

CHARACTERIZATION OF WASTEWATER STREAMS FROM BOR SITE

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ABSTRACT

This paper presents full characterization of wastewater streams within Bor copper mine. Seven different wastewater streams were identified and fully characterized (origin, flow rate, chemical and physical properties) on basis of five year analysis. Taking into consideration chemical composition and flow rate of each wastewater calculations of metal loss through wastewaters was calculated. This characterization is the first step in investigations for best remediation technology of wastewaters all together or individual.

Key words: wastewater, characterization, metal loss

INTRODUCTION

Consequences of pyrometallurgical treatment of copper within RTB Bor are different kind of wastewater effluences, which vary in accordance with wastewater origin, volume and composition. Because of these effluences wastewaters should be treated before discharging to river streams. This is in accordance with European environmental legislation. Before developing suitable treatment technologies wastewaters should be characterized from the aspects of their origin, flow rates and chemical composition. The wastewaters streams origin will be defined according to the different production procedures, while their flow rates will be measured as the average of the daily produced volumes. For the chemical composition characterization of wastewaters, representative samples from each stream will be collected and analyzed by various methods of analysis (AAS, ICP-AES, TOC analyzer and volumetric methods). In Fig 1. map of Bor copper mine is presented.

As it could be seen in Fig 1. there are 7 different places where wastewaters enter natural water streams of Krivelj and Bor Rivers.

They are presented as:

- 1) wastewater from open pit "Veliki Krivelj",
- 2) wastewater of Saraka stream,
- 3) open pit Bor wastewater,
- 4) wastewater of flotation dam 1A of flotation tailings pond "Veliki Krivelj",
- 5) wastewater of flotation dam 3A of flotation tailings pond "Veliki Krivelj",
- 6) wastewater from lake "Robule",
- 7) collective wastewater from open pit Bor and copper smelting and refinery plants.

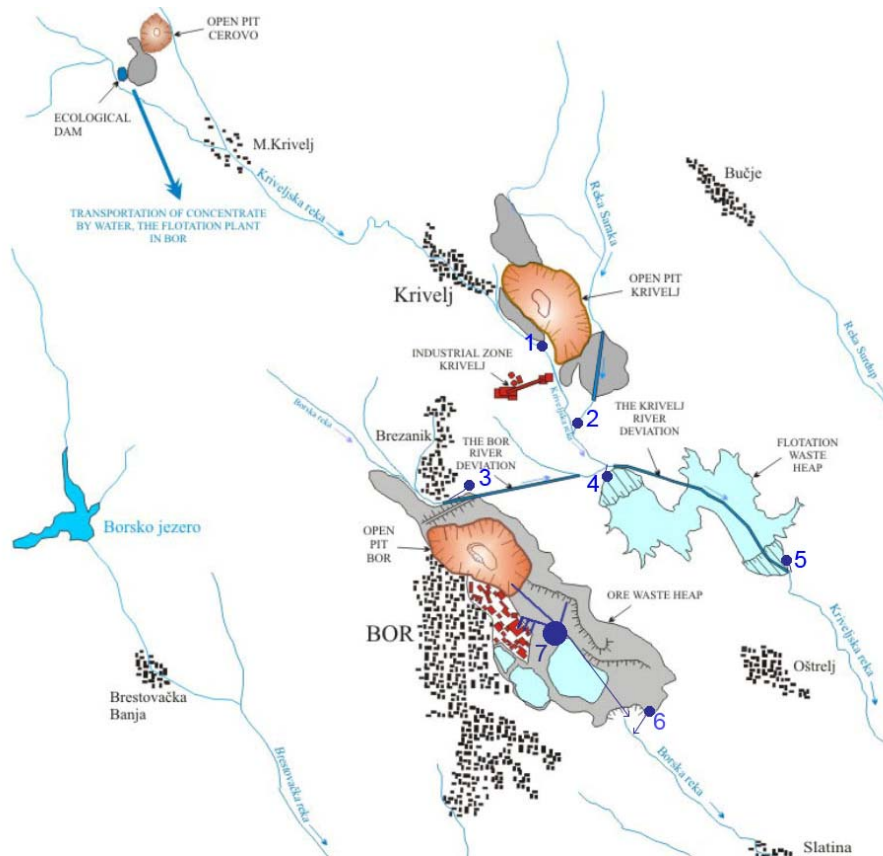


Figure 1. Map of Bor copper mine (Bor-Krivelj-Cerovo)

1. WASTEWATER FROM OPEN PIT “VELIKI KRIVELJ”

This is wastewater accumulated in water collector on the bottom of open pit “Veliki Krivelj”. This wastewater originated from surface (atmosphere) and underground waters. From water collector wastewater is pumping to Krivelj River with average flow rate of 2333 m³/day. In Tab. 1. some of the major characteristic of this wastewater is presented.

Table 1. Characteristics of wastewater from open pit “Veliki Krivelj”

Characteristic	unit	09.06.04	Characteristic	unit	09.06.05
Temperature of water	°C	26.5	Chloride (Cl)	mg/L	150.8
Temperature of air	°C	22	Sulfate (SO ₄)	mg/L	360.0
Color	/	yes	Phosphate (PO ₄)	mg/L	1.34
Odor	/	none	Surfactants	mg/L	n.d.
Floatables	/	none	Phenol	mg/L	/
pH	/	4.4	Oil and grease	mg/L	/

Settleable solids	mL/L	1	Oxygen (dissolved)	mg/L	/
Total suspended solids	mL/L	218	Iron (Fe)	mg/L	0.38
Total solids dried at 105°C	mL/L	560.0	Chromium (Cr)	mg/L	n.d.
KMnO4 consumption	mL/L	52.3	Copper (Cu)	mg/L	127.5
Biochemical oxygen demand (BOD)	mg O ₂ /L	27.7	Nickel (Ni)	mg/L	0.07
Chemical oxygen demand (COD)	mg O ₂ /L	/	Arsenic (As)	mg/L	n.d.
Total organic carbon (TOC)*	ppm	4	Zinc (Zn)	mg/L	3.1
Nitrogen (nitrate)	mg/L	0.42	Lead (Pb)	mg/L	0.00
Nitrogen (nitrite)	mg/L	n.d.	Cadmium (Cd)	mg/L	/
Nitrogen (ammonia)	mg/L	n.d.	Manganese (Mn)	mg/L	/

- Value of TOC on March, 5th 2005

2. WASTEWATER OF SARAKA STREAM

This is wastewater with leach solution from surface water stream Saraka. Above from this stream, on location, is an open pit "Veliki Krivelj" tailings pond. Wastewater from this location flow into Krivelj River with average flow rate of 3802 m³/day. Quantities of this wastewater significantly depend on atmosphere conditions. Basing on analysis for past five years diagram with change of metals concentration versus date could be designed (Fig. 2.).

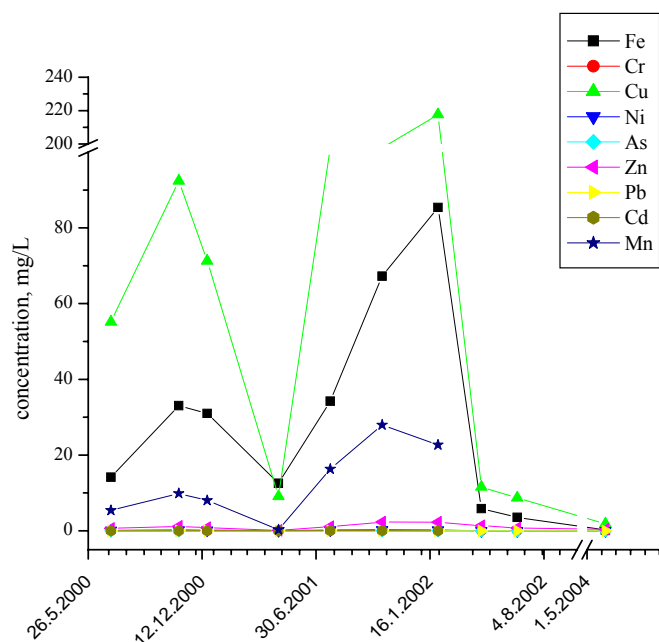


Fig. 2. Change of concentration of all metals found in wastewater of Saraka stream

Table 2. Min, max and mean values of characteristics of wastewater for past 5 years

Characteristic	unit	min	max	mean	Characteristic	unit	min	max	mean
Temperature of water	°C	15	21	17.23	Chloride (Cl)	mg/L	8	61.5	22.14
Temperature of air	°C	16	26	21.33	Sulfate (SO ₄)	mg/L	40.98	319	132.51
Color	/	/	/	/	Phosphate (PO ₄)	mg/L	0.05	3.9	1.07
Odor	/	/	/	/	Surfactants	mg/L	n.d.	0.09	0.02
Floatables	/	/	/	/	Phenol	mg/L	/	/	/
pH	/	3.6	7.74	4.88	Oil and grease	mg/L	/	/	/
Settleable solids	mL/L	0.8	1.5	1.20	Oxygen (dissolved)	mg/L	6.51	15.74	9.00
Total suspended solids	mL/L	93	316	227.82	Iron (Fe)	mg/L	0.21	85.4	26.13
Total solids dried at 105°C	mL/L	6.8	6360	2221.71	Chromium (Cr)	mg/L	0	0.005	0.00
KMnO ₄ consumption	mL/L	8	60	21.70	Copper (Cu)	mg/L	1.855	217.65	76.68
Biochemical oxygen demand (BOD)	mg O ₂ /L	0.08	19.6	4.35	Nickel (Ni)	mg/L	n.d.	0.264	0.11
Chemical oxygen demand (COD)	mg O ₂ /L	7.92	23.81	12.61	Arsenic (As)	mg/L	n.d.	0.013	0.00
Total organic carbon (TOC)	ppm	/	/	/	Zinc (Zn)	mg/L	0.119	2.305	1.02
Nitrogen (nitrate)	mg/L	0.39	2.61	1.14	Lead (Pb)	mg/L	n.d.	0.024	0.01
Nitrogen (nitrite)	mg/L	n.d.	0.002	n.d.	Cadmium (Cd)	mg/L	0.002	0.019	0.01
Nitrogen (ammonia)	mg/L	0	0.75	0.12	Manganese (Mn)	mg/L	0.284	27.95	11.49

3. OPEN PIT BOR WASTEWATER

This is pumped out wastewater from open pit Bor, which flow into Krivelj river, with average flow rate of 3599 m³/day.

In Table 3. some of the major characteristic for the past 5 years of this wastewater is presented. On basis of this table diagrams with metals (all, major and minor) versus date could be designed (Fig. 3.).

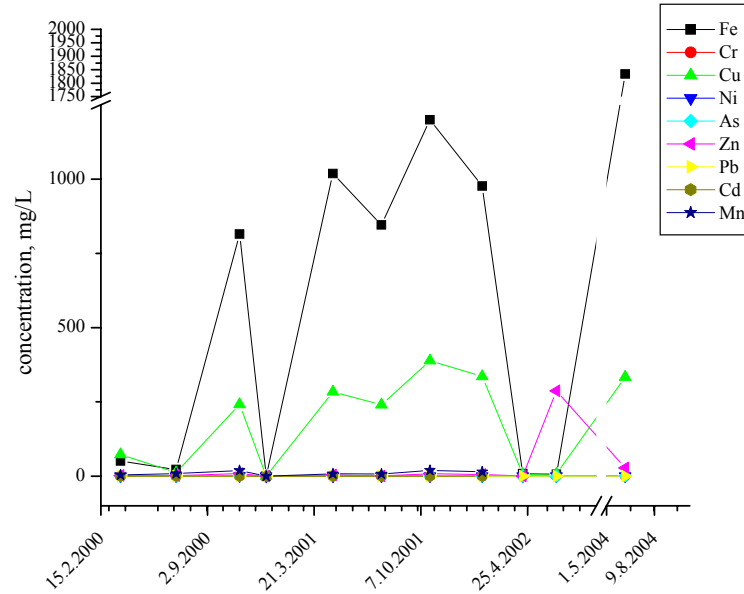


Fig. 3. Concentration of all metals found in wastewater of open pit Bor for the past 5 years

Table 3. Min, max and mean values of characteristics of wastewater for past 5 years

Characteristic	unit	min	max	mean	Characteristic	unit	min	max	mean
Temperature of water	°C	22	26	24.33	Chloride (Cl)	mg/L	6	720	184.09
Temperature of air	°C	17	26	21.67	Sulfate (SO ₄)	mg/L	2.99	829.09	224.79
Color	/	/	/	/	Phosphate (PO ₄)	mg/L	n.d.	1.5	0.37
Odor	/	/	/	/	Surfactants	mg/L	n.d.	0.094	0.03
Floatables	/	/	/	/	Phenol	mg/L	/	/	/
pH	/	2.49	8.27	3.36	Oil and grease	mg/L	/	/	/
Settleable solids	mL/L	2.4	4.6	3.30	Oxygen (dissolved)	mg/L	6.63	19.93	11.64
Total suspended solids	mL/L	0	618	292.55	Iron (Fe)	mg/L	0.15 3	1834	616.20
Total solids dried at 105°C	mL/L	340	12620	5827.00	Chromium (Cr)	mg/L	n.d.	0.015	n.d.
KMnO ₄ consumption	mL/L	6	212	65.95	Copper (Cu)	mg/L	0.028	388.7	174.68

Biochemical oxygen demand (BOD)	mg O ₂ /L	0.19	86.4	19.33	Nickel (Ni)	mg/L	n.d.	0.74	0.15
Chemical oxygen demand (COD)	mg O ₂ /L	1.98	230	63.22	Arsenic (As)	mg/L	n.d.	1.219	0.24
Total organic carbon (TOC)	ppm	/	/	/	Zinc (Zn)	mg/L	0.017	287	31.33
Nitrogen (nitrate)	mg/L	0.45	5.58	5.58	Lead (Pb)	mg/L	n.d.	0.015	0.01
Nitrogen (nitrite)	mg/L	0	0.003	n.d.	Cadmium (Cd)	mg/L	0.001	0.05	0.03
Nitrogen (ammonia)	mg/L	0.05	16	3.51	Manganese (Mn)	mg/L	0.012	19.55	10.04

4. WASTEWATER OF FLOTATION DAM 1A OF FLOTATION TAILINGS POND "VELIKI KRIVELJ"

These are surface, drainage wastewaters of flotation dam 1A of flotation tailings pond Veliki Krivelj. Average flow rate to Krivelj river is 1944 m³/day. In Tab. 4. some of the major characteristic for the past 5 years of this wastewater is presented.

On basis of this table diagrams with metals (all, major and minor) versus date could be designed (Fig. 4.).

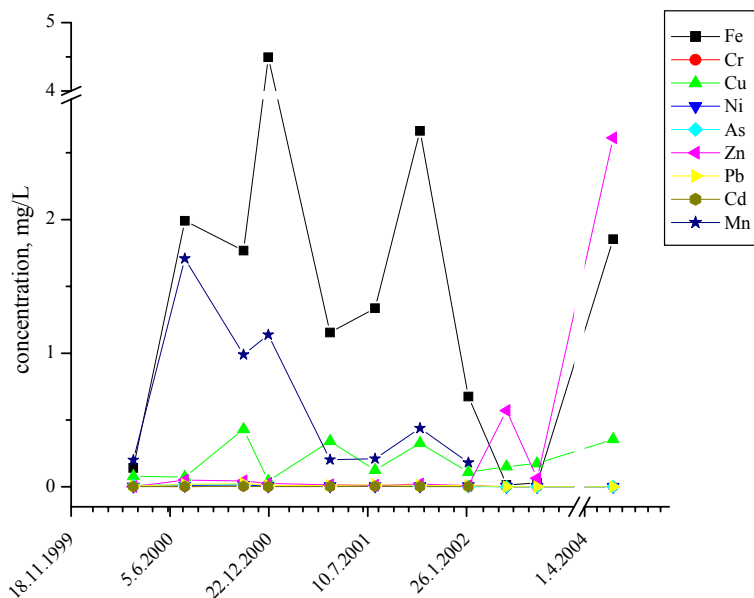


Fig. 4. Concentration of all metals found in wastewater of flotation dam 1A of flotation tailings pond Veliki Krivelj for the past 5 years

Table 4. Min, max and mean values of characteristics of wastewater for past 5 years

Characteristic	unit	min	max	mean	Characteristic	unit	min	max	mean
Temperature of water	°C	15	24	20.33	Chloride (Cl)	mg/L	20	29	23.77
Temperature of air	°C	16	27	21.67	Sulfate (SO ₄)	mg/L	58.74	729.82	167.97
Color	/	/	/	/	Phosphate (PO ₄)	mg/L	0.05	4	0.72
Odor	/	/	/	/	Surfactants	mg/L	n.d.	0.13	0.03
Floatables	/	/	/	/	Phenol	mg/L	/	/	/
pH	/	6.08	8.12	7.21	Oil and grease	mg/L	/	/	/
Settleable solids	mL/L	0.3	0.4	0.37	Oxygen (dissolved)	mg/L	4.71	14.75	9.31
Total suspended solids	mL/L	n.d.	137	58.18	Iron (Fe)	mg/L	0.014	4.492	1.46
Total solids dried at 105°C	mL/L	296	2680	1731.27	Chromium (Cr)	mg/L	n.d.	0.009	n.d.
KMnO ₄ consumption	mL/L	5	28.7	12.58	Copper (Cu)	mg/L	0.043	0.43	0.20
Biochemical oxygen demand (BOD)	mg O ₂ /L	0.12	13.6	3.52	Nickel (Ni)	mg/L	n.d.	0.014	n.d.
Chemical oxygen demand (COD)	mg O ₂ /L	1.52	72	24.54	Arsenic (As)	mg/L	n.d.	0.016	0.01
Total organic carbon (TOC)	ppm	/	/	/	Zinc (Zn)	mg/L	0.001	2.612	0.31
Nitrogen (nitrate)	mg/L	0.15	0.9	0.9	Lead (Pb)	mg/L	n.d.	0.024	0.01
Nitrogen (nitrite)	mg/L	n.d.	0.002	n.d.	Cadmium (Cd)	mg/L	0.001	0.003	n.d.
Nitrogen (ammonia)	mg/L	n.d.	0.5	0.10	Manganese (Mn)	mg/L	0.181	1.708	0.63

5. WASTEWATER OF FLOTATION DAM 3A OF FLOTATION TAILINGS POND "VELIKI KRIVELJ"

These are drainage wastewaters of flotation dam 3A of flotation tailings pond Velliki Krivelj. Average flow rate to Krivelj river is 3024 m³/day. In Tab. 5. some of the major characteristic for the past 5 years of this wastewater is presented.

On basis of this table diagrams with metals (all, major and minor) versus date could be designed (Fig. 6.).

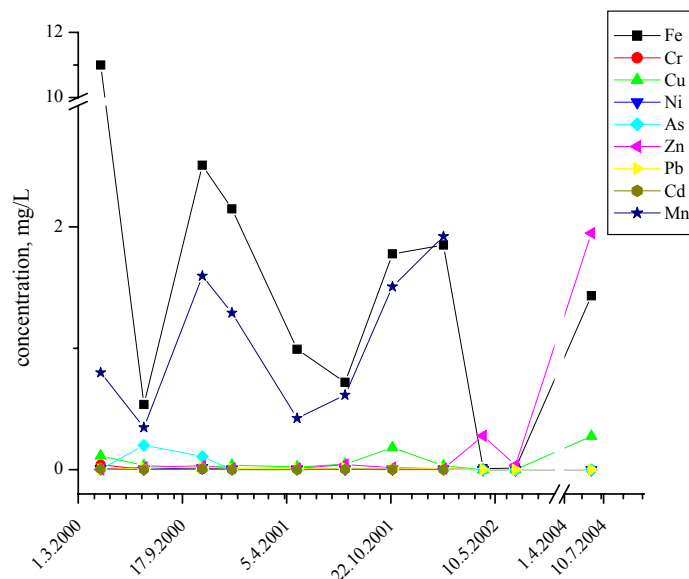


Fig. 5. Concentration of all metals found in wastewater of flotation dam 3A of flotation tailings pond Veliki Krivelj for the past 5 years

Table 5. Min, max and mean values of characteristics of wastewater for past 5 years

Characteristic	unit	min	max	mean	Characteristic	unit	min	max	mean
Temperature of water	°C	14	17	15.50	Chloride (Cl)	mg/L	12	25.6	19.24
Temperature of air	°C	22	27	24.50	Sulfate (SO ₄)	mg/L	11.69	700.73	183.30
Color	/	/	/	/	Phosphate (PO ₄)	mg/L	0.05	0.52	0.23
Odor	/	/	/	/	Surfactants	mg/L	n.d.	0.23	0.05
Floatables	/	/	/	/	Phenol	mg/L	/	/	/
pH	/	4.6	8.24	7.18	Oil and grease	mg/L	/	/	/
Settleable solids	mL/L	0.6	2.4	1.30	Oxygen (dissolved)	mg/L	3.42	7.83	5.33
Total suspended solids	mL/L	2	317	87.73	Iron (Fe)	mg/L	0.009	11	2.09
Total solids dried at 105°C	mL/L	440	2980	1908.55	Chromium (Cr)	mg/L	n.d.	0.041	0.01
KMnO ₄ consumption	mL/L	7	26.4	12.83	Copper (Cu)	mg/L	n.d.	0.276	0.07
Biochemical oxygen demand (BOD)	mg O ₂ /L	1.07	12.8	4.43	Nickel (Ni)	mg/L	n.d.	0.015	n.d.

<i>Chemical oxygen demand (COD)</i>	mg O ₂ /L	4	69	25.89	<i>Arsenic (As)</i>	mg/L	n.d.	0.201	0.04
<i>Total organic carbon (TOC)</i>	ppm	/	/	/	<i>Zinc (Zn)</i>	mg/L	0.001	1.95	0.22
<i>Nitrogen (nitrate)</i>	mg/L	0.03	1.81	1.81	<i>Lead (Pb)</i>	mg/L	n.d.	0.022	0.01
<i>Nitrogen (nitrite)</i>	mg/L	n.d.	0.002	0.00	<i>Cadmium (Cd)</i>	mg/L	0.001	0.009	n.d.
<i>Nitrogen (ammonia)</i>	mg/L	0.05	6	0.72	<i>Manganese (Mn)</i>	mg/L	0.348	1.922	1.06

6. WASTEWATER FROM LAKE "ROBULE"

Wastewater from lake Robule originate from accumulation of leach solution from pit Bor tailings pond. This lake is constant, because of accumulation from external sources. Average flow rate to Bor river is 484 m³/day. In Tab. 6. some of the major characteristics are presented.

Table 6. Characteristics of wastewater from lake Robule

<i>Characteristic</i>	unit	08.02.05			
<i>Temperature of water</i>	°C	6	<i>Chloride (Cl)</i>	mg/L	42
<i>Temperature of air</i>	°C	8	<i>Sulfate (SO₄)</i>	mg/L	4145.45
<i>Color</i>	/	yes	<i>Phosphate (PO₄)</i>	mg/L	0.05
<i>Odor</i>	/	none	<i>Surfactants</i>	mg/L	0.06
<i>Floatables</i>	/	none	<i>Phenol</i>	mg/L	/
<i>pH</i>	/	2.97	<i>Oil and grease</i>	mg/L	/
<i>Settleable solids</i>	mL/L	/	<i>Oxygen (dissolved)</i>	mg/L	11.92
<i>Total suspended solids</i>	mL/L	199.6	<i>Iron (Fe)</i>	mg/L	895
<i>Total solids dried at 105°C</i>	mL/L	20040	<i>Chromium (Cr)</i>	mg/L	0.002
<i>KMnO₄ consumption</i>	mL/L	16.1	<i>Copper (Cu)</i>	mg/L	55.16
<i>Biochemical oxygen demand (BOD)</i>	mg O ₂ /L	4.63	<i>Nickel (Ni)</i>	mg/L	0.322
<i>Chemical oxygen demand (COD)</i>	mg O ₂ /L	4.02	<i>Arsenic (As)</i>	mg/L	0.001
<i>Total organic carbon (TOC)*</i>	ppm	3.4	<i>Zinc (Zn)</i>	mg/L	26.5
<i>Nitrogen (nitrate)</i>	mg/L	6.33	<i>Lead (Pb)</i>	mg/L	0.01
<i>Nitrogen (nitrite)</i>	mg/L	0.004	<i>Cadmium (Cd)</i>	mg/L	0.034
<i>Nitrogen (ammonia)</i>	mg/L	/	<i>Manganese (Mn)</i>	mg/L	125

* Value of TOC on March, 5th 2005

7. COLLECTIVE WASTEWATER FROM OPEN PIT BOR AND COPPER SMELTING AND REFINERY PLANTS

This wastewater is collective wastewater pumped out from open pit Bor (closed in 1992.), from metallurgical plants (electrolysis, factory of H₂SO₄, PM plant, regeneration and other S&R plants) and drainage waters. Average flow rate to Bor river is 2323 m³/day. In Tab. 7. some of the major characteristics are presented.

Table 7. Characteristics of collective wastewater

Characteristic	unit	08.02.05	Characteristic	unit	08.02.05
Temperature of water	°C	17	Chloride (Cl)	mg/L	22
Temperature of air	°C	11	Sulfate (SO ₄)	mg/L	1670
Color	/	yes	Phosphate (PO ₄)	mg/L	3.93
Odor	/	none	Surfactants	mg/L	0.31
Floatables	/	none	Phenol	mg/L	/
pH	/	2.35	Oil and grease	mg/L	/
Settleable solids	mL/L	/	Oxygen (dissolved)	mg/L	0
Total suspended solids	mL/L	63	Iron (Fe)	mg/L	322.5
Total solids dried at 105°C	mL/L	4156	Chromium (Cr)	mg/L	0.009
KMnO ₄ consumption	mL/L	159.2	Copper (Cu)	mg/L	54.04
Biochemical oxygen demand (BOD)	mg O ₂ /L	/	Nickel (Ni)	mg/L	1.046
Chemical oxygen demand (COD)	mg O ₂ /L	39.8	Arsenic (As)	mg/L	0.017
Total organic carbon (TOC)*	ppm	7.2	Zinc (Zn)	mg/L	1.92
Nitrogen (nitrate)	mg/L	0.45	Lead (Pb)	mg/L	2.083
Nitrogen (nitrite)	mg/L	0.003	Cadmium (Cd)	mg/L	0.225
Nitrogen (ammonia)	mg/L	2.43	Manganese (Mn)	mg/L	9.63

* Value of TOC on March, 5th 2005

This wastewater is actually composed from several wastewater streams (Fig 6.).

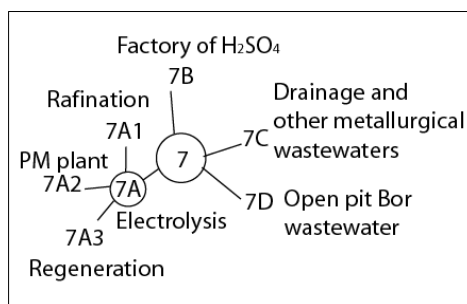


Fig. 6. Collective wastewater from open pit Bor and copper smelting and refinery plants schematic preview

Flow rate, min, max and average content of copper and sulfuric acid for wastewater streams from rafination, PM plant, regeneration and H₂SO₄ plant are presented in Tab. 8.

Table 8. Flow rate, min, max and average content of copper and sulfuric acid for wastewater streams on locations 7A and 7B

Location	V. m ³ /year	Cu, mg/L			H ₂ SO ₄ , mg/L		
		min	max	mean	min	max	mean
7A1	2874.00	0.55	14.70	4.8	1.96	47.04	16.63
7A2	1946.00	0.00	20.19	2.85	0.98	245.98	15.30
7A3	1070.68	10.90	20.95	15.15	328.00	450.00	385.98
7B	34944.00	0.012	0.070	0.041	0.61	0.99	0.81

CONCLUSION

Within RTB Bor, as presented, there are different wastewaters by origin, chemical composition and flow rate. To Krivelj and Bor river flow in mixture of atmosphere, drainage, mining and metallurgical wastewaters. With Krivelj and Bor river all wastewaters flow in trough Timok river into Danube and then to Black sea.

Distribution of concentration for past five years is basically lognormal. Only results for nitrite and for lead in some analysis (Saraka stream and open pit Bor) are questionable.

Losses of metals through wastewater disposal are presented in the table 9.

Table 9. Losses of metals through wastewater disposal

WW	loss. t/year								
	Fe	Cr	Cu	Ni	As	Zn	Pb	Cd	Mn
1	0.324	0.000	108.860	0.065	0.000	2.647	0.000	0.00	0.00
2	36.356	0.003	106.691	0.157	0.006	1.419	0.012	0.015	15.987
3	811.776	0.004	230.117	0.203	0.321	41.270	0.009	0.035	13.230
4	1.042	0.002	0.143	0.003	0.005	0.221	0.007	0.001	0.450
5	2.313	0.007	0.076	0.005	0.045	0.242	0.010	0.003	1.177
6	158.491	0.000	9.768	0.057	0.000	4.693	0.002	0.006	22.136
7	275.352	0.008	46.140	0.893	0.015	1.639	1.778	0.192	8.222
Σ	1285.655	0.024	501.795	1.383	0.391	52.132	1.818	0.252	61.202

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