

## THE EFFECT OF OXIDANTS THROUGH A TAILING DUMP DEPTH AND THE LEACHING OF COPPER

<sup>1\*</sup>Zoran STEVANOVIC, <sup>2</sup>Milan ANTONIJEVIC, <sup>2</sup>Grozdana BOGDANOVIC, <sup>1</sup>Mile BUGARIN, <sup>1</sup>Vlastimir TRUJIC, <sup>1</sup>Radmila MARKOVIC & <sup>3</sup>Dragutin NEDELJKOVIC

<sup>1</sup>Mining and Metallurgy Institute Bor, 35 Zelene bulevar, P. O. Box 152, 19210 Bor, Serbia;

\*E-mail: zoran.stevanovic@irmbor.co.rs

<sup>2</sup>University of Belgrade, Technical Faculty Bor, VJ 12, P. O. Box 50, 19210 Bor, Serbia

<sup>3</sup>University of Belgrade, Institute of Chemistry, Technology and Metallurgy, Njegoseva 12, 11000 Belgrade, Serbia

**Abstract:** The research results of the oxidants influence on Cu leaching recovery from the old Bor flotation tailing dump from the Bor mining facilities, located in eastern Serbia, will be present. Leaching experiments were carried out on samples of tailings taken from the surface of tailing dump down to the depth of 20 m, per depth intervals of 5 m. Copper content in the initial samples ranged from 0.026 % (surface) to 0.43% (20 m depth). Tests of copper leaching were carried out in the acid media (0.01 M solution of H<sub>2</sub>SO<sub>4</sub>) without an oxidant, with addition of hydrogen peroxide and oxygen. All three combinations of tests were done with and without the previous rinsing of samples so that total of six different series of experiments emerged. During previous rinsing of samples with distilled water, high degree of copper leaching (up to 75.33%) was achieved in some samples indicating the presence of copper sulfate and other soluble copper oxides. The highest copper recovery were obtained in the experiments with 3% solution of hydrogen peroxide and amounted to 88.93% and 62.63% for samples with and without rinsing, respectively. These results indicate on extremely high mobility of copper ions and the risk in terms of pollution the surrounding water system and soil.

**Key words:** copper leaching, hydrogen peroxide, oxygen, flotation tailings, copper recovery, copper sulphate

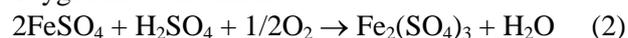
### 1. INTRODUCTION

Flotation tailings, formed from non operational copper ore processing facilities, usually have low pH value and contain high concentration of heavy metals and other toxic elements. Depending on the porosity and permeability of tailing, toxins are distributed over the volume of tailing dump and surrounding soil (Benzaazoua & Kongolo, 2003) causing a serious pollution of the environment. Various metal sulfides are present in tailings and the oxidation occurs when the tailing is exposed to the air and atmospheric precipitation (Balderama, 1995; Markovic et al., 2011). Pyrite (FeS<sub>2</sub>) is the most common sulfide mineral present in the flotation tailings and serves as a precursor for the development of acid mine drainage (AMD). AMD products contain high amount of sulfate ions, metal ions and metalloids and the pH value of the solution is between 2.5 and 4.5 (Parker & Robertson, 1999; Conesa et al., 2006; Pérez-López, et

al., 2007; Simón et al., 1999; Andrade et al., 2006; Stjernaman Forsberg et al., 2006). Generally, the oxidation of pyrite from the flotation tailings under atmospheric conditions can be represented by the following consecutive reactions (Bonniessel-Gissinger et al., 1998; Singer & Stumm, 1970; Lawson, 1982; Rosso et al., 1999; Kamei & Ohmoto, 1999; Borda et al., 2004). Oxidation of pyrite by oxygen dissolved in water:

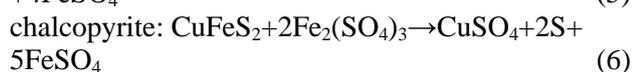
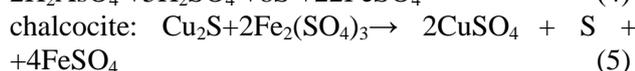
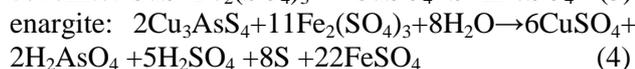
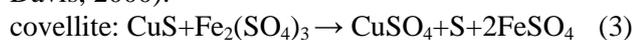


Oxidation of the formed iron (II) sulfate with oxygen in acidic media:



The atmospheric oxygen dissolves in the tailing solution of the metal sulfides and act as an oxidant for the pyrite oxidation (Mizutani & Rafter, 1973; Tayler et al., 1984; Toran & Haris R, 1989; Krouse et al., 1991). Therefore, a degree of pyrite oxidation is directly dependent on concentration of dissolved oxygen and environment humidity

(Bornstein et al., 1980). The bacteria commonly present in the sulfide ore of a various metals (e.g. *Ferrobacillus ferrooxidans*, *Ferrobacillus thiooxidans* and *Thiobacillus thiooxidans*) can also enhance the degree of a pyrite oxidation (Chaudhury et al., 1989; Battaglia et al., 1998; Edwards et al., 2000; Baker & Banfield, 2003; Gonzáles-Toril et al., 2003; Bryan et al., 2006). As a product of a pyrite oxidation, ferric sulfate and sulfuric acid are formed, as it is described in equations 1 and 2. In the presence of the AMD, ferric sulfate and sulfuric acid oxidize sulfides of other metals forming soluble salts of heavy metals. By this mechanism, heavy metal ions are released in the surrounding environment as pollutants (Gleisner & Herbert, 2002). The main metallic ion of the acid drainage solution from the copper mine flotation tailing is copper. The oxidation of various copper sulfides that are used for the copper smelting can be presented as (Smalley & Davis, 2000):



Various chemical elements can be present in the AMD (Fe, As, Zn, Mn etc.), depending on the composition of the primary rock. The other parameters that influence the distribution and behavior of the heavy metal ions include: geological and hydrological characteristics of the terrain, climate of the area and water permeability of the flotation tailings (Dold, & Fontbote, 2001). As the tailing dump usually contains huge amount of sludge, the pollution periods are usually measured in decades after the mining activities had been stopped.

For the investigation presented in this paper, the samples were taken from the old flotation tailing dump of the Mining and Smelting Complex Bor (RTB Bor). This tailing dump was chosen as a typical example of source of contamination through acid mine drainage processes. This pollution affects east Serbia, northwest Bulgaria and southwest Romania.

The average copper content in the old Bor flotation tailing dump is about 0.2%, which means that the total amount of tailings, about 27 million tons, contain about 54 000 t of copper (Nikolić, 2001). Obviously, tailing with such amount of a copper is a potential basis for the further copper recovery (Antonijević et al., 2008; Stevanović & Bugarin, 2007). On the other hand, the same

material without any treatment is a constant pollution emitter to water, air and soil. The highest rate of an unprovoked copper self-leaching is observed on the surface of the dump as a consequence of a higher concentration of oxygen and moisture from the air. As the concentration of copper in deeper layers of a dump increases, the main focus of the research presented in this paper is the influence of non-treated flotation tailing dumps to the environment.

The leaching experiments were conducted on samples from eight drill holes with the depth increment of 5m (1 m, 5 m, 10 m, 15 m and 20 m). The sample from the depth of 15 cm was also taken to represent the surface of a dump. Experiments were carried out in reactors exposed to the air with 0.01M sulfuric acid solution and with or without presence of an oxidizer (hydrogen peroxide or oxygen). Two parallel sets of experiments were done, and one set include previous rinse of samples with distilled water to determine the content and behavior of easily soluble copper compounds.

## 2. EXPERIMENTAL

### 2.1 Characteristics of the Old Bor flotation tailing dump

The Old Bor flotation tailing dump was formed in 1933, and was in function until 1987 when the flotation tailings from the Flotation Plant Bor were disposed in the valley of the Bor River. During the operation, the tailing dump was divided into three sectors separated by sand dams. Each field of dump contained large amounts of sludge the tailing as following (Nikolić, 2001):

- Field I:	3.922.146 t
- Field II:	22.846.122 t
Total:	26.768.268 t

On the basis of the geological analysis of a tailing dump, the average contents of elements were found as 0.2% of copper, 0.3 g / t of gold, 2.5 g / t of silver and 10.5% of sulfur.

### 2.2. Characteristics of flotation tailings samples

The samples used for the experiments presented in this paper are taken from drill holes implemented in 2007 (Stevanović & Bugarin, 2007). The drill holes were carried out in the Field I of the flotation tailing dump along according to the following sections (Longitudinal section: I – I', and Transversal section: II – II'). The position of the sections and the position of the flotation tailing dump

in the area of the town of Bor is presented on figure 1.

Eight drilling holes (B1 – B8) were digged in total. Six of them (B1 - B6) were in the longitudinal profile (I - I') (distance 20 m), while the drill holes B7 and B8 were placed in the transversal section (II - II'), which passes through the drill hole B4. The distance between B4 and B7 was 20m and the distance between B4 and B8 was 40m. The reason for the latter was to avoid the influence of the town sewage collector that is located below the tailing dump (Fig. 1). The size distribution of the grains from the old flotation tailings was determined by the standard Tyler sieve series and presented in table 1.

Table 1. Grain size distribution of samples from the old flotation tailings

Size range (mm)	Partial participation		Cumulative participation	
	m (g)	w (%)	R (%)	D (%)
- 1.168 + 0.833	0.1	0.1	0.1	100.0
- 0.833 + 0.589	0.1	0.1	0.2	99.9
- 0.589 + 0.417	0.8	0.8	1.0	99.8
- 0.417 + 0.295	3.3	3.3	4.3	99.0
- 0.295 + 0.212	8.2	8.2	12.5	95.7
- 0.212 + 0.147	8.5	8.5	21.0	87.5
- 0.147 + 0.104	11.5	11.5	32.5	79.0
- 0.104 + 0.074	12.2	12.2	44.7	67.5
- 0.074 + 0.053	15.2	15.2	59.9	55.3
- 0.053 + 0.036	14.8	14.8	74.7	40.1
- 0.036 + 0.000	25.3	25.3	100.0	25.3
Σ	100.0	100.0	-	-

The chemical composition of samples from the old flotation tailings was determined by the Atomic emission spectrometer with induced plasma (ICP - AES) and presented in table 2.

Table 2. Chemical composition of the initial composite samples per depth of tailing dump

El. (%)	Sample from the depth of tailing dump (m)					
	0	1	5	10	15	20
Cu	0.026	0.032	0.25	0.42	0.33	0.43
Fe	4.46	4.19	7.54	8.38	14.24	13.96
Zn	0.0016	0.014	0.012	0.020	0.017	0.019
Pb	0.0066	0.0066	0.0075	0.010	0.010	0.010
As	0.0031	0.0039	0.015	0.021	0.016	0.021
Mn	0.0030	0.0042	0.0089	0.012	0.021	0.019

Mineralogical analysis, performed using a polarizing microscope in reflected light in air (Carl Zeiss-Jena "JENAPOL-U"), was carried out on composite samples. The average value of sulfide mass was 22.2%, with average amount of free mineral grains of 89%. The most common sulfide mineral was pyrite, and the most common barren mineral were quartz and other silicate minerals with concentrations of 21.57% and 76.98% respectively. The Cu minerals were mostly covellite (0.21%), chalcopyrite (0.16%), enargite (0.14%) and chalcocite (0.04%). The mean value of free grains was 38.7%; 24.7 % of the aggregates appear as impegtrations in quartz, 20.8% of the complex mesogens with pyrite and quartz is and 15.8% of simple mesogens with pyrite or quartz.

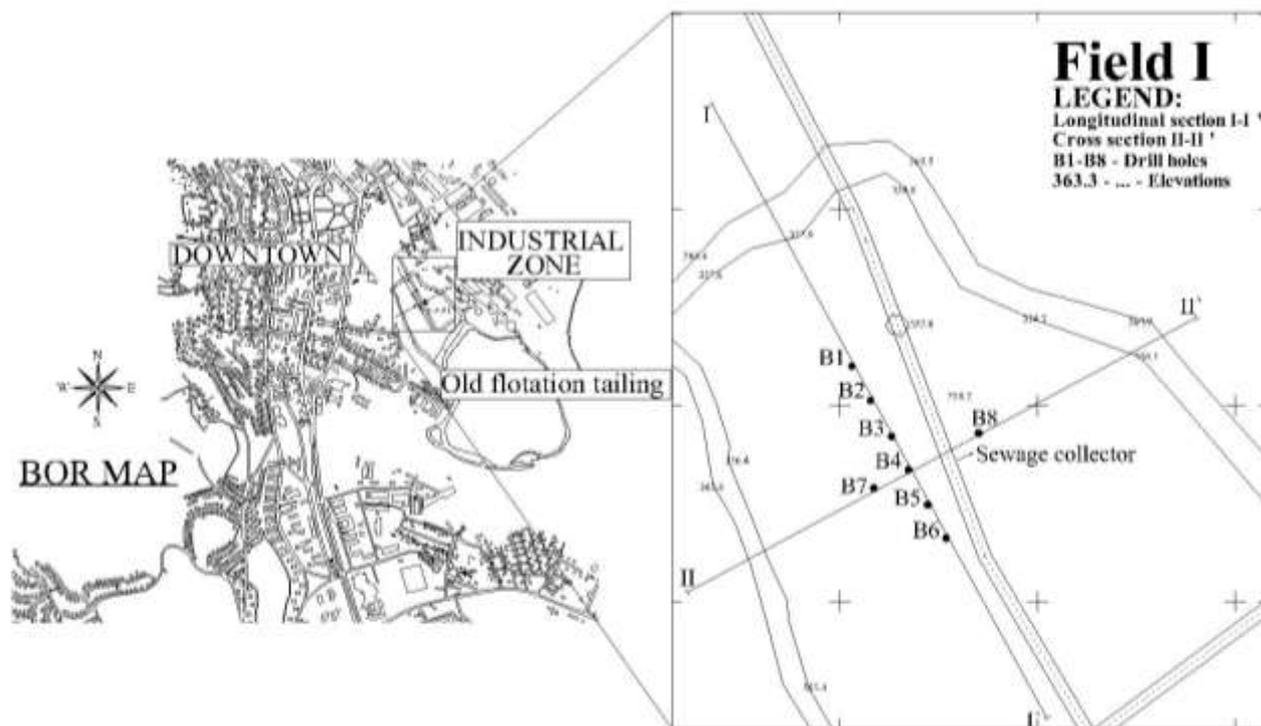


Figure 1. Location of drill holes and the flotation tailing dump.

### 2.3. Experimental setup

Experiments were carried out in open reactors of 1000 ml without stirring in order to simulate the conditions in the tailing dump. Distilled water (pH = 5.58), and 95% H<sub>2</sub>SO<sub>4</sub> were used for the experiment and 30% H<sub>2</sub>O<sub>2</sub> or oxygen were added as an oxidant. Experiments were carried out in reactors exposed to the air with 0.01M sulfuric acid solution and with or without presence of an oxidizer (hydrogen peroxide or oxygen). Six series of samples were prepared from composite samples of the flotation tailings as follows:

I series: 0.01M H<sub>2</sub>SO<sub>4</sub> without oxidant. Samples pre-rinsed;

II series: 0.01M H<sub>2</sub>SO<sub>4</sub> without oxidant. Samples without previous rinsing;

III series: 0.01M H<sub>2</sub>SO<sub>4</sub> + H<sub>2</sub>O<sub>2</sub>. Samples pre-rinsed;

IV series: 0.01M H<sub>2</sub>SO<sub>4</sub> + H<sub>2</sub>O<sub>2</sub>. Samples without previous rinsing;

V series: 0.01M H<sub>2</sub>SO<sub>4</sub> + O<sub>2</sub>. Samples pre-rinsed;

VI series: 0.01M H<sub>2</sub>SO<sub>4</sub> + O<sub>2</sub>. Samples without previous rinsing;

Leaching solution was prepared from distilled water and sulfuric acid (as a pH regulator). For the series III and IV, 3% solution of H<sub>2</sub>O<sub>2</sub> was added on the start of the experiment. Every three days 3% of fresh hydrogen peroxide (recalculated for every addition to keep the same concentration) was added. In the series V and VI, oxygen was added directly to the solution on the start, and every three days for five minutes with the flow rate of 25 l/min. During all of the experiments, the ratio solid/liquid was 1/1 (500 ml of leaching solution and 500 g of samples). The duration of experiment was four months. The sampling of the liquid phase was done 6 and 24 hours after the start of experiment. The sampling period in the first month was 10 days, and for the rest of the experiment was 15 days. 20 ml of the sample were filtered and analyzed. The corrections of concentrations of the elements in the tailing dump were calculated due to the taking of 20ml of a liquid phase.

## 3. RESULTS AND DISCUSSION

### 3.1 Pre-rinsing of samples

The samples of the series I, III and V were rinsed with distilled water in five cycles in order to remove soluble compounds from the sample and to determine differences in solubility of heavy metals in comparison to the non-rinsed samples. Each cycle had lasted for 10 minutes with the manual stirring of the immersed sludge pulp (ratio S:L = 1:1). After the cycle has been finished,

the pulp was filtered and fresh distilled water was added to the solid residue. The amount of the monitored elements in the cumulative solution of the filtrates was determined. The results of the analysis of the initial sample are presented in table 3.

Table 3. Analysis of filtrate after rinsing the initial depth composite samples

Sample	Filtrate		Concentration (C) and Cu leaching degree (X)	
	Volume (dm <sup>3</sup> )	pH	C <sub>Cu</sub> (g/dm <sup>3</sup> )	X <sub>Cu</sub> (%)
0m	6.00	4.29	0.0045	6.92
1m	6.65	2.84	0.033	45.72
5m	6.89	3.55	0.410	75.33
10m	7.00	3.68	0.400	44.44
15m	7.93	3.77	0.320	51.26
20m	7.34	3.03	0.280	31.86

As it can be observed from table 3, minimum level of Cu leaching was 6.92% on the surface and maximum level was 75.33% (sample from depth of 5m). The Cu concentrations in filtrates were 0.0045 g/dm<sup>3</sup> to 0.410 g/dm<sup>3</sup> respectively. The high degree of Cu leaching implies the alleged presence of copper sulfate that came as a result of a long period of copper sulfide oxidation (Edwards et al., 2000; Antonijević et al., 2008). Low degree of the Cu leaching on the surface can be explained by the natural process of gas removal by the atmospheric oxygen and water. The leaching degree is not directly correlated to the amount of Cu in the initial sample. Possible reason can be that due to the shape of the lower parts of a tailing dump, contact between the oxygen and the tailing is shorter. The other possible reason is the non-uniform distribution of pyrite that directly influences the reactivity and mobility of present sulfide minerals.

### 3.2. Leaching in the acid media (0.01M H<sub>2</sub>SO<sub>4</sub>) without addition of oxidants (Series I and II)

Leaching experiments of the Serials I and II were done with 0.01M H<sub>2</sub>SO<sub>4</sub>, at room temperature and at a solid/liquid ratio of 1:1. Contrary to the previous works (Antonijević et al., 2008), the reaction mixture was stirred manually and periodically rather than mechanically and continuously. The reason was to allow for the better contact between the leaching liquor and floating particles during the experiment. The dependence of Cu leaching degree and pH value on time of series I are presented on figures 2 and 3 while the analogous results for serial II are presented on figures 4 and 5. The dependence of Cu leaching degree and Cu concentration in a solution on the depth of the flotation tailing dump is presented in figure 6.

From figure 2, it can be observed that the highest degree of Cu leaching was obtained at the sample from the depth of 5m (34.73%; concentration of Cu in the leaching solution 0.213 g/dm<sup>3</sup>). The leaching degrees of the samples from the surface and 1m depth were 17.10% (Cu concentration 0.036 g/dm<sup>3</sup>) and 20.67% (Cu concentration 0.040 g/dm<sup>3</sup>) respectively. The leaching degree of samples from greater depths of tailing dump (10-20m) ranges from 7.19% (at 20 m) to 13.94% (at 15 m). It can also be observed that the leaching degree rapidly increases in first 264 hours (11 days) and remains approximately constant in the later stages of the experiment. The reason is that the most of soluble Cu is mobilized at the beginning of experiment and the remaining part is from less soluble Cu minerals. It is also obvious that the degree of Cu leaching decreases depthwards in the tailing dump, while the Cu concentration in the leaching solution increases. The reason for this behavior is a limited amount of available oxygen in the deeper layers of the tailing dump. Degree of pyrite reactivity is also lower at greater depths of the tailing dump as indicated by slightly higher pH values during the experiment on samples from greater depth of tailing dump (Fig. 3).

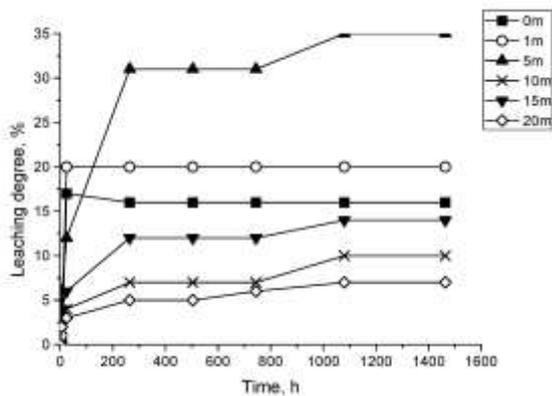


Figure 2: Change of Cu leaching degree with time in the Series I

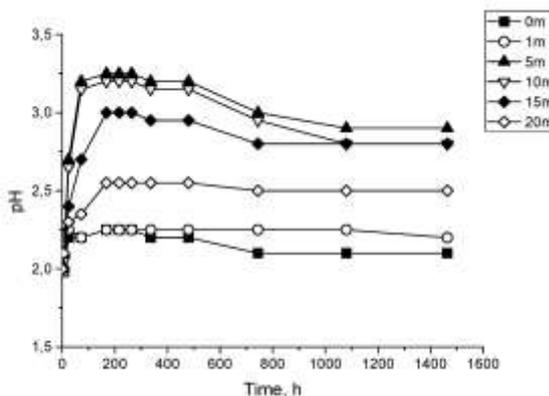


Figure 3. Change of pH value with time in the Series I

Comparing the Cu leaching degree in experiments conducted on Series I and II, it is

obvious that the higher leaching degrees were obtained for Series I. This behavior can be explained by the presence of Cu ions that are removed by rinsing in Series II. The changes in pH were similar for both rinsed and non-rinsed samples (Figs. 3 and 5). In the Series I, the highest leaching degree was obtained for the sample from 15m depth (48.92%; Cu concentration in the leaching solution 1.614 g/dm<sup>3</sup>); followed by the sample from the depth of 20m (46.31%; Cu concentration of 1.992 g/dm<sup>3</sup>).

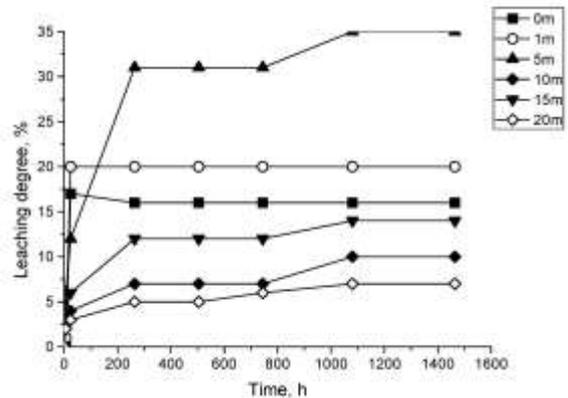


Figure 4. Change of Cu leaching degree with time in the Series II

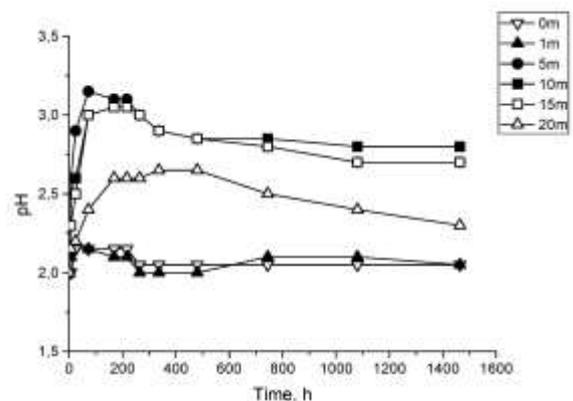


Figure 5. Change of pH value with time in the Series II

Comparing the results of the Series II to the Series I, it can be seen that Cu leaching degrees are generally lower as the alleged minerals are removed during the rinsing. For example, hydroxides of iron are being oxidized, resulting in the formation of ferric ions. The oxidation of Cu is enhanced by the ferric ions. The Cu in the tailing dump is mainly present in the form of covellite (Dutrizac & MacDonald, 1974; Hirato et al., 1989). The dependence of the covellite solubility on the concentration of the ferric ions was investigated. The two parameters are in direct dependence for the concentration of ferric ions lower than 0.28g/l. Analyzing figure 6, it is obvious that that degree of Cu leaching and Cu concentration in leaching solution increases with the increase of the depth of a tailing

dump. The achieved Cu leaching degrees in the leaching of samples without prior rinsing and calculated degrees of leaching, obtained by addition of leaching through previous rinsing of samples are presented in table 4.

Table 4. The effect of previous rinsing of samples on total Cu leaching in the experiments on Series I and Series II

Total leaching, $\Sigma X_{Cu}$ (%)	Sample from the depth (m)					
	0	1	5	10	15	20
$\Sigma X_{Cu}$ without rinsing	19.23	26.96	39.62	38.10	48.92	46.31
$\Sigma X_{Cu}$ with rinsing	23.46	56.61	83.94	89.87	58.01	36.76

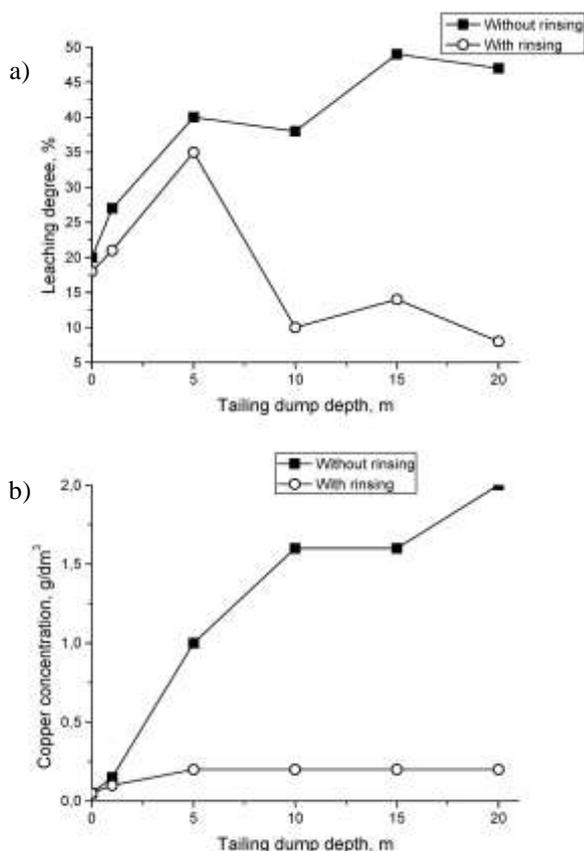


Figure 6. The results of leaching experiments of Series I and Series II depending on depth of tailing dump: a) Change of Cu leaching degree; b) Change of Cu concentration in leaching solution

Analyzing the data presented in table 4 the pre-rinsing of the samples if the oxidants were not added has significant influence to the overall degree of a Cu leaching for samples from all the depths except the sample from 20 m. Results presented in Table 4 imply that residual sulfide minerals dissolve efficiently which results in significantly higher leaching degrees for some samples (1 m, 5 m, 10 m). As a contrast, the rinsing of the sample did not have any influence to the leaching degree of the sample from 20m depth. The

possible reason is a lower initial degree of oxidation of the minerals that enhance the oxidation of remaining sulfides at this depth and their removal by the rinsing. As a support of this statement, there is also a trend of total degree of Cu leaching in the experiments with previous rinsing, which increase till the 10 meter of depth and then decreases with increasing of depth of the tailing dump.

### 3.3. Leaching in the acid media (0.01M $H_2SO_4$ ) with addition of 3% $H_2O_2$ solution (Series III and IV)

The leaching experiments of the Series III and IV were done in acid solution (0.01M  $H_2SO_4$ ) with addition of 3%  $H_2O_2$  solution as an oxidant. All of the experiments were conducted on the room temperature with a solid/liquid ratio of 1:1. The dependence of the Cu leaching on time of the samples from series III is presented on figure 7, and from series IV on figure 8. Figure 9 shows the dependence of Cu leaching degree on depth of a tailing dump.

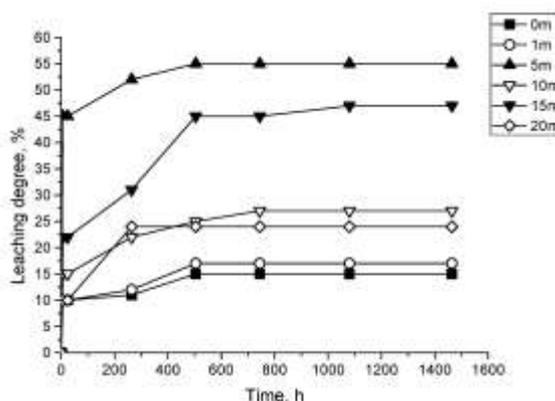


Figure 7. Change of Cu leaching degree with time (Series III)

The highest level of Cu leaching in the series III was obtained on the sample from the depth of 5m, similarly to the series I. The Cu leaching degree was 55.38% (compared to the 34.73% of the sample without the oxidant). The concentration of Cu was  $0.360 \text{ g/dm}^3$  (compared to the  $0.507 \text{ g/dm}^3$  in the analogous without oxidant). Unlike the experiments on samples from Series I (Fig. 6a), after the highest level of leaching on a sample at depth of 5 m in the experiments on Series III (Fig. 9a), slightly lower results were obtained on samples at depths of 15 m, 10 m and 20 m (46.65%, 28.17% and 23.86%, respectively) and the lowest were the results in the surface layers of tailing dump. These observations indicate strong influence of the hydrogen peroxide to the oxidation of a Cu sulfide, mainly in the deeper levels of the tailing dump. Additionally, obtained Cu leaching degree in Series III at the beginning of the

experiment (up to 6 h), was a steep slope of curves with the jumps of the recovery that leads to increased reactivity of Cu ions. This is significantly faster compared to the Series I (Figs. 2 and 7). Other results are in good accordance with previous research that confirmed H<sub>2</sub>O<sub>2</sub> as strong oxidant for metal sulfides (Aydogan et al., 2005). Change in pH value was in the same range as in the case of Series I (pH was between 2.0 and 2.7).

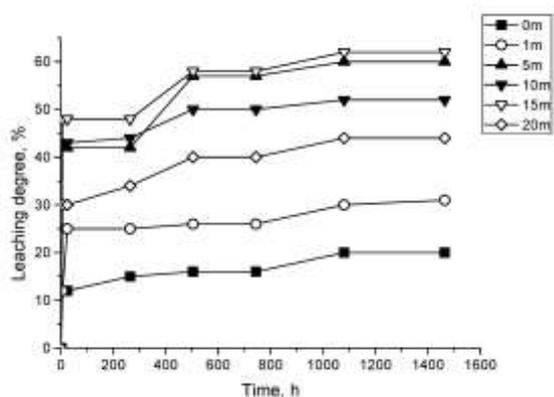


Figure 8. Change of Cu leaching degree with time (Series IV)

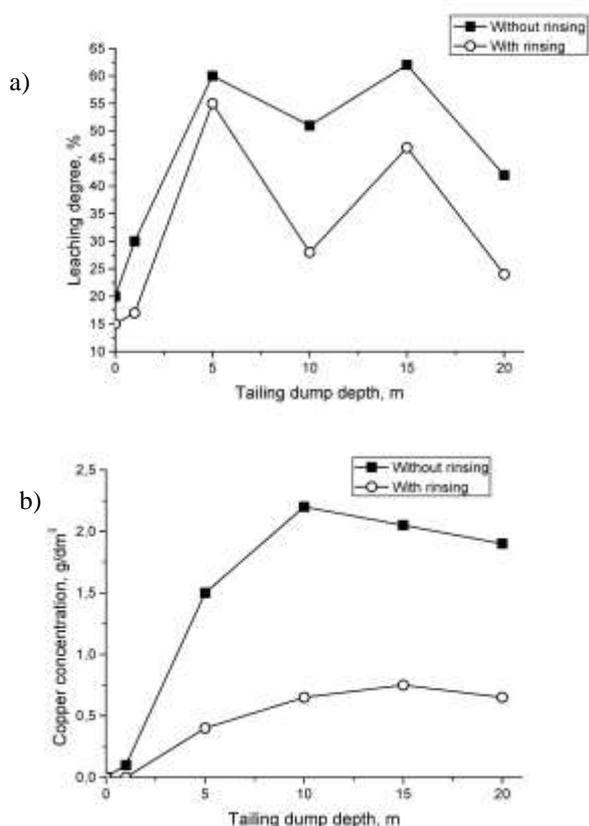


Figure 9. The results of leaching experiments Series III and Series IV per depth of a tailing dump: a) Change of Cu leaching degree; b) Change of Cu concentration in leaching solution

The experiments of Cu leaching of the samples from Series IV show slightly higher values of the

leaching degree than in Series III, but the trend of the leaching level was the same as in the samples of Series III. Range of the pH values was the same as in the previous cases (from 1.8 to 2.5). The highest degree of Cu leaching was achieved on samples from the tailing dump depth of 15 m and 5 m (62.63% and 59.88%, respectively), with Cu concentration in the leaching solutions of 2.067 g/dm<sup>3</sup> and 1.497 g/dm<sup>3</sup>, respectively.

Analogously to the samples from the Series III, the highest degree of Cu leaching were obtained during the first 6 hours of the experiment, with the slight increase during next 104 days and the constant value during the last 16 days of the experiment.

The results obtained in the experiments with the samples from Series III and IV show that presence of the hydrogen peroxide as an oxidant increase the mobility of the Cu ions in samples from all depths of the tailing dump. The concentration of the Cu in leaching solutions in samples taken from 5m depth or deeper was higher than 1.5 g/dm<sup>3</sup>, with the highest concentration of 2.188 g/dm<sup>3</sup> observed in the sample from the depth of 10m. This value is well above the demands of current SX-EW process for commercial hydrometallurgical Cu production (Kordosky, 2002). The results of a Cu leaching of samples in Serial III and IV as a function of a depth of sampling are compiled in table 5.

Table 5. Effect of previous rinsing of samples on total Cu leaching in the experiments on Series III and Series IV

Total leaching, $\Sigma X_{Cu}$ (%)	Sample from the depth (m)					
	0	1	5	10	15	20
$\Sigma X_{Cu}$ without rinsing	19.98	30.96	59.88	52.11	62.63	42.90
$\Sigma X_{Cu}$ with rinsing	21.68	54.69	88.93	60.06	73.97	48.12

As it can be seen in table 5, in the case of the experiments in presence of hydrogen peroxide oxidant, pre-rinsing has a significant effect on a total Cu leaching degree. Contrary to the experiment without oxidizer additives, high leaching degrees were obtained for the sample taken from the depth of 20m, which implies the influence of the oxidizing agent to the Cu sulfide from the bottom layers of tailing dump. However, comparing total leaching degrees of sample from the depth of a 10m with prior rinse, in the presence and absence of a hydrogen peroxide it can be seen that leaching degree is significantly higher in the absence of hydrogen peroxide. A possible reason for this is that the products of reaction of hydrogen peroxide with soluble sulfide minerals induce passivation of the surface of the Cu minerals. In general, the strongest effect of the presence of hydrogen peroxide on a Cu leaching degree is the mobilization of Cu ions, while the differences in the amount of final

leaching degrees, after the overall time of experiment (4 months), are very small.

### 3.4. Leaching in acid media (0.01M H<sub>2</sub>SO<sub>4</sub>) with addition of oxygen (Series V and VI)

The same procedure was followed for the experiments on samples from Serial V and VI. The experiments were conducted in acid solution (0.01M H<sub>2</sub>SO<sub>4</sub>), and the oxygen was added at the same experimental conditions as in previous cases. The results regarding the dependence of a Cu leaching degree on time of samples from Series V are presented in figure 10, and the same dependence of Series VI is presented in figure 11. The Cu leaching degree and the changes of a Cu concentration as a function of depth of a tailing dump are presented on figure 12.

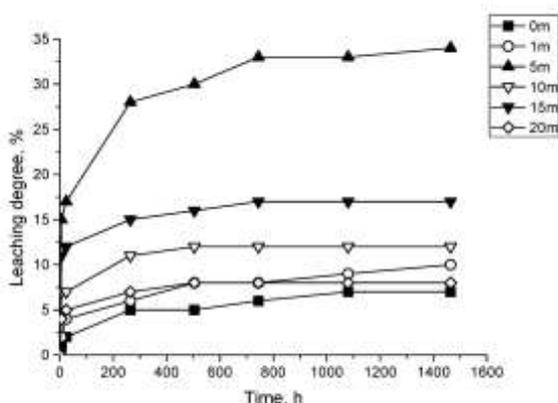


Figure 10. Change of Cu leaching degree with time (Series V)

The highest Cu leaching degree in the Series V, analogously to the Series I and III, is obtained on the sample taken from the depth of 5m (33.93%; Cu concentration in leaching solution 0.208 g/dm<sup>3</sup>). This value of Cu recovery is significantly lower than in the case of the addition of hydrogen peroxide (Series III), and is at the same order of magnitude as in the experiments without added oxidant (Series I; 0.8% difference in leaching degree and 0.005 g/dm<sup>3</sup> difference in Cu concentration). Those results indicate that the periodic addition of oxygen has no influence to the oxidation of copper sulfides. Final observed leaching degree of the samples of Series V taken at the surface layer was below the leaching degree of analogous sample of the Series I, while the leaching degree of the samples from deeper levels were higher for Serial V than in Serial I. The addition of oxygen increased the mobility of the Cu ions at the beginning of the experiment (first six hours). However, the mobilization rate was significantly lower than in the case of hydrogen peroxide. Based on these observations, it can be concluded that the introduced amount of oxygen was insufficient for the efficient oxidation of sulfide

minerals. The pH value was similar to the experiment without addition of an oxidant.

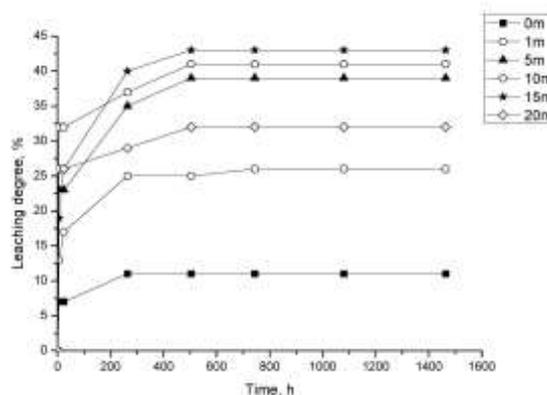


Figure 11. Change of Cu leaching degree with time (Series VI)

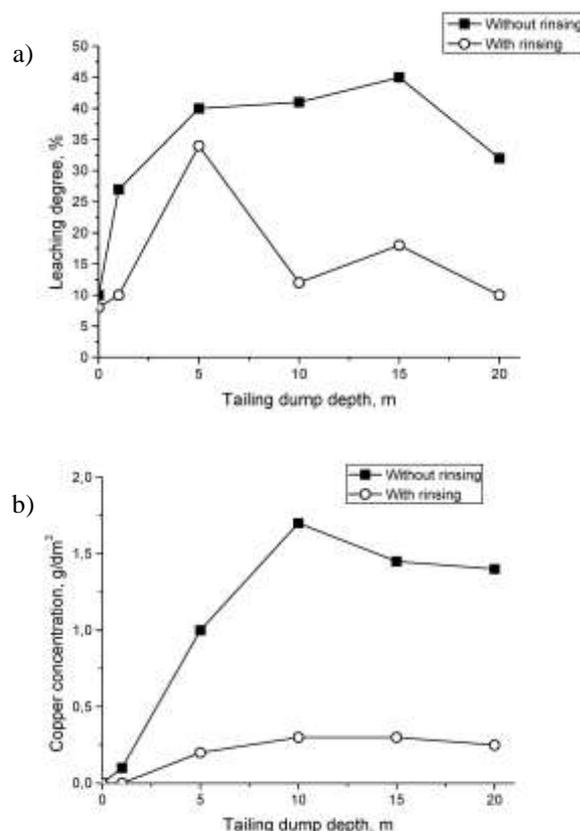


Figure 12. The results of leaching experiments Series V and Series VI with the depth of depth of tailing dump a) change of Cu leaching degree; b) change of Cu concentration in leaching solution

The similar parallel changes might be observed in the comparison of samples from Series VI and II. The general trend of the leaching degree trough the depth is similar in the cases of Series VI and II, as well as the change of pH value. The higher degrees of Cu leaching were observed on the samples from the depths of tailing dump of 15 m, 10 m and 5 m (43.89%, 41.02% and 39.47%, respectively), with Cu

concentration in leaching solutions of 1.448 g/dm<sup>3</sup>, 1.723 g/dm<sup>3</sup> and 0.986 g/dm<sup>3</sup>, respectively. These results are good starting points for considering the material from the tailing dump as a raw material for Cu recovery. The achieved Cu leaching degrees of the samples of Series V and VI are presented in table 6.

Table 6. Effect of prior rinsing of samples on total Cu leaching in the experiments on Series V and Series VI

Total leaching, ΣX <sub>Cu</sub> (%)	Sample from depth (m)					
	0	1	5	10	15	20
ΣX <sub>Cu</sub> without rinsing	10.69	26.58	39.47	41.02	43.89	32.50
ΣX <sub>Cu</sub> with rinsing	14.31	51.02	83.73	51.49	59.60	37.96

Analogously with the previous sets of experiment (Tables 4 and 5), it can be observed from the Table 6 that rinsing process has strong influence to the leaching degree of a copper. Presented results imply high economic potential of the flotation dump treatment in order to recover the present copper. A possibility of introduction of a phase of a copper pre-concentration should also be taken into consideration in order to optimize the operating costs of the complete hydrometallurgical process.

#### 4. CONCLUSION

Flotation tailings contain finely crushed material (55.3% of particles are smaller than 0.074 mm), and are a good predisposition for increase the reactivity of sulfide minerals in acid drainage. The dominant minerals in AMD were sulphides (mainly pyrite) followed by silicates and carbonates. The copper is mainly present in the form of covellite, chalcopyrite, enargite and chalcocite, with the overall copper concentration in AMD products up to 0.43%. The copper (II) sulfate was observed in the top layers of the tailing dump as a consequence of the exposure to the atmospheric oxygen and air. The samples were taken from the various depths of a tailing dump, and the leaching degree was measured in the acid solution without oxidizing agent, and with two types of oxidizer (hydrogen peroxide and oxygen). All experiments were conducted in two parallel paths, one of them with previous rinsing with distilled water, and the other one without rinsing. The highest degree of copper leaching was observed in the presence of 0.01M H<sub>2</sub>SO<sub>4</sub> with addition of 3% solution of H<sub>2</sub>O<sub>2</sub> as an oxidant. The leaching degree is not directly related to the copper concentration in the initial sample due to the lower degree of oxidation of sulfide minerals in deeper parts of tailing dump, unequal distribution of pyrite in tailing dump as well as unequal degree of its oxidation or reactivity. The highest copper leaching degrees were

obtained on the samples taken from the depth of 15 m: with 0.01M H<sub>2</sub>SO<sub>4</sub> without an oxidant (48.92%), with 0.01M H<sub>2</sub>SO<sub>4</sub> with addition of 3% H<sub>2</sub>O<sub>2</sub> (62.63 %) and with 0.01M H<sub>2</sub>SO<sub>4</sub> with addition of O<sub>2</sub> (43.89 %). The copper concentrations in leaching solutions were 1.614 g/dm<sup>3</sup>, 2.067 g/dm<sup>3</sup> and 1.448 g/dm<sup>3</sup>, respectively. The highest total degrees of copper leaching in the experiments with previous rinsing of samples, were obtained with 0.01M H<sub>2</sub>SO<sub>4</sub> without and oxidant (89.87% on a sample from depth of 10 m), with 0.01M H<sub>2</sub>SO<sub>4</sub> with addition of 3% H<sub>2</sub>O<sub>2</sub> (88.93% on a sample from depth of 5 m) and with 0.01M H<sub>2</sub>SO<sub>4</sub> with addition of O<sub>2</sub> (83.73% on a sample from depth of 5 m). The highest effect of previous rinsing the samples was recorded on samples from depth of 5 m in the experiments: with 0.01M H<sub>2</sub>SO<sub>4</sub> without oxidant (44.32%), with 0.01M H<sub>2</sub>SO<sub>4</sub> with addition of 3% H<sub>2</sub>O<sub>2</sub> (29.05 %) and with 0.01M H<sub>2</sub>SO<sub>4</sub> with addition of O<sub>2</sub> (44.26%). The highest copper concentrations in leaching solution in treatment the non-rinsed samples were measured in the experiments on samples from the deeper levels of tailing dump (10 m - 20 m): with 0.01M H<sub>2</sub>SO<sub>4</sub> without oxidant (1.614 g/dm<sup>3</sup> – 1.992 g/dm<sup>3</sup>), with 0.01M H<sub>2</sub>SO<sub>4</sub> with addition of 3% H<sub>2</sub>O<sub>2</sub> (1.780 g/dm<sup>3</sup> – 2.188 g/dm<sup>3</sup>) and with 0.01M H<sub>2</sub>SO<sub>4</sub> with addition of O<sub>2</sub> (1.412 g/dm<sup>3</sup> – 1.723 g/dm<sup>3</sup>). High degrees of copper leaching shows that the flotation tailing dumps are potentially good basis for the further obtaining of a copper and at the same time has the great influence to the decrease of the pollution of surrounding soil and water systems. On the other hand, the results obtained on fresh samples from realized drill holes also indicate the real possibility of use some metallurgical methods for recovery of the present copper. This suggests the necessity of a complex approach, which should solve the environmental problem with possible achievement in terms of certain economic effects.

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