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Waste waters from copper ores mining/flotation in 'Bučim' mine: characterization and remediation

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Abstract

Open pit mining, ore dressing and flotation in Bučim mine are accomplished by using vast amount of water. A complex water circulation scheme is employed, and this one is necessarily accompanied by water losses. In this process, part of the flotation waste water enters the nearby watercourses, thus contaminating them with heavy metals, organic tensides, etc. Resulting contamination is further spread up to the Vardar River and Aegean Sea.

Smaller part of the ponds (and other out-of-pipe) water reaches the underground aquifers and lowers the quality of water used in nearby villages wells.

Acid mine leaching of copper minerals in the overburden disposal site as well as mine waters also contribute in stream pollution. The waste waters from overburden leaching are extremely concentrated and contain up to 840 mg/L Cu^{2+} and 360 mg/L Mn^{2+}, in an average flow of 2 L/s.

1. Introduction

Republic of Macedonia is rich in poly-metallic complex sulfide ore deposits. They are used for production of base and precious metals, as e.g. copper, zinc, lead, silver and gold. The exploitation of sulfide ores requires a complex treatment during which the low-grade ore is enriched. This is achieved by flotation aimed at the removal of copper bearing particles in the ore. As a result of flotation, copper concentrate is produced which is later transformed into blister copper and finally into electrolytic copper of 99.95–99.97% Cu purity.

The exploitation of copper ore deposits, together with metal extraction that follows, causes severe environmental pollution problems, such as contamination of surface and ground water with high loads of toxic and heavy metals as well as with organic pollutants.

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In order to solve the environmental pollution problems one should first of all identify and characterize the pollution sources and then to suggest measures how to minimize and prevent future contamination, as well as how to remediate past groundwater contamination.

Copper works in Bučim, near town of Radovis, named Mine & Flotation 'Bučim' was constructed and is in operation since 1979, with a short pause in the period 2003–2004. Open pit mining is applied with a capacity of some 4 million t/y ore with an average content of 0.25% Cu, 0.9 g/t Ag, 0.4 g/t Au, etc. Flotation efficiency is 1.2% (m/m) and the separation of useful components is 85, 35, and 60% respectively, for Cu, Ag and Au. As a result, a quantity of an average of 40,000 000 t/y Cu-concentrate, containing 20% Cu, 30 g/t Ag; 30 g/t Au is produced annually. After metallurgical treatment, that takes place elsewhere, annual metal production averages 8000 t/y Cu, 800 kg/y Au, 800 kg/y Ag.

Water economy did impose construction of a dam that forms a pond with adequate capacity. By using and recycling of the water from this pond few important segments of the operation procedure are achieved, such as (i) separation of copper sulfide minerals and their collection into a concentrate, (ii) gravitational transportation back to the dam of flotation tailings suspended in water, (iii) settling down of suspended particles and (iv) pumping of the clarified water again back to the flotation unit. Thus, the whole process of water supply, flotation and transportation is completed in one water circulation cycle.

2. Sources of water pollution

From the environmental point of view, such a process of intensive and spread over a significant land area, water handling process inherently has some negative consequences. Recycled water accumulates residues of both treated ore and used flotation agents, such as alkansulphonates, alkylsulfates, phosphoric acids esters, etc. (see Table 1).

Other waste waters are formed as a result of occasional leaching of copper ore in the open pit and in the overburden and waste rock dumps. The main source for the generation of acid mine drainage is the natural oxidation of sulfide minerals exposed to the combined action of water and oxygen. A quantity of some 150 million tones of open pit overburden and waste rock material were accumulated during the past mine operation. It contains up to 0.12% Cu that is continuously oxidized and leached with the rainfalls. This waste water appears to be the most contaminated with Cu^{2+} ions of all hot spots, as shown later.

Part of these contaminated waste waters escapes or is disposed into nearby rivers without

Table 1
Analysis of samples taken from copper mine Bucim [1]

Contamination by heavy metals	Cu	Cr	Zn	Ni	Mn	Pb	Cd
Waste water from brook, 2.5 km from factory, mg/L	200.4	<0.005	1.60	0.77	56.0	0.055	<0.005
Waste water from mine, mg/L	50.5	<0.005	0.46	0.23	16.2	<0.02	<0.005
Sediment from brook, mg/kg	2145	14	21	15	731	15	<10
Contamination by organic matter	Carbonic acids (C_{16}–C_{18})		Phthalates (DBP, etc.)		Ionic and non-ionic tensides from flotation		
Waste water from brook, 2.5 km from factory	10 mg/L		0.5 mg/L		Present		

any treatment, and finally reaches the Vardar River. After some 100 km, all the contamination ends in the Aegean Sea, near the Gulf of Thessalonica.

3. Extent of water pollution

Preliminary data on the contamination of the waste waters are given in Table 1. Copper ions concentration reaches up to 200 mg/L, while the concentration of flotation agent is up to 10 mg/L (for carbonic acids) and 0.5 mg/L (for phthalates). These figures are higher than the corresponding legal limits, as illustrated in [2]*. For comparison, German quality objective for copper in surface water is 4 μg/L.

More detailed insight in the waste water composition is given in Tables 3 and 4, where samples from the hot spots characterized in Table 2 were subject of analysis.

Results presented in Tables 3 and 4 indicate that waste water from Bučim mine and flotation works are characterized by:

(1) Low acidity: In most cases pH value is higher than 6. The most acid (as low as pH = 4.6) are the samples from the spots where acid mine drainage takes place, i.e. overburden and waste rock dump's leachates and leachates from the open pit mine.

(2) High Cu^{2+} ions concentration: A value as high as 840 mg/L was registered in waste waters from the overburden and waste rock dump (during the off period, when the leachates were not diluted by other waste waters).

(3) High SO_4^{2-} ions concentration: This is again due to the acid mine drainage process.

Table 2
Location and intensity of water flow in the selected hot spots

Hot spot no.	Location	Flow, L/s
1	Pond water, downstream of the dam	16–22
2	Overburden and waste rock dump leachates	10–12
3	Leachates from the open pit mine	0.5–2.0
4	Collective waste waters before inlet in the local river	25
5	Underground water downstream of the factory	/
6	Watercourse formed by inlet of Stream 1 in Stream 2	up to 40

Together with other waste water characteristics this is an evidence of intensive waste water pollution that requires serious measures for prevention and remediation.

4. Pollution prevention measures

Pollution prevention measures were planned (and some of them are already realized) aimed at

*Maximum permitted values of heavy metal concentrations (μg/L) according to the Macedonian Regulation for classification of water sources [2] are:

	Class I–II	Class III–IV	Class IV
Arsenic	30	50	>50
Copper	10	50	>50
Zinc	100	200	>200
Cadmium	0.1	10	>10
Chromium (VI)	10	50	>50
Manganese	50	1000	>1000
Nickel	50	100	>100
Lead	10	30	>30
Iron	300	1000	>1000

Table 3
Chemical analysis (mg/L) of waste water samples (7 November 2004)

Parameter		Hot spot no.				
		1	2	3	4	5
pH		6.01	5.20	5.34	6.13	6.70
Suspended matter		16.6	94.7	60.3	98.3	17.2
Dry residue 105°C		862	5859	4550	894	904
Dry residue 600°C		720	4500	3500	734	741
COD ($KMnO_4$)		10.6	22.1	12.9	12.6	4.92
Cations	Cu	2.41	840	163	31.0	0.09
	Pb	0.02	0.06	0.04	0.01	0.01
	Fe	0.84	4.44	4.44	0.35	0.45
	Mn	2.20	360	270	14.0	–
	Zn	0.25	11.2	19.5	0.52	0.15
	Ca	185	304	372	209	324
	Mg	17.3	9.70	8.60	10.3	19.6
Anions	SO_4^{2-}	237	2067	1230	393	316
	Cl^-	80.0	76.5	82.7	69.5	70.3

both minimization of the quantity of waste waters as well as of the pollutant concentrations.

Acid mine drainage control techniques, such as preventive and containment methods are planned to be applied in order to eliminate the most serious source of environmental pollution. Theoretically, acid generation could be prevented by excluding the contact of sulfides with oxygen or water. Use of appropriate cover, e.g. vegetative, organic, or composite is suggested as an effective measure for prevention of oxygen diffusion. Elimination of the bacteria responsible for the catalytic reactions, and increase of pH by means of alkaline agents (limestone or fly ash) was also suggested [3,4]. By preventing water flow into the overburden dump site (as, e.g. by construction of diversion trenches) [5,6] the spreading of acid drainage is reduced.

Effective collecting and recycling of waste waters was and still is the immediate measure. Only after their possibilities will be exhausted, measures aimed at further treatment of waste waters, are to be employed.

There are many other pollution management measures that also help to achieve a level of better compliance with the progressively strengthening environmental legislative.

Among the methods suggested for minimization of acid mine drainage we did accept the method of immobilization of copper in the overburden heap by means of mixing it with lime, fly ash (waste from coal burning in power plant) and bentonit. Preliminary results show that substantial decrease (90–95%) of leaching rate is achieved with addition of typically 10% of these substances. A study is in course that is aimed at determining the optimal set of conditions that lead to the most effective immobilization of copper in this mine's solid waste.

5. Waste water treatment measures

Waste waters from copper mining and flotation activities can be treated in many different ways, such as by:

- Leaching aimed to recover the heavy metals contained in the solid wastes. Chemical leaching (with citric and oxalic acids), as well as bacterial leaching (mainly *T. Ferrooxidans*) processes are considered as the most promising.
- Selective recovery of metals from waste waters by electrochemical methods.
- In-situ immobilization of heavy metals by transforming them into less-soluble compounds. This should be done by lower cost and environmentally safe agents (as e.g. fly ash) that reduce waste's permeability, stabilize the heavy metals and subsequently minimize their load in the leachates.
- Remediation of leachates by means of reactive barriers, as e.g. limestone, bentonites, zeolites, volcanic tuff etc., that adsorb the toxic load from the polluted waters.
- Recovery of metals and removal of sulfates from the waste waters by photochemical process, as e.g. formation of strong metal complexes with organic ligands, before waste water neutralization.

Table 4
Chemical analysis (mg/L) of waste water samples (23 March 2005)

Parameter		Hot spot no.					
		1	2	3	4	5	6
pH		6.72	4.62	4.68	5.30	6.53	4.90
Suspended matter		64.0	109	36.8	175	22.4	304.0
Dry residue 105°C		1086	16,658	4664	2674	974	2450
Dry residue 600°C		836	11590	3734	2274	780	1746
BOD_5		2.52	5.05	2.60	1.50	0.62	–
COD ($KMnO_4$)		6.44	11.6	7.18	5.72	1.39	6.62
Cations	Ca	107	435	350	328	167	142
	Mg	24.1	12.0	9.83	15.6	8.90	18.3
	K	20.3	14.1	7.80	9.60	0.90	19.1
	Na	141	64.1	64.1	70.3	62.1	78.9
	As	0.01	0.35	0.02	0.01	0.01	0.01
	Cu	0.10	603	32.0	31.2	0.09	65.0
	Pb	0.006	0.011	0.005	0.006	0.004	0.005
	Mn	1.05	241	46.0	21.0	–	24.0
	Zn	0.99	5.38	3.40	1.88	0.79	1.55
	Fe	–	2.86	–	–	0.05	–
Anions	Cl^-	101	59.5	77.3	68.0	67.1	86.5
	SO_4^{2-}	537	2495	1127	1002	389	614
	HCO_3^-	–	–	–	–	112	–

Recently, various electrochemical and hydrometallurgical processes, alternative to chemical precipitation, have been developed. These technologies, such as electrolysis (cementation), solvent extraction, adsorption, ion exchange and membrane separation, are able to recover heavy metals from waste waters as pure materials. Moreover, they control environmental pollution since the secondary wastes are avoided and the treated water can be recycled in closed loop processes.

Moreover, electrochemical processes succeed in destructing pollutant species like strong complex-forming agents, cyanide and others by anode oxidation in the electrochemical reactor, simultaneously with metal recovery.

For the adsorption of metals from waste waters, a variety of adsorption media is used. These media are either proprietary materials, as iron hydroxide-coated sand, alumina, organic polymers etc., or solid wastes from different processes, like fly ash, red mud and biological material.

Currently, chemical precipitation is the most widely used technique for copper removal from waste waters. Chemical precipitation is a convenient process for most metals that are precipitated as hydroxides, carbonates or sulfides. Metal precipitation involves conversion of soluble metal compounds to insoluble ones that are precipitated through a reaction of metal ions under appropriate pH conditions. Usually, cheap alkaline agents are used as precipitants, while others are used as coagulants to enhance colloid particles aggregation and increase the effectiveness of subsequent solid-liquid separation. Although chemical precipitation is an attractive process, there are also several disadvantages, such as: generation of large

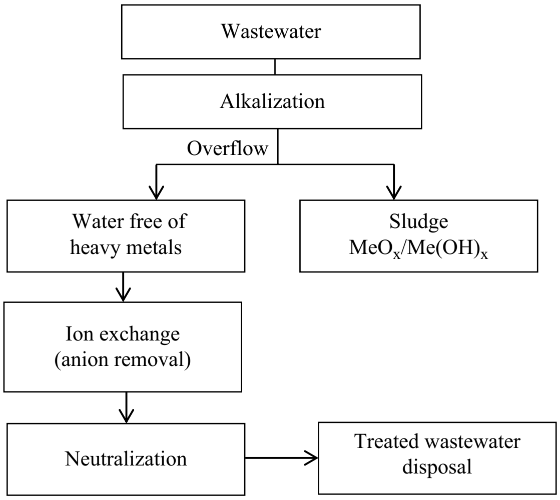

Fig. 1. Schematic of waste water treatment procedure.

sludge volumes, the need for further treatment of sludge to meet the disposal criteria, and loss of the valuable metals.

In our study we did apply a complex scheme for treatment of waste waters. In Fig. 1 a schematic is given that explains the treatment procedure.

Waste water is alkalized up to pH 10.5 so that heavy metal cations are transformed into practically insoluble oxide and/or hydroxide. After sedimentation, the clear water is paste through an anion exchange resin (Amberlite IRA 900) in sulfate form, so that anions, first of all chlorides, are removed. The last operation is neutralization back to pH 7–8.5. On such a way the concentration of pollutants in the waste water is brought within the discharge limits.

6. Conclusions

(1) Applied operational procedure in the Bučim copper mine and flotation necessarily results in generation of significant quantities of waste waters contaminated with heavy metals and organic residues of flotation agents.

(2) Acid mine drainage of open pit mine overburden also takes place and produces waste waters that contain as much as 840 mg/L Cu^{2+} ions.

(3) A number of measures for prevention and remediation of waste water pollution were planned according to the identified nature and intensity of pollution and the available reference experience.

(4) Results of already applied prevention measures are in favour of further search for the most convenient, the most efficient and cost-effective measures to decrease or eliminate the negative effects of mine and flotation operations.

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