MINE WATERS AND WATERS OF COPPER DEPOSIT TAILING DISPOSALS OF SERBIA AND ENVIRONMENTAL PROTECTION. HYDROGEOCHEMICAL ASPECT

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ABSTRACT

Copper ore deposits are located in eastern parts of Serbia, in the "Timocka eruptive area". Apart from copper mine Bor, established 1903. there are few more mines: Majdanpek, Veliki Krivelj and Cerova. Hydrogeochemical processes in deposits aeration zone, mining works and surrounding tailing dumps, caused forming of groundwater with high mineralization and non-complying chemical composition. These are acid sulfate waters, with high contents of Fe, Al, Cu and other elements, such as Zn and As, and their compounds. These mine groundwaters, mostly without technological processing, are discharged directly to the streams. Thus, these waters pollute surface and ground waters in alluvial and carbonated aquifers. Abandoned mines and test mine gurmys, from which mine waters with non-complying chemical properties have been discharged into surrounding streams for a many years, represent specific environmental protecting problem in this area.

INTRODUCTION

Physico-chemical and biochemical processes in the zone of aeration and directly in mining work - sulphide ore tailing disposals result in the pollution of surface and groundwaters owing to uncontrolled discharge, namely removing from mining work, mine waters or uncontrolled ore waste dumping (Kelly, 1988).

Ideal conditions for more intensive oxidation of certain sulphide minerals in mining work in the zone of aeration were made by copper deposits exploitation of eastern Serbia starting at the beginning of this century. It resulted in forming mineralized acid sulphate waters with high concentrations of total Fe (Fe^{2+}+Fe^{3+}, relate to whole paper), Al, Cu, As, Zn and other elements and their compounds.

Forming of mighty tailing disposals most often representing low percentage copper ore waste dumps follows the exploitation of copper sulphide ore. They are exposed to atmospheric influence and degradation resulting in different physico-chemical and biochemical processes, primarily those of oxidation, in which case waters are formed in their physico-chemical characteristics, identical to mine waters.

Forming of ore tailing disposal in this part of Serbia is often not followed by adequate surface and groundwater protection measures in the zone of inflow. Ore tailing disposals of scale of more then million m^3 were dumped and are still dumped in depressions, mainly representing river beds resulting in direct hydraulic connections of tailing disposals and river flow waters. In several occurrences tailing disposals are often dumped over the bottom made by water bearing rocks as pebbles, sands and limestones contaminating these aquifers.

Negative impact of mine waters and tailing disposals waters on environment is pointed out on the examples of active copper mine Bor, the abandoned mine Gornja Lipa and ore tailing disposals of the mine Veliki Krivelj (Figure 1).

PHYSICO-CHEMICAL AND BIOCHEMICAL-MICROBIOLOGICAL PROCESSES AT COPPER DEPOSITS AND ORE TAILING DISPOSALS

Complex physico-chemical and biochemical-microbiological processes occur when groundwater and free oxygen are present conditioning more intensive degradation of sulphide and petrogenic mineral deposits at the zone of copper deposit hypergenesis. The research of the late forties pointed out the influence of microorganisms in sulphide mineral oxidation, bacteria of the genus *Thiobacillus* (particularly species

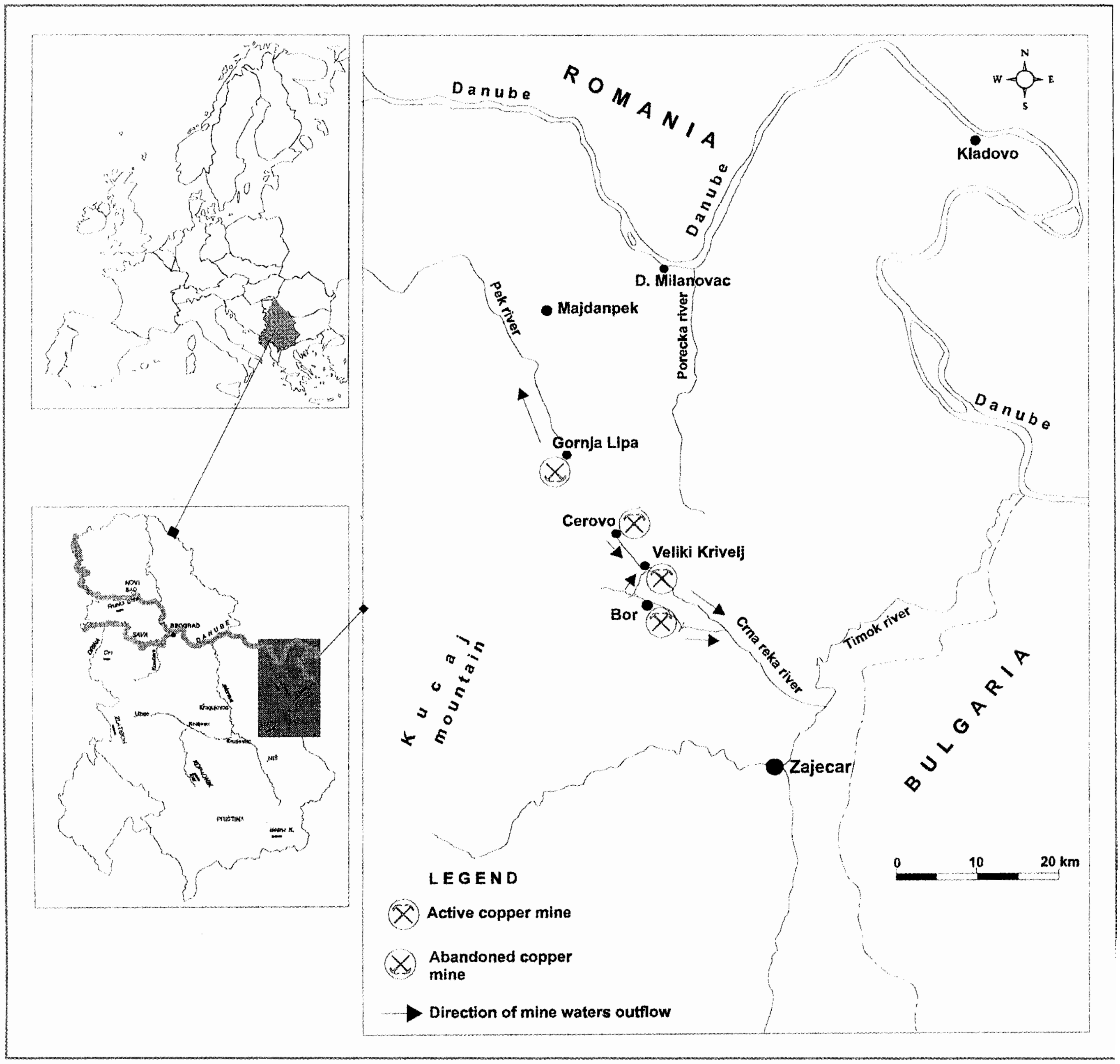


Figure 1. Physical setting of the investigating area.

Thiobacillus ferrooxidans) having the main role among them (Colmer and Hinkle, 1947).

Copper sulphides are the most common minerals present in hydrothermal copper deposits: chalco-pyrite ($CuFeS_2$), chalcocite (CuS_2), covelline (CuS), bornite (Cu_5FeS_4), enargite (Cu_3AsS_4) etc. Besides numerous sulphides, there are present minerals weakly dissolving in water, but when O_2 and CO_2 are present, they oxidize and turn into copper sulphate having high solubility in water. At the zone of oxidation copper sulphides transforms, forming secondary sulphides, oxides, hydroxides, sulphates, carbonates, arsenates, silicates and other minerals.

Pyrite (FeS_2) is a-permanent companion of these deposits. The presence of pyrite is of particular interest for forming chemical composition of copper deposit mine waters, and in general, sulphide deposits. The significance of pyrite reflects in its stability to chemical transformations conditioned by pH value of the environment. Pyrite is stable to spontaneous oxidation in water, namely effect of oxygen at pH values lower than 5.5 and reverse at the values higher than 5.5. Thus, for example, if water pH value is between 2 and 3.5, the oxidation speed is very slow and half-time of oxidation on pH = 3 amount 1000 days in conditions when only oxygen is present. This process is sped up considerably by microorganisms of *Thiobacillus* genus (species *Thiobacillus ferrooxidans* and *Thiobacillus thiooxidans*) (Fenchel and Blackburn, 1979).

Consequently, microbiological process is dominant in mine waters of pH value lower than 5, while chemical oxidation processes influenced by dissolved O_2 are more distinguished for mine waters of lower acidity. Investigations pointed out that, except by pH values, oxidation speed of pyrite is also conditioned by partial pressure of dissolved oxygen.

Chemical reactions occurring at metal oxidation process from sulphide in the presence of pyrite may be pointed out by the following equations (Brierley, 1978; Lundgren, 1980; Vrvic 1986,1991):

$FeS_2 + 3.5\ O_2 + H_2O \longrightarrow FeSO_4 + H_2SO_4$

Thiobacillus ferrooxidans

$MS \longrightarrow MSO_4$ M - bivalent metal; chemical

$2\ FeSO_4 + 0.5\ O_2 + H_2SO_4 \longrightarrow Fe_2(SO_4)_3 + H_2O$

Thiobacillus ferrooxidans

$MS + Fe_2(SO_4)_3 \longrightarrow MSO_4 + 2\ FeSO_4 + S$ chemical

$S + 1.5\ O_2 + H_2O \longrightarrow H_2SO_4$

Thiobacillus ferrooxidans and *Thiobacillus thiooxidans*

The equations point out that process of bacterial and chemical oxidation occurs in two ways:

- By direct oxidation of sulphide minerals;
- Indirectly, by iron(III) sulphate regeneration and originating of sulphur acid, by oxidation of pyrite that is a permanent companion of sulfide copper deposits. The originated sulphur acid dissolves sulphides, as well as iron(III) sulphate, which is a strong oxidant. Reduced iron(III) sulphate is again bacterially oxygenated, so the cycle is closed.

Iron(III) sulphate is a good source of sulphur acid originating as a product of hydrolysis according to summary equation.

$$3\ Fe_2(SO_4)_3 + 12\ H_2O \longrightarrow 2\ H[Fe(SO4)_2 \times 2\ Fe(OH)_3] + 5\ H_2SO_4$$

However, base iron(III) sulphates are deposited on ore mineral particles making the contact with bacteria impossible, thus slowing down the process considerably. The given equations applied to oxidation of copper and chalcopyrite ($CuFeS_2$) minerals, chalcocite (CuS_2), covelline (CuS) and enargite (Cu_3AsS_4) have the forms summary (Brierley, 1978; Lundgren, 1980):

$$2\ CuFeS_2 + 8.5\ O_2 + H_2SO_4 \longrightarrow 2\ CuSO_4 + Fe_2(SO_4)_3 + H_2O$$

$$Cu_2S + 0.5\ O_2 + H_2SO_4 \longrightarrow CuS + CuSO_4 + H_2O$$

$$CuS + 2\ O_2 \longrightarrow CuSO_4$$

$$4\ Cu_3AsS_4 + 35\ O_2 + 10\ H_2O \longrightarrow 12\ CuSO_4 + 4\ H_3AsO_4 + 4\ H_2SO_4$$

Described processes on copper mineral example are similar to other sulphides (Vrvic, 1986, 1991; Dragisic, 1992). Groundwaters with increased content of Cu, Pb, Zn, Al, As and other micro components are formed in the result of stated processes.

SURFACE AND GROUNDWATER CONTAMINATION UNDER THE IMPACT OF MINE WATERS OF ACTIVE MINES

At the moment there are four active copper mines in eastern Serbia (Bor, Veliki Krivelj, Majdanpek and Cerova). None of the mentioned mines has solved the problem of mine waters, so they are let out to the nearest streams contaminating surface and groundwaters of neighbouring aquifers.

The copper mine Bor is the oldest for copper ore exploitation dating from the beginning of 20th century. Copper ore deposit Bor has been originated by volcanic rocks and their pyroclastic equivalents, hydrothermally altered igneous rocks and sedimentary rocks. Ore bodies of massive -sulphide, -impregnation and porphyry type can be found at the deposit. Covellyne, chalcocite, enargite, bornite and chalcopyrite, among ore minerals are represented. The stated physico-chemical and microbiological processes conditioned mineralized sulphate waters formation with low pH values and increased content of particular metals (Table 1).

Mine waters from underground mining are thrown out directly into the stream of the Bor river, led near the mine to the Kriveljska river, where mine waters of Veliki Krivelj and Cerovo mines flow into. This results in excessive surface water pollution in the mentioned streams, as well as in groundwater pollution in alluvial and karst aquifers in the wide surroundings of the mentioned mines.

For example, about 9 km to the east from the mine, after joining of the Borska and Kriveljska streams, on the basis of particular parameter determination of chemical composition, in a long period the following water characteristics have been stated (Dragisic, 1992): pH: 3.7-6.5; $SO4^{2-}$: 880-3235 mg/l; Fe: 0.8-223 mg/l; Cu: 0.5-315 mg/l.

Components	Values
Organoleptic properties	
Temperature (°C)	18.5
Colour	Light yellow
Basic chemical properties	
Dry residue (mg/l)	4322
Electrical conductivity (μS/cm)	4560
pH value	3.8
Eh (mV)	604
Total hardness (°dH)	89.60
Temporary hardness (°dH)	<0.01
Permanent hardness (°dH)	89.60
Primary macrocomponents (mg/l)	
Chlorides (Cl^-)	<0.1
Hydrocarbonates (HCO_3^-)	<0.1
Sulphates (SO_4^{2-})	3480.90
Sodium (Na^+)	115.8
Calcium (Ca^{2+})	356.2
Magnesium (Mg^{2+})	184.4
Silica (SiO_2)	73.2
Secondary macrocomponents (mg/l)	
Potassium (K)	4.70
Iron (Fe)	275.30
Boron (B)	0.08
Strontium (Sr)	2.28
Nitrites (NO_2)	0.001
Nitrates (NO_3)	0.20
Microcomponents (mg/l)	
Copper (Cu)	173.00
Barium (Ba)	0.03
Zinc (Zn)	12.9
Aluminium (Al)	162.20
Arsenic (As)	0.0007
Lead (Pb)	0.045
Gaseous components (mg/l)	
Dissolved O_2	7.20
Dissolved CO_2	<0.01
Microbiological components (number/ml)	
TB[a]	<10
AN[b]	<10
SM[c]	8
DN[d]	<4
TB[e]	25
TF[f]	14000

Note: TB[a]-number of total mesophilic aerobic chemoorganoheterotrophic bacteria; AN[b]- number of total mesophilic anaerobic and facultative anaerobic chemoorganoheterotrophic bacteria; SM[c]-spores of malds; DN[d]-number of total microorganisms denitrification; TB[e]-number of total thionic bacteria (liquid medium with thiosulphate at pH 4.5); TF[f]-number of Thiobaccilus ferrooxidans (liquid medium with ferrous ion at pH 3.5).

Table 1. Physico-chemical and microbiological characteristics of mine waters of the "Bor" copper mine.

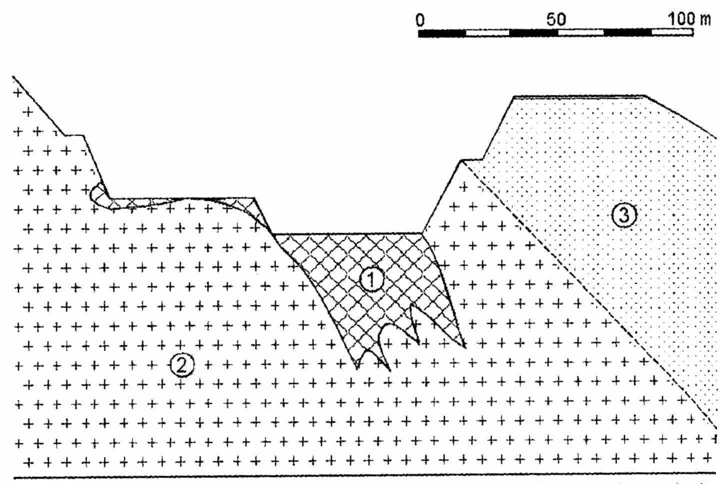
It should be stated that waters from copper melting and electrolysis processes are let out into the water basin of the Borska river contaminating additionally this stream. The flow originating by joining of the Borska and Kriveljska rivers is called the Crna reka (Black river) belonging to the basin of the Veliki Timok, namely the Danube. That is the most polluted stream in Serbia, and perhaps in Europe as well.

SURFACE AND GROUNDWATER POLLUTION UNDER THE IMPACT OF MINE WATERS OF ABANDONED MINES

There is a large number of abandoned mining works, in the area of copper deposit occurrences in eastern Serbia, letting out mineralized sulphate waters with high content of iron and other metals for years. These waters flow off directly into river streams contaminating their waters. It can be seen on the example of the abandoned mine Gornja Lipa how drastic the impact of these waters on the environment can be.

The abandoned mine Gornja Lipa is situated on the northern slopes of the mountain Crni Vrh, close to the river Lipa representing the spring part of the Veliki Pek (Figure 1). The mine was closed in the middle of the sixties, when 500,000 tons of the ore were left unworked (Jankovic, 1990). Copper ore of energetic type was exploited by open pit mining in this mine.

Copper ore mineralization was placed in hydrothermally altered hornblende-augite andesite and volcanic breccia. The main ore body consisted of Fe and Cu sulphides, while important place belonged to enargite, besides pyrite. The floor part of ore body is represented by pyrite impregnation's with insignificant share of copper mineralization (Figure 2). Surrounding ore



1. Ore body, 2. Kaolinizated, silificated and pyritizated hornblend-augite andesite 3. Carbonizated and sericitizated andesites

Figure 2. Geological profile through copper deposit "Gornja Lipa". (Jankovic, 1990).

Components	Values
Organoleptic properties	
Temperature (°C)	2.5
Colour	Red
Basic chemical properties	
Dry residue (mg/l)	2102
Electrical conductivity (µS/cm)	1430
pH value	3.8
Eh (mV)	604
Total hardness (°dH)	39.48
Temporary hardness (°dH)	<0.01
Permanent hardness (°dH)	39.48
Primary macrocomponents (mg/l)	
Chlorides (Cl^-)	7.1
Hydrocarbonates (HCO_3^-)	<0.01
Sulphates (SO_4^{2-})	1500.0
Sodium (Na^+)	5.10
Calcium (Ca^{2+})	182.0
Magnesium (Mg^{2+})	61.10
Silica (SiO_2)	42.4
Secondary macrocomponents (mg/l)	
Potassium (K)	0.58
Iron (Fe)	210.80
Boron (B)	0.03
Strontium (Sr)	0.60
Nitrites (NO_2)	0.001
Nitrates (NO_3)	6.50
Microcomponents (mg/l)	
Copper (Cu)	11.30
Barium (Ba)	0.01
Zinc (Zn)	5.48
Aluminium (Al)	60.80
Arsenic (As)	0.003
Lead (Pb)	0.016
Gaseous components (mg/l)	
Dissolved O_2	7.4
Dissolved CO_2	<0.01
Microbiological components (number/ml)	
TB[a]	<10
AN[b]	65
SM[c]	2
DN[d]	<4
TB[e]	115
TF[f]	<10

Table 2. Physico-chemical and microbiological characteristics of mine waters of the abandoned mine "Gornja Lipa" - open pit.

rocks are represented by intensively kaolinizated, silificated and sericitizated andesites. By deposit exploiting a depression was made in relief filled with water originating from atmospheric precipitation, wandering surface waters from surrounding slopes and groundwaters from mineralized andesites.

Regardless of finished deposit exploitation, one part of enargite copper ore remained at the walls and floor of the mine being succumbed to hypergenic processes even today, resulting in forming mine waters with many physico-chemical and biochemical peculiarities (Table 2).

Mine waters accumulating into gravity area of the mine in drought period are drained thought adit, the entrance of it being placed on the left bank of the river Lipa, about 20 m far from it. The adit is mainly broken, but mine waters flow out of it constantly. During rain and snow melting periods mine waters overflow the mine directly into the river (Figure 3).

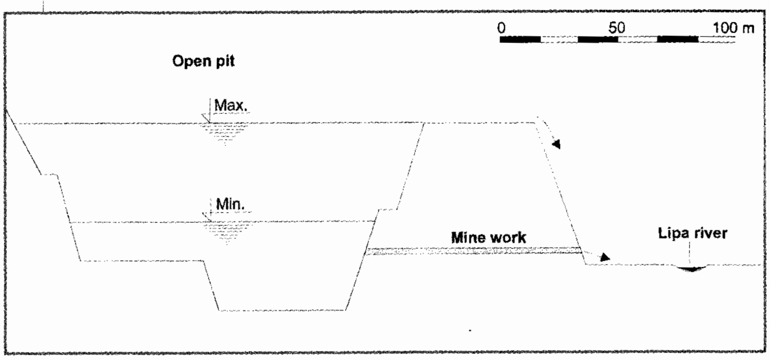


Figure 3. Profile through abandoned open pit Gornja Lipa.

Mine waters from the abandoned mine and the edit, together with the waters draining abandoned tailing disposal, flow out directly into the river Lipa undisturbed, conditioning drastic changes of chemical composition of its waters.

Before running into the zone of the abandoned mine, the river Lipa is characterized by clear low mineralized water, rich in river flora and fauna. From the mine, close to its joining with the Boza's river, iron hydroxide, manganese and aluminium deposits cover the riverbed, while waters themselves are characterized by increased content of iron and heavy metals (Table 3). Besides surface waters, ground waters of alluvial aquifer in direct hydraulic connection with the river waters are contaminated as well.

Locality	Metal content (mg/l)
River Lipa (100 m downstream of the mine)	Fe=2.9; Cu=1.10; As=0.95; Zn=0.46
River Lipa (200 m downstream of the mine)	Fe=3.0; Cu=0.95; As=1.90; Zn=0.38
River Lipa (500 m downstream of the mine)	Fe=9.7; Cu=1.65; As=0.94; Zn=0.46

Table 3. The content of metals in surface waters of the river Lipa downstream from the abandoned mine Gornja Lipa (Dragisic, 1998).

SURFACE AND GROUNDWATER CONTAMINATION UNDER THE IMPACT OF ORE TAILING DISPOSAL

The forming of copper ore tailing disposal in the eastern Serbia is not followed by adequate measures of surface and groundwaters charge aria. Ore tailing disposals were deposited in the nearest depressions, representing mainly riverbeds, where there is direct hydraulic connection between tailing disposal waters and river stream waters.

Ore tailing disposals represent most often low percentage copper, so groundwaters being formed in them have characteristics of mine waters of copper deposits. Groundwaters of ore tiling disposals of such composition flow out uncontrolled to surface streams and together with mine waters pollute surface and groundwaters in the neighbouring area of the mentioned mines. The stated tailing disposals are often deposited either on limestone base or at basin of particular karstic springs, direct hydraulic connection of karst groundwaters and waste waters of tailing disposals being made. This results in complete pollution of karst groundwaters, it endangers particular speleology objects, as well as the living world in them (Dragisic, 1994).

On the example of the mine Veliki Krivelj, negative impact of ore tailing disposal on environment is pointed out (Table 4). The ore-tailing disposal Veliki Krivelj has been formed at the southeast board of the mine in the basin of the little river Saraka. Fragments and blocks of volcanic and hydrothermal altered igneous rocks, partially mineralized by pyrite - chalcopyrite mineralization build ore tailing disposal.

The tailing disposal, formed in the basin of the river Saraka, arises mainly from the karstic spring Korkan (Q=10 l/s in drought period), characterized by exceptionally low mineralized hydrocarbonated-calcium waters. Owing to activity of physico-chemical and biochemical-microbiological processes the waters of specific physico-chemical characteristics are formed in ore tailing disposals. Partly, these waters infiltrate directly karst aquifer contaminating it while in the main part they flow out into the river resulting in drastic changes of physico-chemical characteristics of surface waters.

Components	Values
Organoleptic properties	
Temperature (°C)	8.0
Colour	Blue
Basic chemical properties	
Dry residue (mg/l)	459.9
Electrical conductivity (μS/cm)	6.6
pH value	7.25
Eh (mV)	402
Total hardness (°dH)	19.34
Temporary hardness (°dH)	8.40
Permanent hardness (°dH)	10.94
Primary macrocomponents (mg/l)	
Chlorides (Cl^-)	10.20
Hydrocarbonates (HCO_3^-)	183.0
Sulphates (SO_4^{2-})	192.0
Sodium (Na^+)	5.40
Calcium (Ca^{2+})	118.20
Magnesium (Mg^{2+})	12.20
Silica (SiO_2)	17.30
Secondary macrocomponents (mg/l)	
Potassium (K)	0.84
Iron (Fe)	3.04
Boron (B)	0.01
Strontium (Sr)	0.21
Nitrites (NO_2)	0.002
Nitrates (NO_3)	1.58
Microcomponents (mg/l)	
Copper (Cu)	9.26
Barium (Ba)	0.03
Zinc (Zn)	0.25
Aluminium (Al)	14.36
Arsenic (As)	0.006
Lead (Pb)	0.003
Gaseous components (mg/l)	
Dissolved O_2	8.60
Dissolved CO_2	20.00
Microbiological components (number/ml)	
TB[a]	10
AN[b]	<10
SM[c]	17
DN[d]	15
TB[e]	<4
TF[f]	10

Table 4. Physico-chemical and microbiological characteristics of river Saraka mine waters downstream from Veliki Krivelj mine tailing disposal.

CONCLUSIONS

- On the basis of physical, physico-chemical, chemical and microbiological parameters of mine waters and tailing disposal waters, namely neighbouring and connected streams, an attempt has been made to deal with complex hydro-geo-chemical processes thoroughly, using the example of some copper deposits in Serbia (the mine Bor, the abandoned mine Gornja Lipa and the tailing disposal of the mine Veliki Krivelj);
- It is characteristic of all mine waters, tailing disposal waters and neighbouring and connected streams, in relation to surface and ground water values, not con-

nected with sulphide mineralizations in the zone of oxidation: low pH value, high Eh, high mineralization, drastically high sulphate concentrations, total iron (Fe^{2+}+Fe^{3+}), copper and other elements, as arsenic for enargite mineralization of abandoned mine Gornja Lipa;

- The presence and number of specific "biological agents"-tionic bacteria, of especially Thiobacillus ferrooxidans genus, as specific sulphide deposits in wide range of ecologic abiotic factors, proves the significance of contribution of biochemical-microbiological component to the acceleration and oxidation processes and solubilization of sulphide and their influence on water composition;
- Phenomenological parameters of the streams up and down connected with, copper, mineralization, as well as their hydrogeochemical aspects, point out important impact of polluters on quality as well as flora and fauna in surface, and obviously, in groundwaters;
- Mine waters and tailing disposal waters for examined localities flow into surface streams and aquifers without previous treatment and because of that they are a serious problem of pollution and environment protection on the local and regional level.

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