulation of water in the tailing pond. Accumulation of water might cause leakage of solid material from the tailing pond and/or dam instability. Therefore, from an ecology point of view, one solution might be to cover the tailing with watertight layer together with remediation activities to prevent AMD origination and maintain tailing pond stability. Choosing a further route and sequence of activities to solve ecological problems in an observed location should be the result of complex consideration with special attention paid to the RTB Bor development strategy and the environmental impact on the wider area.

4. Conclusions

Based on the results from this study, the following conclusions could be drawn.

- The flotation tailing represents very fine grained waste material with 55.3% of the particles <0.074 mm, which is a propitiatory circumstance for increased sulphide reactivity.
- Copper, zinc and arsenic were present in significantly high concentrations in the cumulative composite sample, 3000, 250 and 130 $mg \cdot kg^{-1}$, respectively.
- The highest concentrations of copper, zinc and arsenic were determined at a depth of 10 m from the surface. The highest concentrations of copper (6700 $mg \cdot kg^{-1}$; B3), zinc (550 $mg \cdot kg^{-1}$; B2) and arsenic (290 $mg \cdot kg^{-1}$; B6) were determined in the layers at depths of 15, 10 and 15 m, respectively, from the surface of the tailing.

- The dominant sulphide mineral was pyrite with a total mass participation of 21.57%, whereas gangue minerals, represented by quartz, silicates and carbonates, had cumulative participation of 77%. Other metal sulphides and oxides had a cumulative mass participation of 1.43%, of which 0.8% was oxides and 0.63% sulphides.
- The liberation of sulphide minerals was 89%, whereas the separate liberation of pyrite was 90.9%, which represents a large reactivity capacity in the presence of water and atmospheric oxygen.
- The average liberation of copper minerals was 38.7%.
- The main copper minerals present were covellite, chalcopyrite, enargite, chalcocite, bornite and tetrahedrite. Based on the mass participation of minerals and their dissolution characteristics, the main sources for the release of copper ions and of environmental pollution are covellite, enargite and chalcocite.
- Main sources for pollution by arsenic ions are enargite and arsenopyrite; sphalerite is the only source of zinc ions.
- The acidity of the flotation tailing was very high, with pH values between 2.25 and 4.22, with variations along the depth of the tailing pond.
- The differences between the pH_{H_2O} and pH_{KCl} values along the depth of the drilling holes were very small, indicating that the flotation tailing had achieved a very high reactivity of pyrite and other sulphide minerals.
- The flotation tailing represents a permeable waste material owing to its highly increased acidity from the surface down to the base of the tailing pond. This, combined with the increased concentrations and liberation of heavy metals, indicates ideal conditions for the origin of long-term acid mine drainage.

References

[1] M. Benzaazoua and M. Kongolo, *Physico-chemical properties of tailing slurries during environmental desulphurization by froth flotation*, Int. J. Miner. Process. 69 (2003), pp. 221–234.

[2] N.H. de Leeuw, S.C. Parker, H.M. Sithole, and P.E. Ngoepe, *Modeling the surface structure and reactivity of pyrite: Introduction a potential model for FeS_2*, J. Phys. Chem. B 104 (2000), pp. 7969–7976.

[3] J.D. Rimstidt and D.J. Vaughan, *Pyrite oxidation: A state of the art assessment of the reaction mechanism*, Geochim. Cosmochim. Acta 67 (2003), pp. 873–880.

[4] E.C. Todd, D.M. Sherman, and J.A. Purton, *Surface oxidation of pyrite under ambient atmospheric and aqueous (pH 2 to 10) conditions: electronic structure and mineralogy from X-ray absorption spectroscopy*, Geochim. Cosmochim. Acta 67 (2003), pp. 881–893.

[5] M.J. Borda, D.R. Strongin, and M.A. Schoonen, *A vibrational spectroscopic study of the oxidation of pyrite by molecular oxygen*, Geochim. Cosmochim. Acta 68 (2004), pp. 1807–1813.

[6] C.R. Usher, C.W. Paul, J. Narayasamy, J.D. Kubicki, D.L. Sparks, D.L. Strongin, and M.A.A. Schoonen, *Mechanistics aspects of pyrite oxidation in an oxidizing gaseous environment: an* in situ *HA TR–IR isotpe study*, Environ. Sci. Technol. 39 (2005), pp. 7576–7584.

[7] P.C. Singer and W. Stumm, *Acidic mine drainage: the rate determining step*, Science 167 (1970), pp. 1121–1123.

[8] S.L. Balistrieri, S.E. Box, A.A. Bookstrom, and M. Ikramuddin, *Assessing the influence of reacting pyrite and carbonate minerals on the geochemistry of drainage in the Coeur d'Alene Mining District*, Environ. Sci. Technol. 33 (1999), pp. 3347–3353.

[9] M. Simón, I. Ortiz, I. Garcia, E. Fernández, J. Fernández, C. Dorronsoro, and J. Aguilar, *Pollution of soils by the toxic spill of a pyrite mine (Aznalcollar, Spain)*, Sci. Total Environ. 242 (1999), pp. 105–115.

[10] G. Kamei and H. Ohmoto, *The kinetics of reaction between pyrite and O_2-bearing water revealed from* in-situ *monitoring of DO, Eh and pH in a closed system*, Geochim. Cosmochim. Acta 64 (1999), pp. 2585–2601.

[11] M. Gleisner and R.B. Herbert Jr, *Sulfide mineral oxidation in freshly processed tailings: batch experiments*, J. Geochem. Expl. 76 (2002), pp. 139–153.

[12] B.J. Baker and J.F. Banfield, *Microbial communities in acid mine drainage*, FEMS Microbiol. Ecol. 44 (2003), pp. 139–152.

[13] S. Andrade, J. Moffett, and J.A. Correa, *Distribution of dissolved species and suspended particulate copper in an intertidal acosystem affected by copper mine tailings in Northern Chile*, Mar. Chem. 101 (2006), pp. 203–212.

[14] L. Stjernaman Forsberg and S. Ledin, *Effect of sewage sludge on pH and plant availability of metals in oxidising sulphide mine tailings*, Sci. Total Environ. 358 (2006), pp. 21–35.

[15] B. Jovanović and M. Đorđević, *100 years of Bor mining*, Megatrend University, Beograd, 2005 (in Serbian).

[16] V. Dragišić, *The characteristics of mine waters in copper depozit of Bor (east Serbia), Yugoslavia*, Int. J. Mine Water, special ed. Vol. 1, SPGZLIGGG and INWA, Portschach, Austria, 1991, pp. 31–38.

[17] V. Dragišić, *Hydrogeological characteristics of Timok eruptive area volcanic rocks*, Proceedings of the VII Yugoslav Hydrogeology Congress, Novi Sad, Vol. 1, 1982, p. 253 (in Serbian).

[18] M. Korać and Ž. Kamberović, *Characterization of wastewater streams from Bor site*, Metalurgija J. Metall. 13 (2007), pp. 41–51.

[19] N. Milošević, *Annual meteorological report for Bor municipality*, Mining and Metallurgy Institute, Bor, 2010 (in Serbian).

[20] Z.O. Stevanović, *Kinetics of copper and gold leaching from the flotation tailings*, M.Sc. Thesis, University of Belgrade, 2001.

[21] M.M. Antonijević, M.D. Dimitrijević, Z.O. Stevanović, S.M. Šerbula and G.D. Bogdanović, *Investigation of the possibility of copper recovery from flotation tailings by acid leaching*, J. Hazard Mater. 158 (2008), pp. 23–34.

[22] Z. Mitrović and R. Jovanović, *100 years of Bor mining – 75 years of basin flotation plants*, Megatrend University, Beograd, 2007 (in Serbian).

[23] O. Hisamitsu, *Case study, setting the course for reconstructing the mining industry base*, Master Plan for Promotion of Mining Industry in Republic of Serbia Workshop, Japan International Cooperation Agency, Economic Development Department, Belgrade, 2007.

[24] G.G. Fennemore, W. Chad Neller, and A. Davis, *Modeling pyrite oxidation in an arid environment*, Environ. Sci. Technol. 32 (1998), pp. 2680–2687.

[25] H.K. Hansen, J.B. Yianatos, and L.M. Ottosen, *Speciation and leachability of copper in mine tailings from porphyry copper mining: influence of particle size*, Chemosphere 60 (2005), pp. 1497–1503.

[26] G. Parker and A. Robertson, *Acid drainage. A critical review of acid generation from sulfide oxidation. Processes, treatment and control*, Australian Minerals and Energy Environment Foundation, Melbourne, Australia, Occasional Paper 11, 1999.

[27] R. Pérez-López, J.M. Nieto, and G. Ruiz de Almodóvar, *Immobilization of toxic elements in mine residues derived from mining activities in the Iberian Pyrite Belt (SW Spain): laboratory experiments*, Appl. Geochem. 22 (2007), pp. 1919–1935.

[28] R.M. Balderama, *Tailings reprocessing as source of acid rock drainage*, Proceedings of the XIX International Mineral Processing Congress, Society for Mining, Metallurgy & Exploration (SME), Englewood, USA, Vol. 4, 1995, p. 115.

[29] M.M. Antonijević and G.D. Bogdanović, *Investigation of the leaching of chalcopyritic ore in acidic solutions*, Hydrometallurgy 73 (2004), pp. 245–256.

[30] Ž. J. Kamberović, *Cleaner metallurgical industry in Serbia: a road to sustainable development*, Chem. Ind. Chem. Eng. Q. 15 (1) (2009), pp. 1–4.

[31] EIA Study, *New Smelter and Sulphuric Acid Plant Project*, Vols 1 & 2, TMF, Belgrade, Serbia, 2010, available at http://www.rtb.rs/documents.