Mine Waste Water Management in the Bor Municipality in Order to Protect the Bor River Water

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http://dx.doi.org/10.5772/51902

1. Introduction

The fact is generally known that all human societies depend on the availability of natural resources (coal, iron, nonferrous metals, precious metals, industrial minerals, etc.) and possibility of their use [1]. One of three main conclusions of The World Summit on Sustainable Development, held in Johannesburg from 08/26/2002 - 4/9/2002, was that the concept of sustainable development underlines that long term efficient development, both for developed and developing countries, has to be based on three favorite topics: environmental protection, economic development and social cohesion, both on national and global levels.

The used minerals to obtain different products are very important for everyday life. Also, they are raw materials for various industries, including ceramics, construction, cosmetics, detergents, drugs, electronics, glass, metal, paint, paper and plastics. Mining and mineral processing has played a vital role in the history and economy of the following Western Balkan countries, comprising Albania, Bosnia and Herzegovina, the Former Yugoslav Republic of Macedonia, Kosovo (Territory under the Interim UN Administration), Montenegro and Serbia. Mining the polymetallic ores, jointly with the metal extraction process, is one of the most powerful industrial sectors. In the period until early 1990, this area was the main European source of copper, lead and zinc but, with disintegration the Yugoslav common market, led to worsening the economic conditions in the region, and after this period came to a sharp fall in industrial production, closing the mines. In a short period, the pollution was reduced as the result of active mining, but at the same time the conditions were created for continuation of pollution as the result of unclear and incomplete defined legal procedures that did not precisely establish the environmental responsibility in leaving or privatization the mining and mining-metallurgical plants [1].

Very extensive activities, both by the open pit and underground mining, are the essential characteristics of mining activities. These activities in conjunction with metallurgical activities further continue to cause a serious negative impact on the environment generating large amounts of solid waste and hazardous substances, air pollution, negative impacts on the land use and biodiversity, pollution and water availability. Noise and vibrations, the use of energy sources, visual effects are also negative consequences of mining and metallurgical activities. In addition to the active sites, thousands of "old" or "depleted" sites are scattered in the region. Reduction the risk of accident situations and prevention the environmental pollution, with the problems that occur with unresolved issues of ownership of the same locations in such places, is technically and economically very difficult.

Problems of mining sites as a part of industrial hot spots on the Balkan Peninsula are the subject and topic of the Project carried out by the UNDP-led Western Balkans Environment Programme with the support of the Dutch Government and others. Large amounts of solid and liquid waste contain harmful and toxic substances such as cyanides, heavy metals and other harmful and dangerous substances, which have a negative impact on the eco and biosystems [2, 3]. Cyanide discharge into the Baia Mare River in Romania is the result of incidences the failure of tailing dams at the Baia Mare Gold Mine in Romania and Aznalcollar Zinc, Lead and Copper Mine in Spain that cause many years of pollution the river Rio Tinto in Spain. In general, the environmental impacts of metal mining are likely to be greater than for other minerals, due to the often used toxic chemicals in the separation of minerals [1,2,4].

Copper is one of the essential materials to man since the time of pre-history. The fact that one of the eras of human history called the "Bronze" age and the name comes from copper alloy - bronze. It has found its very wide use thanks to good physical-chemical properties (fatigue resistance, strength, and excellent electrical and thermal conductivity, corrosion resistance). It remains one of the most used and reused of all metals. The demand for copper is due to its good strength and fatigue resistance, excellent electrical and thermal conductivities, outstanding resistance to corrosion, and ease of fabrication. Copper offers the moderate levels of density, elastic modulus and low melting temperature. It is used in the electrical cables and wires, switches, plumbing, heating, roofing and building construction, chemical and pharmaceutical machinery. It is also used in the alloys such as brass and bronze, alloy castings, and electroplated protective coating in the undercoats of nickel, chromium, and zinc.

According to data about the world copper mine production expressed in million metric tons of Cu content for the first years of twenty first century [5], it is clear that there is an almost steady increase of world copper mine production from 12.8 to 14.9 million tones of Cu content in the period from the end of twentieth century till nowadays. The copper ore deposits in Europe are limited and found in Poland, Serbia, Montenegro, Portugal, Bulgaria, Sweden and Finland [6].

http://dx.doi.org/10.5772/51902

The first mining operations in the Republic Serbia, related to the exploitation of copper ore in Bor, began in the early 20th century, more precisely in 1903. Exploitation of copper sulfide ores is carried out both by underground mining and open pit mining. Further course of ore processing requires a complex treatment in which the low-grade ore is enriched in the flotation concentration process in order to obtain the copper concentrate. This operation is used for material preparation for the pyrometallurgical process to obtain the anode copper. The final stage in the process of cathode copper production, purity minimum 99.95 wt. % Cu, is the process of electrolytic refining the anode copper.

In the period until the 1990s, the copper production from copper sulfide concentrates, which is concentrated in Serbian in the Mining and Smelting Basin (RTB) Bor, presented almost 50%, and since 2003 it accounts 20% of the total European copper production [7,8]. Due to the confirmed ore reserves of about 700 million tons, and the presence of Au and other precious metals, the mining and metallurgical activities on this site are also expected in the future. Exploitation of these ore reserves in RTB Bor and extraction of metals lead to the pollution of region by contamination of soil, air, surface and groundwater. Mining and metallurgical activities also have a negative impact on the health of population of this region.

Due to the imperfection of technological process of ore processing in the immediate vicinity of Bor, it was delayed about 250 000 t of open pit overburden and 88 000 t of flotation tailings which contain hazardous and dangerous materials such as copper, nickel, arsenic, zinc, antimony, mercury, chromium, bismuth. Such large quantities of mining waste require large areas for disposal [9]. In the area of disposal the mining waste, the acid mine water is generated acid mine drainage (AMD) from the mine wastes containing sulfide-rich minerals. Sulfide minerals, mainly pyrite (FeS_2), often present in the mine wastes, can generate AMD when they come in contact with water and O_2. The oxidation of pyrite produces H_2SO_4 reducing pH in solution. Generally, the pH drops to values below 4, which causes toxic metals to dissolve. Low pH conditions involve the growth of acidophilic bacteria Thiobacillus ferroxidans [10]. These bacteria have the ability to oxidize aqueous Fe(II) to Fe(III) which is then the principal agent for pyrite oxidation in an aerobic or anaerobic environment. At pH <2.5, a near-steady-state cycling of Fe occurs via the oxidation of primary sulfides by Fe^{3+} and the subsequent bacterial oxidation of regenerated Fe^{2+} [11]. These reactions cannot be carried out without dissolved O_2 [12].

Waste water, generated during metallurgical treatment of copper ore, also leads to transfer of harmful and dangerous materials into local water ways. There are many new processes for treatment of these wastes and some of them using the cheap, locally available adsorbents [13,14].

The following block diagram (Figure 1) shows a simplified diagram of the production process of cathode copper with the indication of place where the waste solutions are generated.

Treatment of waste solutions, produced during the mining and metallurgical activities in the process of ore mining to the finished product – cathode copper, is the basic pre-condition for their release into local water ways.

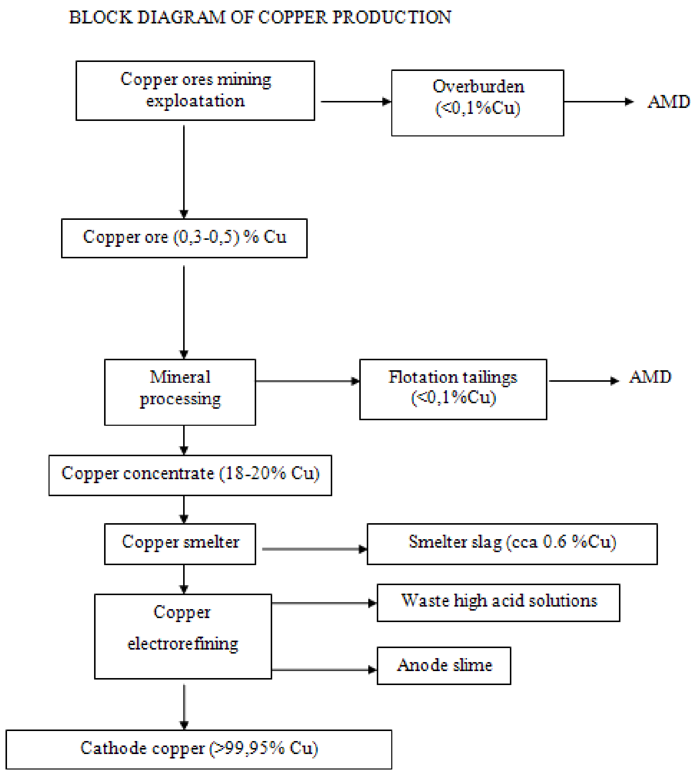

Figure 1. Block diagram of copper production in RTB Bor

Many different biological and chemical technologies exist for treatment of acid mine drainage (AMD) and smelter effluents but neutralization is the most commonly used process for the removal of metals from industrial wastewaters because it offers a most cost effective solution applicable to large operating units [15,16] until different electrochemical and hydrometallurgical processes are often used in recent years [17-21]. Lime neutralization is most applicable largely due to the high efficiency in removal of dissolved heavy metals combined with the fact that lime costs are low in comparison to alternatives. This treatment essentially consists in bringing the pH of the raw water to a point where the metals of concern are insoluble. These metals therefore precipitate to form minuscule particles. A separation of these precipitates is then required to produce a clear effluent which meets regional discharge criteria. The solid/liquid separation forms a sludge which, depending on the applied process, can contain 1 to 30 wt. % of solids. This sludge must be disposed of in an environmentally acceptable manner. Many studies have demonstrated efficiency of the precipitation in removing various metals (for example, nickel, copper, zinc, cadmium and lead) as sulphide, carbonate and phosphate instead of hydroxide. Besides yield and selectivity, a good knowledge of settling, filterability and dewatering characteristics of the metal precipitates produced is also necessary to evaluate the techno economic performance of different metal precipitation methods.

During the period from 1933 to 1970, the flotation tailing completely degraded the valley of the Bor River, White River and partly Timok. Entire length of the Bor River flow to the emp-

http://dx.doi.org/10.5772/51902

ties into the Krivelj River, about 70 hectares of coastal land was polluted by the flotation tailings. It is estimated that the flotation tailings polluted even more than 2000 ha of the most fertile coastal land of the above rivers. In addition to the physical contamination of the coastal land of the Bor River valley by thousands of tons of flotation tailings, the Bor River is constantly polluted by waste water resulting from draining through the flotation tailings and open pit overburden.

Continuous monitoring the quality and quantity of discharged waste water into the Bor River creates a basis for creating the necessary information base that will be the beginning of an integrated waste water management that, as the result of mining and metallurgical activities in RTB Bor, were discharged untreated into the Bor River. The Bor River belongs to the Timok River basin which flows into the Danube, and thus this river and its coastal region are directly polluted by a number of harmful and dangerous metals. In order to determine the impact of flotation tailings on water pollution in the Bor River, the tailings was subjected to the TCLP test as well as the leaching test.

The reason for this characterization is that the drainage water from the flotation tailing dump cannot be physically sampled because this water is drained through the cracks to the municipal sewer where it is mixed with the utility water. Possibility of metal precipitation from drainage water of the Robule Lake will be tested using 10 wt.% lime milk as well as using $FeCl_3$ and $AlCl_3$ as coagulants. Dewatering characteristics of the obtained precipitate will be tested in order to define the conditions for further treatment of the obtained residue. By proper management of mine waste water, the economic effect of copper recovery by chemical or electrochemical methods can be achieved in addition to the environmental effect.

2. Materials and methods

For the purpose of continuous monitoring the quantities and chemical composition of waste water, discharged into the Bor River, at the monthly level, the following samples were taken:

- Drainage water from the Robule Lake,
- Drainage water from the site of flotation tailings deposited on the empty space of the open pit, closed after cessation the exploitation,
- Wastewater generated during metallurgical processes, and
- Water from the Bor River which flows into the above water.

Drainage water of flotation tailing dump cannot be physically sampled because this water is drained into the municipal sewer and thus mixed with the wastewater, utility water. Flotation tailings from Mining and metallurgy copper complex in Bor are deposited on the field, size 380x260 m. Flotation tailing dump, during the earlier period, was sampled in eight drill holes in which the samples in quantities of 5 kg were taken at each 5 m in depth to the value of 20 m [22].

Three samples of 5 kg, originated from the independent drill hole B, were used as representative samples for physic-chemical characterization of determination the material acidity, definition of particle size distribution, apparent density and specific mass, mineralogical analysis as well as the leaching test and TCLP test (B/1-2 m is the sample from depth of 1-2 m from the surface; the sample marked: B/8-9 m is the sample from depth of 8-9 m from the surface and the sample marked: B/15-16 m is the sample from depth of 15-16 m from the surface). The drilling was carried out using the depth prospecting drill set S.K.B-5, by rotary drilling with a simple core tube without the introduction of flush (i.e., dry). Drill holes diameter was 101 mm.

Qualitative-quantitative mineralogical analysis was carried out on a common sample formed from these three samples. Qualitative analysis was carried out using the polarized microscope JENAPOL-U, Carl Zeiss – Jena, and the qualitative analysis was carried out using the software package OZARA v.2.5 in the Pinnacle System for microphotography.

The pH meter WTW INOLAB 720-Series was used to determine the acidity of samples. The sample for determination of acidity was prepared by mixing the flotation tailings with water using the applicable procedure within TCLP test by EPA Test Method 1311 - TCLP.

The water acidity was measured in the field during sampling on the portable waterproof pH meter ROWA as well as in the laboratory conditions after the certain lapse of time using pH meter WTW INOLAB 720-Series.

Flotation tailings is the waste material of extremely uniform structure due to the standard procedure during the flotation process in which the sulfide copper minerals are realized [22]. For these reasons, the sieve analysis of a composite sample, formed from the three samples, was carried out. The method for defining the sieve analysis content depends on the size and type of the raw material. Accordingly, the sieve analysis method was used, in range from 300 to 37 μm. TYLER, MPIF Standard 05 sieving system was used for the sieve analysis, which was confirmed for the last time in 1998 [23].

Atomic emission spectrometry with inductively coupled plasma (ICP-AAS), carried out on a device SPECTRO CIROS VISION, was used to determine Cr, Ni, As, Pb, Cd, Fe and Mn contents in water samples from the Robule Lake, the samples of drainage water from the flotation tailing dump, delayed in the area of empty open pit Bor and water from the Bor River.

In samples of waste water, generated during the metallurgical process, the elements: Cu and Fe were analyzed using the AAS - Atomic Apsorption Spectrophotometer (Perkin-Elmer - 100), the elements: As, Pb, Cd, Zn, Ni and Se using the Atomic Emission Spectrometer with inductively Coupled Plasma-ICP-AES (Spectro Ciros Vision).

For determination the contents of suspended solids, the gravimetric method was used, and the turbidimetry was used to determine the content of SO_4^{2-} ions in the analysis of all samples.

Standard EPA Test Method 1311-TCLP was used to determine the toxicity of a composite sample formed from materials of various depths of B drill hole, and the EN 12457-2 method was used for testing the waste in accordance with the relevant legislation in Serbia.

3. Results and discussion

3.1. Characterization of flotation tailings

a. Mineralogical analysis: The results of quantitative mineralogical analysis showed that pyrite is a dominant mineral and the following: 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. The results of individual samples from drill holes 1-8 [22] show that the composition is very similar for all samples. The average content of a sulphide composite sample, obtained by merging of samples B/1-2 m, B/8-9 m and B/15-16 m is 21.82 wt.%, the average oxide content – 0.454 wt.% and the average ore content does not contain the minerals – 77.8 wt.%.

b. Sieve analysis, Apparent density and Specific mass: Table 1 shows the results of sieve analysis. Since the material reactivity increases with decreasing the particle sizes, and this is about the material in which the content of fractions finer than 0.038 mm is about 40 wt.%, it can be concluded that there are real pre-conditions for generation the acid main drainage AMD [24].

Size class, mm	W (wt. %)	R – sieve oversize (wt. %)	D – sieve undersize (wt. %)
-0.300 + 0.212	1.20	1.20	100.00
-0.212 + 0.106	7.80	9.00	98.80
-0.106 + 0.075	16.80	25.80	91.00
-0.075 + 0.053	19.60	45.40	74.20
-0.053 + 0.038	15.40	60.80	54.60
-0.038	39.20	100.00	39.20

Table 1. Sieve analysis of the flotation tailing sample

The apparent density was calculated by the following formula:

$$\Delta = \frac{m_2 - m_1}{V} \left(\mathrm{kg} / \mathrm{m3}\right) \qquad (1)$$

where:

V- container capacity, m^3

m_1 - mass of container, kg

m_2 - mass of container with sample, kg

Calculated value for apparent density of the wet sample, average value is 2219 kg/m^3

Calculated value for apparent density of the dry sample, average value is 2028 kg/m^3.

The density (q) or a specific mass was defined by the quotient of mass (m) and capacity (V) of homogenuous body. In other side, the density equals the mass per 1 m^3. Density of the actual sample i.e. a specific mass was done by the glass pycnometer. The following formula was used:

$$\rho = \frac{m_2 - m_1}{(m_4 - m_1) - (m_3 - m_2)} \rho^t \left(\mathrm{kg} / \mathrm{m3}\right) \quad (2)$$

where:

m_1- empty pycnometer mass, (kg)

m_2 – pycnometer mass with sample, (kg)

m_3 – pycnometer mass with sample and water, (kg)

m_4– pycnometer mass with water, (kg)

q^t - fluid (water) density at the measuring temperature, (kg/m^3)

The density of the composite sample was 4500 kg/m^3.

c. Acidity of a sample: measurement of acidity showed that the material has higher acidity in the lower depths and the values range from 3.25 in the sample B/1-2 m to 4.35 in the sample B/15-16 m.

After disposal of tailings, the present sulfide minerals are exposed to air and atmospheric effects. As the oxidation process results of present sulfide minerals and above all pyrite, as the predominant mineral, the acid water are created. Generally, the oxidation of pyrite from mining wastes under weathering conditions, and further formation of iron (III) could be represented by the following reactions [25]:

$$FeS_2 + 3^1/_2O_2 + H_2O \rightarrow FeSO_4 + H_2SO_4 \quad (3)$$

$$2FeSO_4 + H_2SO_4 + 1/2O_2 \rightarrow Fe_2(SO_4)_3 + H_2O \quad (4)$$

Products of pyrite oxidation are sulphuric acid and iron (III) which further induce oxidation of other sulphide minerals and generation of contaminated Acid Mine Drainages (AMD) with low pH value (2.5-4.5) and increased content of SO_4 and metals ions (Cu, Zn, Pb, As, Cd, Ni i Mn), metalloids. This is confirmed that pyrite (FeS_2) serves as a precursor for the

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formation of acid mine drainage, which contains high amount of sulfate ions, metal ions and metalloids and the pH value of solution is between 2.5 and 4.5 [22].

d. Chemical characterization: chemical characterization of all three samples (Table 2) showed that the values of content the following elements were below the limits of sensitivity of the used analytical methods: Sn, Sb, Cd, Pb, Ni and Mn, while the values of Cu, Fe, As, Zn and Hg contents ranged as follows: Cu-0.67 wt.% max. and 0.097 wt.% min, Fe – 21.22 wt.% max. and 6.42 wt.% min., As – 0.025 wt.% max. and 0.0038 wt.% min., Zn – 0.034 wt.% max. and min 0.026 wt.% min. Hg-0.0001 wt.%. By comparing these values with maximum allowable values, it can be seen that the values for Cu, Zn and As are higher than maximum allowable values of Cu-100 mg/kg, Zn-30 mg/kg, and As-25 mg/kg and that it is realistic to expect that content of these elements in AMD is higher than maximum allowed [26].

Elements, content	Sample of flotation tailings, B/1-2 m	Sample of flotation tailings, B/8-9 m	Sample of flotation tailings, B/ 15-16 m
Sb, wt %	< 0.005	< 0.005	< 0.005
As, wt %	0.0038	0.015	0.025
Cu, wt %	0.097	0.40	0.67
Hg, g/t	0.2	0.30	0.40
Cd, wt %	< 0.0025	< 0.0025	< 0.0025
Mo, wt %	< 0.001	< 0.001	< 0.001
Ni, wt %	< 0.01	< 0.01	< 0.01
Pb, wt %	< 0.025	< 0.025	< 0.025
Se, wt %	< 0.0040	< 0.0040	< 0.0040
$Cr_{total,}$ wt %	< 0.001	0.012	0.014
Zn, wt %	0.026	0.033	0.034
Fe^{*}, wt %	6.42	5.53	21.22
Al^{*}, wt %	5.62	2.98	2.32
Mn^{*}, wt %	< 0.002	< 0.002	0.0033

Note: values marked with - *- are not regulated by legislation

Table 2. Chemical characterization of copper flotation tailings

e. Leaching and toxicity: Based on the results of leaching test, which was carried out according to standard procedure SRPS EN 12457-2, this waste is classified in a group of hazardous waste. Copper content is much higher than the legally permitted values. Table 3 shows the comparative values of element contents in different samples of tailings and maximum allowed values according to the current legislation

Element	Valid legislation	Sample of flotation tailings (B/1-2 m)	Sample of flotation tailings (B/8-9 m)	Sample of flotation tailings (B/15-16 m)
Limit value of concentration, mg/kg dm*	Concentration, mg/dm^3	Concentration, mg/dm^3	Concentration, mg/dm^3	
Sb	5	< 0.1	< 0.1	< 0.1
As	25	< 0.1	< 0.1	< 0.1
Cu	**100**	**1310**	**1773**	**2202**
Hg	2	< 0.001	< 0.001	< 0.001
Cd	5	< 0.1	< 0.1	< 0.1
Mo	30	< 0.1	< 0.1	< 0.1
Ni	40	/	1,6	1,3
Pb	50	/	9	38
Se	7	< 0.2	< 0.2	< 0.2
Cr_{total}	70	< 0.1	< 0.1	< 0.1
Zn	**200**	180	**237**	**284**
Fe**	/	1290	819	2405
Al**	/	536	495	382
Mn**	/	3,6	4,8	36

Where: dm* - dry mass

** - values are not regulated by the legislation

Table 3. Leaching test, carried out according to the standard procedure SRPS EN 12457-2

Values for the content of following elements: Sb, As, Hg, Cd, Mo, Se, Cr, Bi, Sn, were below the sensitivity limits of the applied chemical methods.

By comparison the obtained values and statutory value for testing the waste and leachate water from the landfills of inert, non-hazardous or hazardous waste, it can be seen that the content of Cu in all samples is far higher than the statutory values by which this waste is classified in a group of hazardous waste; that content of Ni and Pb is within maximum allowable values and that the values for Zn content are above the allowed values for samples (B/8-9 m) and sample (B/15-16 m). The obtained results are in a direct conformity with the results of chemical characterization of tailings (Table 2).

The results of EPA Test Method 1311 - TCLP (Table 4) showed that the value of Cu content of 104.4 mg/dm^3 was registered in the sample B/15-16 m almost four times higher than the allowed value according to the current legislation of the Republic of Serbia which is in

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agreement with the legislation of the European Union, which classifies this waste in a group of toxic waste.

The increased concentration of Cu in the value of 88.1 mg/dm^3 was also registered in B/8-9 m sample while the sample B/1-2 m had lower value than prescribed one. The trend of higher concentrations in samples from lower depths was also observed in other elements that move into eluent during TCLP test.

Element	Valid legislation	Sample of flotation tailings (B/1-2 m)	Sample of flotation tailings (B/8-9 m)	Sample of flotation tailings (B/15-16 m)
Limit value of concentration, mg/kg dm*	Concentration, mg/dm^3	Concentration, mg/dm^3	Concentration, mg/dm^3	
Sb	15	< 0.1	< 0.1	< 0.1
As	5	< 0.1	0.14	0.17
Cu	**25**	**5.7**	**88.1**	**104.4**
Hg	0.2	< 0.001	< 0.001	< 0.001
Cd	1	< 0.1	< 0.1	< 0.1
Mo	350	< 0.1	< 0.1	< 0.1
Ni	20	< 0.1	< 0.1	< 0.1
Pb	5	< 0.1	0.6	2.6
Se	1	< 0.2	< 0.2	< 0.2
Cr_{total}	5	< 0.1	< 0.1	< 0.1
Zn	250	8.5	11.9	13.2
Fe*	/	12.2	28.5	98.4
Al*	/	12.3	14.6	16.6
Mn*	/	0.13	0.31	1.8

Note: The marked elements* are not on the list of parameters for testing the toxic characteristics of waste such as the obtained values in TCLP test were not discussed.

Table 4. TCLP test, carried out according to the standard procedure EPA Test Method 1311

Content values of Sb, As, Cd, Hg, Mo, Ni, Pb, Sr, Cr_t in efluent were below the values of detection the applied chemical methods.

3.2. Characterization of waste water flowing into the Bor River

1. Drainage water from the Robule Lake

Water from the Robule Lake was analyzed over a period of 12 months, from June 2011ending to May 2012 (Table 5). Considering the concentration values corresponding to the surface water requirements of Class IV the applicable Rules on dangerous substances in water, it can be seen that the content of all analyzed elements is above the permissible values of the amounts (mg/dm^3): Cu - 0.1, Zn - 1.0, Cd - 0.01; Ni - 0.1, Fe - 1.0. By comparison the measured pH values and Rules of prescribed values, which range between 6.0-9.0, it is seen that it is acidic water which presents the polluter of local ecosystem (soil, water).

Robule Lake	pH value	SO_4-2 mg/dm3	Cu mg/dm^3	Mn mg/dm^3	Zn mg/dm^3	Cd mg/dm^3	Ni mg/dm^3	Fe mg/dm^3	Total suspended solids, mg/dm^3
06. 2011	4.08	4907.5	71.6	133.8	29.1	0.09	1.0	575.0	33.0
07. 2011	4.20	4604.2	70.2	122.6	26.4	0.08	0.6	526.4	28.0
08. 2011	2.86	8243.1	69.1	96.0	26.3	0.117	0.738	739.0	12.0
09. 2011	3.49	10570.6	66.9	112.4	25.6	0.11	0.75	812.0	55.0
10. 2011	3.26	7905.7	65.3	108.2	24.3	0.093	0.66	626.8	34.0
11. 2011	2.56	7620.2	53.0	104.3	24.6	0.091	0.72	720.0	32.0
12. 2011	2.70	8243.1	69.1	102.1	26.3	0.117	0.738	739.0	12.0
01. 2012	3.52	10570.6	66.9	98.3	25.6	0.11	0.75	812.0	55.0
02. 2012	3.43	10321.4	64.3	98.8	25.8	0.10	0.68	762.3	52.0
03. 2012	3.54	10518.3	63.2	101.4	26.2	0.097	0.67	581.8	57.0
04. 2012	2.70	7731.7	77.2	96.4	30.4	0.089	0.74	835.6	24.0
05. 2012	3.38	7523.9	64.7	102.3	24.4	0.087	0.67	615.6	29.0

Table 5. Drainage water from the Robule Lake

2. Drainage water of flotation tailings, stored in the area of empty open pit, closed after completion the ore mining operation – RTH

The Old Flotation Tailing Dump (fields 1, 2 and 3) was in the operation since 1933 and it was operational until 1987, after which the storage of flotation tailings from the Old Flotation Plant Bor is done in the empty area of the open pit RTH (after ending the ore mining). Large amount of stored open pit overburden presents a generator of acid drainage water (AMD) generated by the action of rainwater and groundwater (often acid rain precipitation formed at the contact of falls and SO_2 gas) in the oxide, sulphate and carbonate copper minerals, contained in the stored open pit overburden and flotation tailings. This water is characterized by slightly higher pH value than the pH value of drainage water from the Robule Lake, what can be seen comparing the shown values in Tables 5 and 6. Also, the content of elements, registered in drainage water of flotation tailings, stored in the area of empty open pit and closed after completion the ore mining operation – RTH, is lower than the content on these elements in the Robule Lake.

RTH water	pH value	SO_4-2 mg/dm3	Cu mg/dm^3	Zn mg/dm^3	Cd mg/dm^3	Ni mg/dm^3	Fe mg/dm^3	Total suspended solids, mg/dm^3
06. 2011	4.60	4366.7	18.9	11.4	0.03	0.5	155.1	111.0
07. 2011	4.86	4022.4	16.8	10.2	0.021	0.32	155.1	106.0
08. 2011	5.30	3882.9	11.0	8.65	0.044	0.227	190.1	81.0
09. 2011	5.17	3878.4	12.4	8.42	0.035	0.25	190	97.0
10. 2011	4.08	4298.2	17.9	10.8	0.032	0.48	160	88.0
11. 2011	5.97	4102.2	12.6	10.2	0.036	0.38	100.1	86.2
12. 2011	3.94	3882.9	11.0	8.65	0.044	0.227	190.1	81.0
01. 2012	3.28	3990.6	14.3	7.8	0.28	0.220	184.2	68.0
02. 2012	3.60	4008.4	16.8	7.4	0.32	0.28	162.1	56.0
03. 2012	3.37	4143.4	27.8	7.1	0.36	0.36	86.6	46.0
04. 2012	2.88	3792.1	29.2	7.7	0.024	0.31	148.2	12.0
05. 2012	3.60	3343.4	27.4	6.73	0.03	0.34	103.1	15.0

Table 6. Drainage water from flotation tailings, stored in the area of empty open pit, closed after completed the ore mining operation (RTH)

Regarding to the concentrations of Cu, Zn, Cd, Ni and Fe with the concentration values that correspond to the requirements of surface water Class IV the applicable Rules on dangerous substances in water, it can be seen that the content of all analyzed elements is above the permissible values. Measured values are not also in the range of values defined by the same Rules and the values indicate the fact that it is acid water.

3. Waste water generated in the metallurgical process

Those are composite samples that present total waste water generated in a part of metallurgical production the cathode copper that includes the following production units: electrolytic copper refining, electrolyte regeneration, production of precious metals and sulphuric acid production (Table 7).

Comparing the concentration values that correspond to the requirements of surface water Class IV the applicable Rules, it can be seen that the content of all analyzed elements is above the permissible values as follows (mg/dm^3) : Cu – 0.1; Pb – 0.1; Zn – 1.0; Cd – 0.01; Ni – 0.1; Se – 0.01; As – 0.05; Fe – 1.0. Considering the measured pH values with the Rules of prescribed values, it is seen that the values are far lower than the prescribed ones, and by comparison with the pH values for drainage water from the Robule Lake and drainage water from the site of RTH tailing dump, it is seen that the acidity of this water is the highest.

Metal. complex water	pH value	SO_4^{-2}	Cu	Pb	Zn	Cd	Ni	Se	As	Fe	Tot. susp. sol.
						mg/dm^3					g/dm^3
06. 2011	3.12	2813.1	514	4.7	457	11	36	8.7	167	3169	2.60
07. 2011	3.24	3228.1	216	5.8	43.9	<0.1	13	31	51.4	3340	2.42
08. 2011	3.62	3567.9	123	4.1	118	2.4	6.4	19.2	45	3760	4.38
09. 2011	3.42	3470.4	335.8	3.7	132	3.7	21	8.2	95	3730	2.80
10. 2011	2.40	5569.1	541	2.8	102	2.4	45	12	134	4766	4.28
11. 2011	2.02	1624.2	86.2	3.0	110.6	2.2	12.1	6.8	120.6	382.2	26.1
12. 2011	2.45	1554.2	58.5	3.1	6.02	0.055	1.53	<0.2	2.55	214.7	71.0
01. 2012	3.06	2880.2	69.2	2.8	8.4	0.080	1.26	<0.2	2.64	368.2	62.2
02. 2012	3.21	3124.6	72.4	1.86	8.8	0.090	1.20	<0.02	2.48	364.2	54.3
03. 2012	2.99	3334.0	75.8	1.50	9.2	0.091	1.15	<0.2	2.85	395.1	48.0
04. 2012	1.89	4976.7	158.2	0.18	8.1	0.033	15.2	<0.2	<0.10	247.5	24.0
05. 2012	2.95	2930.2	158.7	1.6	16.9	0.22	2.2	0.25	3.24	289.0	2.0

Table 7. Waste water from metallurgical process

4. Bor River

Under the old flotation tailing dump is a collector of urban water utilities and due to the frequent delays of the Flotation Plant in Bor, the flotation tailings from the Flotation Plant Bor was directly discharged into the town sewer and through it into the water flow of the Bor River. Thus, in the period from 1933 to 1970, the flotation tailing completely degraded the Bor River valley. The entire length of the Bor River flow to the flows into the Krivelj River, about 70 hectares of coastal was polluted with flotation tailings of the following composition (wt.%): Cu $_{tot}$.- 0.127; Cu $_{ox}$- 0.032; Al_2O_3-13.51; SiO_2=58.54; S-7.32; Fe-6.33%, also the Bela River and partly Timok. It is estimated that the tailings of similar chemical composition has contaminated over 2000 ha of the most fertile coastal land of the above rivers, which after pollution has never been used for agricultural production. View of the Bor River and the point of connection the Bor River and Krivelj River are shown in Figures 2 and 3. The Krivelj River flows into the River Danube and in that way this river and its riverside are directly polluted with harmful and dangerous materials.

Figure 2. Downstream view of the Bor River Valley, 30/04/2012

Figure 3. Point of connection the Bor River and Krivelj River, 30/04/2012

Characterization of water from the Bor River is given in the Table 8:

Bor River	pH	SO_4 -2 mg/dm3	Cu mg/dm^3	Pb mg/dm^3	Zn mg/dm^3	Cd mg/dm^3	Ni mg/dm^3	Fe mg/dm^3	Total suspended solids, g/dm^3
06. 2011	3.26	1234.0	10.9	<0.1	3.3	0.03	0.4	85.3	166.0
07. 2011	4.10	1138.0	12.8	<0.1	3.4	0.04	0.6	88.6	184.0
08. 2011	4.26	1157.5	19.2	0.830	3.35	0.031	0.420	86.8	376.0
09. 2011	5.16	998.3	9.9	0.33	2.3	<0.02	0.30	35.6	272.0
10. 2011	4.84	1111.9	14.9	<0.1	2.7	<0.02	0.50	2.3	218.0
11. 2011	5.05	110.3	27.0	0.75	3.1	<0.02	0.48	130.0	342.6
12. 2011	4.53	1157.5	19.2	0.83	3.35	0.031	0.42	86.8	376.0
01. 2012	4.60	998.3	9.9	0.33	2.3	<0.020	0.30	35.6	272.2
02. 2012	5.20	1086.2	8.7	0.24	3.0	<0.02	0.26	12.3	234.2
03. 2012	5.83	1130.0	10.2	<0.1	2.0	<0.020	0.13	2.6	256.0
04. 2012	5.99	782.7	1.5	<0.1	0.98	<0.020	0.16	1.1	219.0
05. 2012	5.67	674.2	2.25	<0.1	1.0	<0.02	0.12	3.32	196.0

Table 8. Water in Bor River

Content of some elements in the Bor River water is also higher than maximum permitted content of for water of Class IV, and the Bor River water must fall into the water with hazardous substances that may endanger the life or health of humans, fish and animals.

Waste water flow from the specified locations is measured quarterly and values are shown in Table 9, where it is seen that the lowest value was measured during the winter while the values for the fall and spring are close.

3.3. Neutralization process and dewatering characteristics of metal precipitate

The principle of lime neutralization of acid mine drainage (AMD or ARD for acid rock drainage) lies in the insolubility of heavy metals in alkaline conditions. By controlling pH to a typical set point of 9.5, metals such as iron (Fe), zinc (Zn), and copper (Cu) are precipitated. Other metals such as nickel (Ni) and cadmium (Cd) require a higher pH, in the range of 10.5 to 11 to effectively precipitate the hydroxides. The precipitates can be formed individually as minuscule particles smaller than a single micron.

Neutralization and metal precipitation process was carried out by adding 10 % lime milk in the sample from Robule Lake. The mass of lime is calculated relative to chemical composition of waste water. Compounds $FeCl_3$ and $AlCl_3$ were used as coagulants. The effect of different operating parameters on the precipitate characteristic was investigated. The precipitation process is stopped on pH = 9.88. Obtained precipitate settling, compaction and dewatering characteristics were studied too, as a part of this research.

Flow rate measured in autumn 2011		
Waste water	Month of measurement	Flow rate, m^3/h
Robule Lake	September 2011	7.20
RTH drainage	September 2011	32.4
Metallurgyical ww	September 2011	312.8
Bor river	September 2011	2106.4
Flow rate measured in winter 2011		
Waste water	Month of measurement	Flow rate, m^3/h
Robule Lake	Nov/Dec 2011	5.40
RTH drainage	Nov/Dec 2011	28.6
Metallurgical ww	Nov/Dec 2011	302.2
Bor river	Nov/Dec 2011	1620
Flow rate measured in spring 2012		
Waste water	Month of measurement	Flow rate, m^3/h
Robule Lake	April/May 2012	6.78
RTH drainage	April/May 2012	30.3
Metallurgical ww	April/May 2012	305.5
Bor river	April/May 2012	1818

Table 9. Flow rates measured in period September 2011 – May 2012

3.3.1. Precipitation process experimental procedure

Neutralization process was carried out on 50 dm^3 of real waste water from Robule Lake with the next characteristics (mg/dm^3): Cu - 71.3; Ni - 0.7; As <0.1; Fe - 788; Mn - 133.8; Zn – 31; Cr < 0.02; Pb <0.1; Cd – 0.17; SO_4^{2-} = 10047.2; Cl^- - 14.71; NO_2^- - 0.1; NO_3^- - 38.6; consumption $KMnO_4$ – 41.08; solid residue at 105 °C – 16664.0; Total suspended matters – 23.0, pH value - 2.48.

First step of the neutralization process is lime dissolution. This lime must first be hydrated and fed to the process as slurry. The hydrated lime then dissolves to increase pH. The increased pH then provides hydroxide ions which combine with the dissolved metals to produce precipitates. The following equation shows the general reaction for produce the metal precipitate [27]:

$$M^{n+} + n\,OH^- \Rightarrow M(OH)_n \quad (5)$$

The reaction (5) is characteristic for the next metal cations involved in waste water from Robule Lake: Al^{3+}; Co^{2+}; Cu^{2+}; Fe^{2+}; Fe^{3+}; Ni^{2+}; Pb^{2+}; Zn^{2+}.

Neutralization process was carried out by adding 10 % lime milk (sample 1). Mass of lime is calculated relative to chemical composition of wastewater. Compounds $FeCl_3$ *(sample 2)* and $AlCl_3$ *(sample 3)* were used as coagulants. The effect of different operating parameters on the sludge characteristic was investigated. The neutralization process is stopped on pH = 9.88.

Chemical analysis of water during the neutralisation process were performed on a laboratory portable device DR/890 Colorimeter HACH and the results for the Cu and Fe are presented in Table 10.

	pH	Cu, mg/dm^3	Fe, mg/dm^3
start	2.49	71.3	788
I st step	5.34	3.47	4.57
II nd step	7.40	0.04	< 0.1
III rd step	9.88	< 0.1	< 0.1

Table 10. Waste water characterization during the neutralization process

The complete chemical characterization of water samples after the neutralization process showed that the values of Cu, Fe, Mn, Cd, Ni, Zn were below the sensitivity of applied chemical methods

3.3.2. Dewatering characterization

The mass of sample of 5 g was transferred to a measuring cylinder of a 50 ml. The sample level was measured. After adding the volume of 30 ml distillated water, the level of suspension was measured. Then water was added to ratio solid: liquid = 1: 8. After the manual stirring, solution was left to settle and measured the time of settling. Filtration was carried out by gravitational and vacuum methods. Water volume, which can be separated by gravity, was measured in measuring cylinder using filtration of suspension with filter funnel through filter paper marked Quantitative Ashless, 100 circles 5A, 125 mm, and ash contents of filter paper 0.11 mg /circle. Protocols of experiments were the same for both methods gravitational and vacuum and in both cases of neutralization. Only difference was that, in the case of vacuum method of dewatering, the suspension was vacuum filtered through glass filter crucible, G3.

Dewatering by gravitational method

Obtained results are presented in Table 11 and it could be seen that for all samples are similar. The addition of different coagulant reagents did not give a difference in results of dewatering in different samples. Filtration times are similar too.

Obtained results show that settling of sludge comes in a short time and the content of liquid phase in samples after filtration is about 90 %.

http://dx.doi.org/10.5772/51902

Description	unit	sample1	sample2	sample3
Dry sample mass	g	5	5	5
DM water vol.	ml	40	40	40
Sample volume	ml	4.5	4.5	5
Vol.of suspen.	ml	44.5	44.5	45
Settling time	s	25	25.2	26
Filtration time	s	38	40	42
Wet sam. mass	g	9.75	9.25	9.6

Table 11. Parameters and results of dewatering analysis of sludge obtained after gravimetric filtration.

Dewatering by vacuum method

The obtained results for vacuum filtration are similar. By comparing the values for dry and wet samples it is obvious that the usage of vacuum filtration achieves better dewatering of liquid phase from sample, percentage of water in the samples is about 50 %.

Description	unit	sample1	sample2	sample3
Dry sample mass	g	5	5	5
DM water vol.	ml	40	40	40
Sample volume	ml	4.5	4.5	5
Vol.of suspen.	ml	44.5	44.5	45
Settling time	s	25	25.2	26
Time vac. filt.	s	15	15.6	15.8
Wet sam. mass	g	7.24	7.35	7.4

Table 12. Parameters and results of dewatering analysis of sludge obtained after vacuum filtration.

4. Conclusion

The results of leaching and toxicity tests of flotation tailings, i.e. the solid waste, originated as the result of mining-metallurgical activities in the area of East Serbia, showed that it is a dangerous and toxic waste. This waste is a constant source of water, soil and air pollution.

The results of chemical analyses of waste water, generated from the investigated sites, showed that water individually presents a pollution source of the Bor River.

The precipitation process of water from the Robule Lake has confirmed the effective purification of this water prior to discharge into the Bor River.

Content of some elements in the Bor River is higher than the statutory maximum allowable lead content for water of the Class IV, and that neither this water should be discharged into the local water ways. It can be said that the Bor River water must be placed into the water with dangerous substances that may endanger the life or health of humans, fish and animals.

The proposed Waste Water Management, in order to reduce the water pollution in the Bor River, cannot immediately or within a short time bring in a properly and clean condition one “dead” river and the black ecological point (or rather the river in which even the bacteria cannot survive). However, what gives a practical contribution of this work to cleaner water in the Bor River, in the coming period, is to establish a mechanism for waste water management. The implementation of waste water management creates the conditions for gradual reduction the newly-formed acid mine water, with the ultimate aim of completely control its creation in the future.

Acknowledgment

This work is financially supported by the Ministry of Science, Republic of Serbia: “The Impact of Mining Waste from RTB Bor on the Pollution of Surrounding Waterways with the Proposal of Measures and Procedures for Reduction the Harmful Effects on The Environment”, No. TR 37001.

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