Investigation of the possibility of copper recovery from the flotation tailings by acid leaching

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Abstract

The flotation tailings pond of the Bor Copper Mine poses a great ecological problem not only for the town of Bor but also for the surrounding soils and watercourses. Since the old flotation tailings contain about 0.2% of copper on the average, we investigated their leaching with sulphuric acid in the absence and presence of an oxidant. The aim was to determine the leaching kinetics of copper and iron as affected by various factors such as: the pH value of the leach solution, stirring speed, pulp density, particle size, concentration of ferric ions, temperature and time for leaching. The average copper and iron recovery obtained was from 60% to 70% and from 2% to 3%, respectively. These results indicate that the old flotation tailings pond represents an important source of secondary raw material for the extraction of copper and that it should be valorized rather than land reclamation. At the end of the paper, a mechanism of dissolution of copper and iron minerals from the tailings was described.
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Keywords: Flotation tailings pond; Leaching; Sulphuric acid; Copper

1. Introduction

Mining is the most obtrusive of man's modification of the environment and mining activities are well known for their deleterious effect on the environment. A harmful effect of mining activities is reflected in the degradation of large areas of land (open pits), disposal of large volumes of solid waste and the occurrence of acid mine drainage [1,2]. This is typical of copper extraction from sulphide ores [3,4]. For instance, in the Aitic Copper Mine in northern Sweden, which is one of the biggest copper mines in Europe, the mass of the extracted copper per ton of ground ore is only 3 kg, whereas the average Cu content in the ore is 0.4%, which is about the world average [5]. In copper recovery from such low-grade sulphide ores, it is customary to use hydrometallurgical processes (leaching, solvent extraction and electrowinning) or beneficiation is performed by froth flotation (including crushing, grinding, flotation, thickening and drying of the concentrate), which is followed by pyrometallurgical treatment of the concentrate and electrolysis.

According to the data of KGHM Company, Polska MEIDZ S.A., the greatest flow of waste, about 94% of the mined material arises in the flotation process representing flotation tailings. In El Teniente-Codelco copper mine this percentage is in the range 90–95% [4]. Regarding data from 1998, froth flotation has 44% in total amount copper lost (around 25% of the copper contained in the initial reserves is not extracted) [6]. Disposing of the flotation tailings, which usually consist of sand, mud, pyrite, residual metal sulfides and reagents, can cause serious ecological problems with time if the tailings pond is not properly stabilized. This is particularly characteristic of the municipality of Bor (East Serbia), in which mining and metallurgical operations cause air, soil and water pollution.

Mining production in Bor started in 1903 by underground mining. The open pit operations started in 1912 and were performed until 1986. There are two more copper mines in the municipality—at Veliki Krivelj (opened in 1979) and Cerovo (opened in 1990). The Bor Copper Mine, that is, the town of Bor is situated in eastern Serbia, 220 km away from Bel-
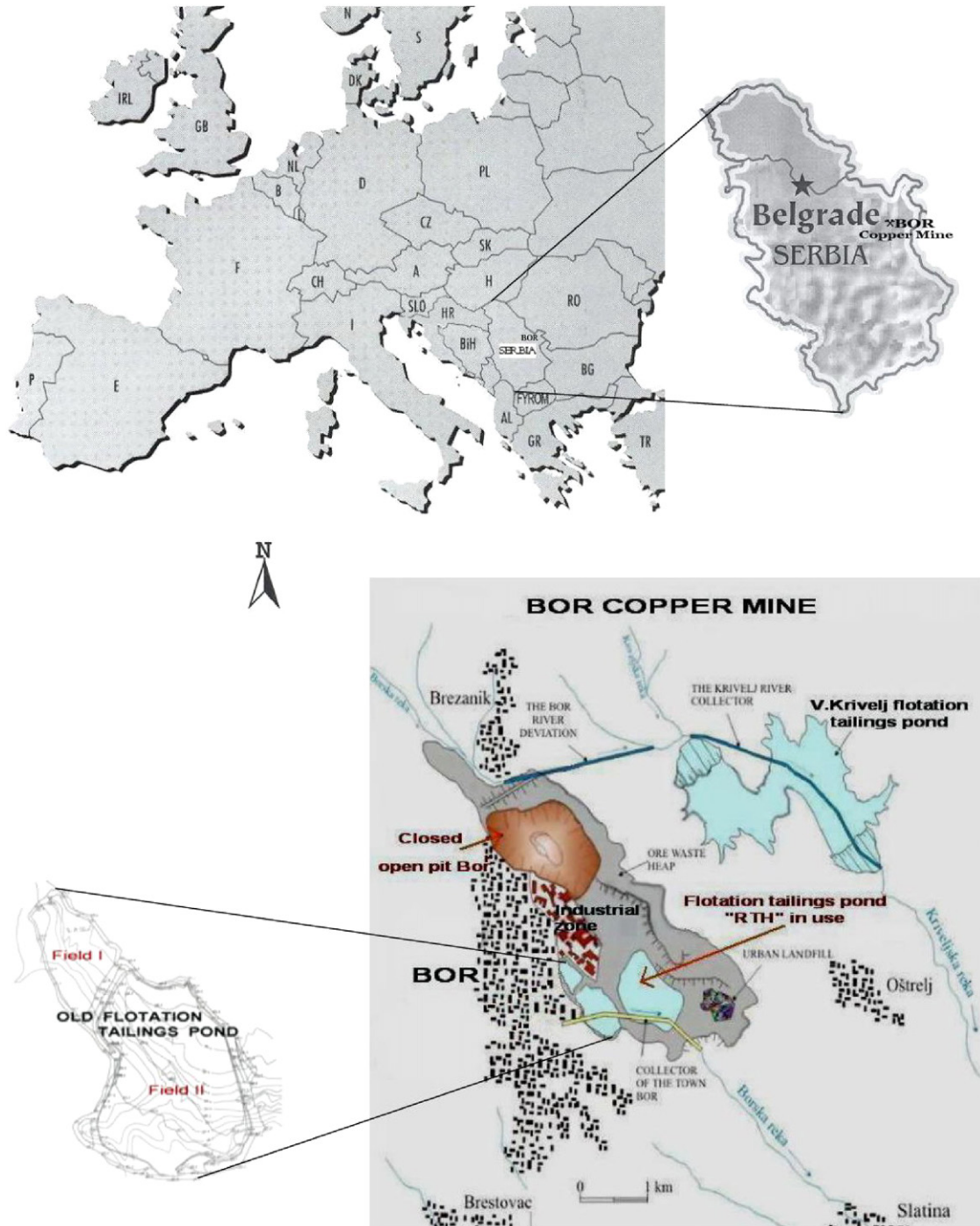
Fig. 1. Location and appearance of the Bor Copper Mine and the flotation tailings pond.

grade and about 30 km away from the Bulgarian border. The mine is located on the northeastern rim of the town so that the open pit and the flotation tailings pond make a boundary between the urban and the industrial zone (Fig. 1). Owing to the fact that the town was built in the near vicinity of the mine, as well as the location of the copper smelting plant and two more mines nearby, which are comprised by RTB Bor (the Copper Mining and Smelting Complex Bor), the town itself represents a serious environmental hot spot of Serbia and Europe.

According to the data for 2002, 207 Mt of flotation tailings, 450 Mt of overburden and 23 Mt of slag were disposed of on the territory of Bor municipality, which amounts to 11333.3 t of waste per inhabitant of the municipality. Over 68% of the Bor mining area has been ruined by waste dumps and tailings ponds [7]. Since remediation is often costly and requires huge investments, many mines in the world (active, closed, derelict) are affected by weathering and are only partly stabilized [5,8–12].

In the Bor Copper Mine, the dam slopes of the flotation tailings pond have been recultived. However, the horizontal area,

Table 1
Results of the previous investigations of copper leaching from the flotation tailings of the Bor Copper Mine

Scientific-research institution	Chemical composition of the sample				t (h)	Experimental parameters			X_{Cu} (%)
	Cu_{cum} (%)	Cu_{ox} (%)	Fe (%)	S (%)		[H_2SO_4] (g/l)	T (°C)	S:L	
IHTM, Institute for Chemistry Technology and Metallurgy	0.17	0.072	8.69	9.22	1	4.9	20	1:5	34.6
					360	4.9	20	1:5	34.7
					1	4.9	20	1:5	30.0
					360	4.9	20	1:5	37.8
ITNMS, Institute for the Technology of Nuclear and Other Mineral Resources, Belgrade, Serbia	0.153	0.061	7.64	8.81	24	15	20	1:1	32.2
					24	30	20	1:1	38.2
					24	40	20	1:1	42.9
					24	40	20	1:1	42.9
					24	40	83	1:1	43.6
					1	40	20	1:1	32.3
					8	40	20	1:1	36.7
					24	40	20	1:1	42.9
Davy Mc Kee, London, England	0.166	0.070	8.24	9.44	24	59	20	1:2	52.7
					24	59	40	1:2	53.8
					24	59	60	1:2	54.8
					2	59	20	1:1	34.9
					5	59	20	1:1	36.1
					24	59	20	1:1	47.9
					48	59	20	1:1	52.7
					24	20.8	20	1:1	34.9
					24	30.8	20	1:1	38.6
					24	41.8	20	1:1	44.0
					24	59	20	1:1	52.7

which is a source of mineral dust, has not been recultived. Consequently, the dust is dispersed towards the urban area and the areas of fertile land depending on the wind rose and precipitation.

The Bor flotation tailings pond was created by disposing of tailings from the flotation plant in the period from 1933 to 1987. It is located in the Borska River valley, whereas the municipal sewage collector is located underneath. This collector was damaged in the 1950s causing the tailings spill which turned the banks of the Borska and Veliki Timok Rivers into a wasteland. On that occasion more than 2500 ha of the most fertile land were ruined. Apart from being the greatest source of mineral dust, this tailings pond, since it has been out of use for 18 years, has become the source of acid mine drainage waters which contain heavy metals and pollute the nearby soil as well as surface and underground waters. In addition, considerable amounts of copper and the accompanying valuable metals are lost. Considering the current price of copper in the world, and predictions that the demand for this metal will increase, as well as a very low copper content in the ore which is being extracted today (about 0.4%), the flotation tailings pond of the Bor Copper Mine represents an important source of secondary raw material for copper production. This is in accordance with the situation in this field in the world, since scientific and technological development has necessitated and enabled recovery of the valuable components from the raw materials in which copper content is about 0.2–0.3%. At the time when high-grade ore was mined, these tailings were impossible to process economically. A good example which illustrates how these raw materials are processed in the world is the flotation tailings pond of the Miami mine in Arizona which belongs to Magma Corporation [13]. At this mine, 34.5 Mt of

waste with an average copper content of 0.33% (consisting of 55% oxide and 45% sulphide copper) were disposed of in the waste dumps created by open pit mining operations and into the flotation tailings pond. Since 1986, when pyrometallurgical copper production stopped, only chemical methods of copper concentration have been employed at the mine. Waste dumps are heap leached by percolation, whereas a plant for agitation leaching has been built for the treatment of flotation tailings.
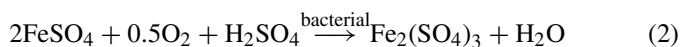
In the period from 1963 to 1987, explorations were performed several times on the borehole samples from the waste dumps with the aim of valorizing the valuable components. Apart from geological investigation, a possibility of copper recovery was investigated, but the obtained results were not satisfactory. Furthermore, a possibility of flotation of pyrite tailings was investigated by applying the flow sheet used at the Bor flotation plant. It was found that a pyrite concentrate of commercial quality can be obtained and the process flow sheet was proposed. It included first acid leaching of copper followed by flotation of pyrite. Unfortunately, for some reason, these explorations have never been completed and can be considered only preliminary. Investigations of the possibility of copper leaching from the flotation tailings of the Bor Copper Mine have been performed by a number of scientific and research institutions. Chemical compositions of the samples, experimental conditions as well as the results obtained in these investigations are presented in Table 1. The results showed that leaching with sulphuric acid resulted in relatively low copper dissolution values, which was a limiting factor for further treatment of tailings [14].

Following the period mentioned above, our country went through a period of economic sanctions, the war and great social
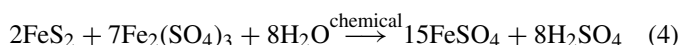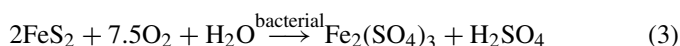
and political changes. These days, environmental and economic considerations coupled with scientific and technological developments have again brought into focus our tailings ponds as potential sources of raw materials. The aim of this paper was to make a modest contribution to resolving the issue of the flotation tailings pond of the Bor Copper Mine.

For that reason, we investigated the leaching of flotation tailings with sulphuric acid in the absence and presence of oxidants. The intention was to determine the kinetics of copper and iron dissolution from flotation tailings and to use the obtained results in planning further activities. This is necessary because with time, the oxidation of pyrite and the accompanying sulphides will create great ecological problems since spontaneous leaching can last tens even hundreds of years.

The oxidation of pyrite from flotation tailings as a result of weathering can be represented by the following reactions [1,15–17]:
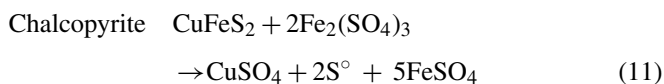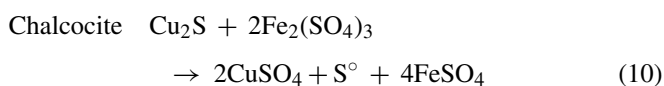
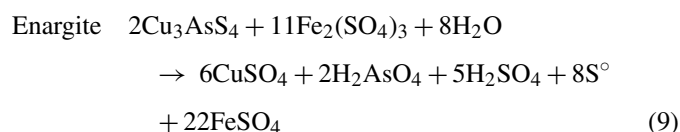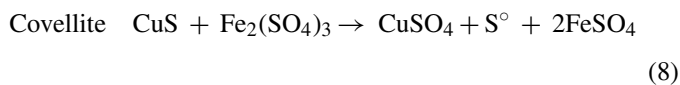$$2FeS_2 + 7O_2 + 2H_2O \overset{chemical}{\longrightarrow} 2FeSO_4 + 2H_2SO_4 \tag{1}$$

$$2FeSO_4 + 0.5O_2 + H_2SO_4 \overset{bacterial}{\longrightarrow} Fe_2(SO_4)_3 + H_2O \tag{2}$$

Summary reaction (1 + 2 = 3)

$$2FeS_2 + 7.5O_2 + H_2O \overset{bacterial}{\longrightarrow} Fe_2(SO_4)_3 + H_2SO_4 \tag{3}$$

$$2FeS_2 + 7Fe_2(SO_4)_3 + 8H_2O \overset{chemical}{\longrightarrow} 15FeSO_4 + 8H_2SO_4 \tag{4}$$

$$FeS_2 + Fe_2(SO_4)_3 \overset{chemical}{\longrightarrow} 3FeSO_4 + 2S^\circ \tag{5}$$

$$S^\circ + H_2O + 1.5O_2 \overset{bacterial}{\longrightarrow} H_2SO_4 \tag{6}$$

The above reactions describe how acidity is generated and maintained in waste dumps as a result of pyrite oxidation through a bacteriochemical process. These reactions occur up to pH 3, whereas pyrite oxidation above pH 3 can be described by the following reaction:

$$FeS_2 + 3.75O_2 + 3.5H_2O \rightarrow Fe(OH)_3 + 2H_2SO_4 \tag{7}$$
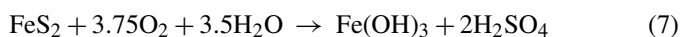
Eq. (3) shows that pyrite oxidation results in the formation of sulphuric acid, iron (III) and heat, since the reaction is exothermic. The reaction products are very harmful because they pollute the drainage waters and can cause autocatalytic pyrite oxidation (reactions (4) and (5)). Furthermore, iron (III) can oxidise other sulphide minerals which release heavy metals maintained in the solution by the acid medium [18–20]. In this particular case, since copper minerals in the tailings are of greatest interest, their dissolution can be represented by the following reactions [16]:

$$Covellite \quad CuS + Fe_2(SO_4)_3 \rightarrow CuSO_4 + S^\circ + 2FeSO_4 \tag{8}$$

$$Enargite \quad 2Cu_3AsS_4 + 11Fe_2(SO_4)_3 + 8H_2O$$
$$\rightarrow 6CuSO_4 + 2H_2AsO_4 + 5H_2SO_4 + 8S^\circ$$
$$+ 22FeSO_4 \tag{9}$$

$$Chalcocite \quad Cu_2S + 2Fe_2(SO_4)_3$$
$$\rightarrow 2CuSO_4 + S^\circ + 4FeSO_4 \tag{10}$$

$$Chalcopyrite \quad CuFeS_2 + 2Fe_2(SO_4)_3$$
$$\rightarrow CuSO_4 + 2S^\circ + 5FeSO_4 \tag{11}$$

Positive results of this investigation would direct further activities towards the treatment of flotation tailings aimed at copper recovery. Negative results would indicate the necessity for immediate phytoremediation activities of the flotation tailings pond as one of the best methods today [21], the application of which has given good results at the RTB Bor.

2. Experimental

2.1. Characteristics of the Bor flotation tailings pond

During the exploitation stage the Bor flotation tailings pond was divided into three fields separated by the cyclone sand dams. Field III is covered with the overburden from the open pit operations and with the ash from the thermoelectric power plant so that only the tailings from Fields I and II were investigated (Fig. 1). Flotation tailings in the form of mud, dust and sand were disposed of in the Borska River valley. Their colour ranges from yellow-grey to dark-grey and black depending on the initial raw materials and various agents. Tailings disposal was performed in a classical way. First, an initial dam, formed out of coarse sand particles and overburden, was built downstream and then flotation tailings were disposed of along the upstream valley of the Borska River.

According to the data from the technical documentation and the existing literature of the Bor Copper Mine, the disposal of the flotation tailings was started by the French in the north part of the Bor brook. This was going on from 1934 to 1941 when the Germans continued disposing of flotation tailings in the lower, southern parts of the Bor brook. Immediately after World War II, upon completion of the reconstruction of the mine, the disposal of tailings continued. In consequence, the whole valley of the Borska River was filled up with flotation tailings and the terrain was roughly flattened and levelled at an approximate elevation of 356 m in the central part of Field I and at an average elevation of 369 m in the flotation tailings pond of Field II.

Specifically, south of flotation Field I, across the Borska River and between the flotation plants, a dam was built consisting of flotation sand, whereas about 600 m downstream another dam was built. Between them the flotation tailings were disposed of in such a way that the coarsest particles were separated and deposited on the banks of the Borska River, whereas the central part was filled with fine flotation tailings.

As it has been previously said, tailings disposal was performed until 1987 and the ultimate heights of dams are:

- upstream dam next to the flotation plants was completed at an elevation of 372 m;

Table 2
Chemical characterization of the flotation tailings

Cu_{cum} (%)	0.20
Cu_{ox} (%)	0.0975
Fe (%)	8.69
Zn (%)	0.003
As (%)	0.014
S (%)	10.58
Au (g/t)	0.35
Ag (g/t)	3.0
SiO_2 (%)	53.34
Al_2O_3 (%)	8.52

- downstream dam was completed at an elevation of 373 m with an average tailings pond elevation of 369 m.

The average tailings pond depth is about 30 m.

The quantity of the discharged tailings amounts to: Field I, 3922.146 t; Field II, 22846.122 t; total, 26768. 268 t.

On the basis of geological drillings performed in 1963 and 1987 it was determined that the copper content in the old flotation tailings averaged about 0.2%, gold between 0.3 g/t and 0.6 g/t, silver 2.5 g/t and sulphur 10.5% [14].

2.2. Characteristics of the flotation tailings sample used in the investigation

For experimental investigations a sample made of exploration borehole cores was used. They were taken at a depth of 16–40 m during the summer of 1998. The tailings from the cores were sorted according to the depth of the boreholes and then dried, vacuum-packed in nontransparent plastic bags and kept in a special storehouse. In order to make a representative sample of the investigated tailings pond, a composite was made of the cores from all the boreholes in Fields I and II.

Particle size distribution in a sample of flotation tailings was determined by the sieve analysis on the standard Tyler sieve series as shown in Fig. 2.

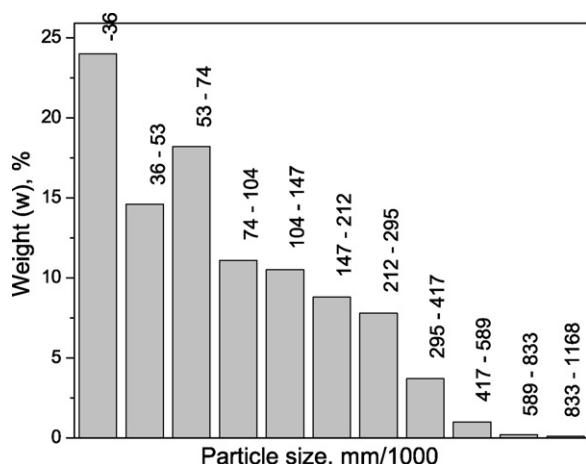Chemical composition of a flotation tailings sample is given in Table 2.

Fig. 2. Particle size distribution in a flotation tailings sample.

Copper and iron contents were determined for certain sieve fractions as shown in Table 3. The last three rows of this table show copper and iron contents for sieve fractions −0.074 mm and +0.074 mm. This is because in mineral processing of copper ores, sieve fraction −0.074 mm is considered standard for determining the degree of liberation of copper minerals.

By qualitative and quantitative mineralogical analysis of tailing sample it was found that content of sulfidic minerals was 21%. In the sample there is 20.81% of pyrite minerals. It found that other minerals (78%) in the sample were silicates, quarc and carbonates, while there are of oxide about 1%. The following copper sulphide minerals were found: covellite (0.081%), enargite (0.037%), chalcopyrite (0.049%) and chalcocite (0.018%). The most abundant copper sulphide is covellite, whereas other minerals appear to a far lesser extent and in the smallest sieve fractions. According to the results obtained by mineralogical analysis in sieve fractions below the 74 μm range, copper minerals are mostly free, whereas a smaller part is associated with quartz and pyrite. Above the 74 μm range, copper minerals are rarely found free, and the most abundant are the intergrowths of covellite and quartz. Since covellite is the main copper bearing mineral in the tailings, its percentage in some sieve fractions is as follows: in the sieve fraction +0.212 mm, 85.7% of covellite is associated with quartz, whereas 14.3% is associated with quartz and pyrite; in the fraction range −0.212 + 0.147 mm 77.8% covellite is associated with quartz; the fraction range −0.147 + 0.074 mm contains 74% of covellite–quartz intergrowths; in the fraction range −0.074 + 0.036 mm only 10% of covellite is associated with quartz and pyrite; in the smallest fraction −0.036 mm 92.1% of covellite is in the free form, whereas 7.6% is associated with quartz and 0.3% with quartz and pyrite.

2.3. Experimental setup

Leaching of the flotation tailings was performed in a 1000-ml glass reactor which was equipped with a mechanical and electromagnetic stirrer. As the leach solutions 500 ml of sulphuric acid and acidified tap water was used. pH value was being adjusted by adding sulphuric acid.

During the experiment the leach solution was first poured into the reactor and then a 100-g sample of tailings (fraction −0.074 mm) was added while stirring, thereby forming the pulp. The experiments were monitored as a function of time and the

Table 3
Copper and iron contents per sieve fractions

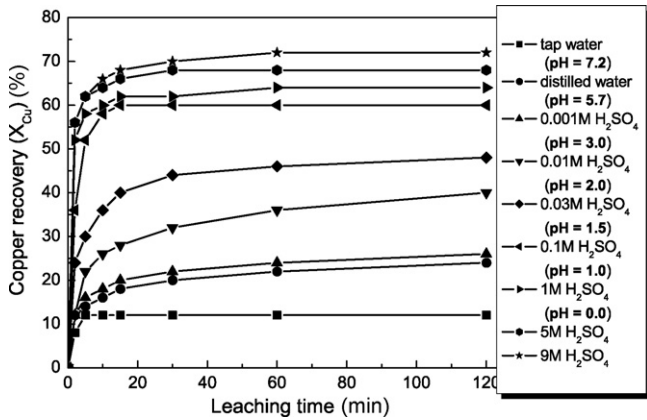| Sieve fraction (mm)	w (%)	Cu (%)	Fe (%)
+0.212	12.8	0.15	6.08
−0.212 + 0.147	8.8	0.14	8.52
−0.147 + 0.074	21.6	0.18	8.26
−0.074 + 0.036	32.8	0.16	7.31
−0.036	24.0	0.36	12.34
Σ	100.0		
+0.074	43.2	0.16	7.60
−0.074	56.8	0.25	9.44
Σ	100.0	0.211	8.645

Fig. 3. Effect of leach solution acidity on copper recovery as a function of time.

stirring was interrupted at regular intervals to enable sampling. Each time a 5-ml liquid-phase sample was pipetted, filtered, diluted with water to 100 ml in a volumetric flask and analysed by the AAS method for the determination of copper and iron contents. Most experiments were carried out at room temperature, at a stirring speed of 600 min^{-1} and during a period of 120 min. In order to investigate the effects of various factors (stirring speed, temperature, time, pulp density, etc.) some of the mentioned parameters were varied within the range defined by the experiment.

2.4. The choice of the leaching agents

The main agent chosen for the leaching of flotation tailings was sulphuric acid, whereas iron (III) sulphate was used as an oxidant. Sulphuric acid was chosen because it is a cheap and easily available reagent which is produced at RTB Bor. However, more importantly, sulphuric acid and iron (III) sulphate are formed by natural leaching of sulphide minerals (FeS_2, $CuFeS_2$) under the influence of the oxygen from the air, water and bacteria (*Thiobacillus ferrooxidans*). The results of the investigation of the effect of these reagents on the leaching of flotation tailings can be used to predict roughly the possible developments in the

Fig. 4. Final percentage of copper and iron leaching recoveries with respect to the initial pH of the leach solution.
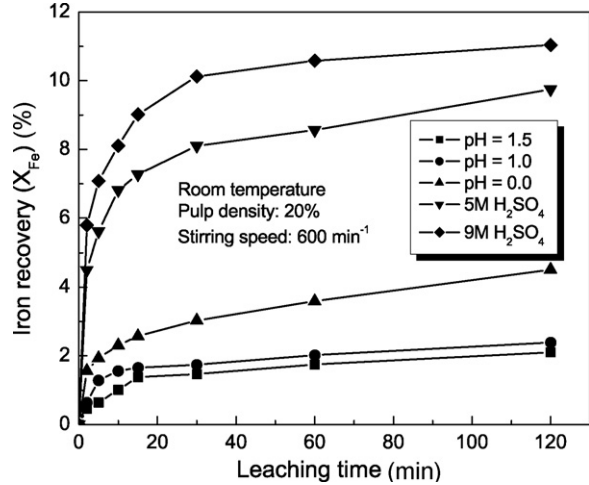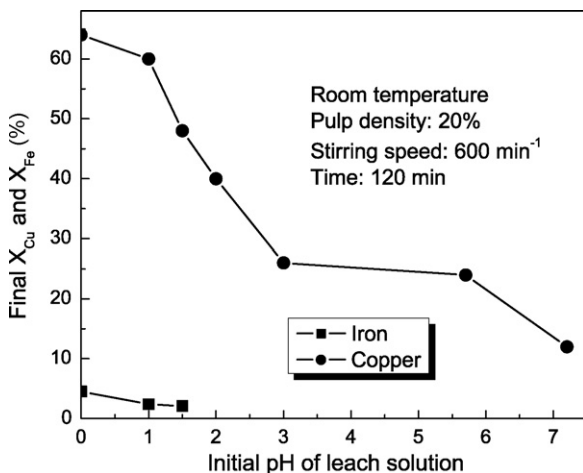

Fig. 5. Effect of leach solution acidity on iron recovery as a function of time.

old flotation tailings pond of the Bor Copper Mine in the next period if it is still exposed to weathering.

3. Results and discussion

3.1. The effect of initial pH

This effect was investigated by leaching flotation tailings with water solutions of various pH values. Depending on the desired pH value, the solutions were prepared from tap water and sulphuric acid, whereas distilled water was used as a leaching agent. The percentage recovery of copper X_{Cu} and iron X_{Fe} was followed over time for a wider pH range (from a neutral to a very acid medium). The obtained results are presented in Figs. 3–5.

During the experiments at pH 1–3, the change of the pH of the leach solution was monitored over time as shown in Table 4.

The presented results show that with increasing concentration of H$^+$ ions in the leach solution, the dissolution of copper and iron increased, which was expected (Figs. 3–5). It can also be seen that, iron minerals (pyrite) occur only at pH values lower than 1.5 (Figs. 4 and 5). This is logical, having in mind the fact that pyrite is a very inert mineral with a high open-circuit potential. In the pulp, pyrite can increase the dissolution rate of the present copper minerals as a result of galvanic interactions with them, whereas it remains undissolved.

Although oxidants were not added during the experiments, except for the oxygen from the air, a relatively high copper dissolution values were achieved indicating the presence of readily leachable copper oxides in the tailings. As shown in
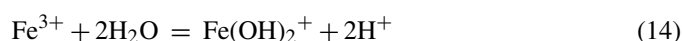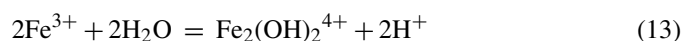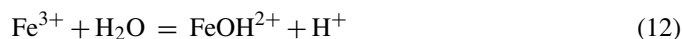
Table 4
The change of the pH of the pulp with time at room temperature, solid-phase concentration of 20% and a stirring speed of 600 min^{-1}

Time (min)	pH 1.0	pH 2.0	pH 3.0
0	1.00	2.00	3.00
30	1.25	2.10	3.08
60	1.30	2.10	3.08
90	1.30	2.10	3.08
120	1.30	2.10	3.08

Figs. 3 and 4 copper dissolution is also noticeable in tap water and distilled water indicating the presence of copper sulphate which is soluble in plain water. Since flotation tailings have been exposed to weathering for many years, it resulted in the oxidation of some copper sulphides and formation of secondary copper minerals such as cuprite Cu_2O, tenorite CuO, chalcanthite $CuSO_4 \cdot 5H_2O$, brochantite $CuSO_4 \cdot 3Cu(OH)_2$, azurite $2CuCO_3 \cdot Cu(OH)_2$, malachite $CuCO_3 \cdot Cu(OH)_2$ i chrysocola $CuO \cdot SiO_2 \cdot 2H_2O$. The minerals are detected in the flotation tailings in prevoius study [22].

The experiments carried out in very acid conditions (1 M, 5 M and 9 M H_2SO_4) enabled a better understanding of the effect of sulphuric acid on copper and iron recoveries. Fig. 3 shows that, although copper recovery increases with increased H_2SO_4 concentrations from 1 M to 9 M, this effect is much less pronounced than in the case of lower concentrations (0.1–0.001 M). Consequently, 0.1 M sulphuric acid concentration (pH 1) can be considered optimal for further investigations considering the obtained results (Fig. 4), H_2SO_4 consumption and negligible iron dissolution (2.39%). Higher iron dissolution occurs only at the highest H_2SO_4 concentrations (5 M and 9 M), which is due to higher dissolution of iron bearing sulphide minerals (chalcopyrite, pyrite). Table 4 indicates that at pH 2 and 3, the pH value of the leach solution is almost constant throughout the experiment (120 min). This is probably the result of the hydrolysis of iron which is represented by the equations

$$Fe^{3+} + H_2O = FeOH^{2+} + H^+ \tag{12}$$

$$2Fe^{3+} + 2H_2O = Fe_2(OH)_2{}^{4+} + 2H^+ \tag{13}$$

$$Fe^{3+} + 2H_2O = Fe(OH)_2{}^+ + 2H^+ \tag{14}$$

The released protons cause an acid reaction in the solution. Thus, sulphuric acid consumption is slightly reduced and the acidity in the solution is partly maintained during the investigated interval.

In the experiment carried out at pH 1, an increase in pH value was observed in the first 30 min, whereas in the next 30 min interval it became constant and remained unchanged until the end of the experiment. Since at such a low pH value, the hydrolysis of iron does not occur to a greater extent, it seems probable that after the reaction with oxides and carbonates no side reactions occur in the solution, which would cause a greater consumption of sulphuric acid. An increase in the pH value, that is, the increased sulphuric acid consumption is logical due to higher copper and

iron dissolution at this pH than at pH 2 and 3 (reactions (15) and (16)). Also, an increase in the pH correlates well with the percentage of copper and iron leached—namely, copper dissolution at initial pH 1 occurs only in the first 15 min whereupon it remains constant. Iron dissolution is also highest at the beginning of the reaction, although, due to low dissolution degree, it cannot significantly affect the pH, that is, the consumption of sulphuric acid.

$$CuO + H_2SO_4 = CuSO_4 + H_2O \tag{15}$$

$$2Fe(OH)_3 + 3H_2SO_4 = Fe_2(SO_4)_3 + 6H_2O \tag{16}$$
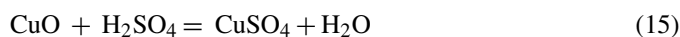
3.2. The effect of pulp density (solid-phase concentration)

This effect was investigated by leaching tailings with 0.1 M H_2SO_4 solution at room temperature and at a stirring speed of $600 \, min^{-1}$. The tailings content in the pulp ranged from 20%, 25%, 33%, and 50% corresponding to the solid–liquid ratio 1:5, 1:4, 1:3 and 1:2. The obtained results are presented in Table 5.

By studying the presented results it can be concluded that the solid reagent concentration has no significant effect on copper and iron dissolution since similar values of dissolution degree were achieved with various pulp densities. For that reason, further experiments were carried out at a solid-phase concentration of 20%.

3.3. The effect of the stirring speed

The effect of stirring on the leaching of flotation tailings was examined at stirring speeds of $300 \, min^{-1}$, $600 \, min^{-1}$ and $900 \, min^{-1}$ in a solution containing 1 M H_2SO_4, at room temperature, and with a pulp density of 20%. In addition, the leaching of the tailings was examined under the same conditions in the absence of stirring. Experimental results (Table 6) show that stirring does not affect copper and iron leaching in the examined range. Somewhat lower copper and iron dissolution values were attained without stirring. The obtained results confirm the previous conclusion that readily soluble copper oxides and sulphides are present in the tailings.

3.4. The effect of particle size

The effect of the particle size on the rate copper and iron leaching was examined with various sieve fractions rang-

Table 5
The effect of solid-phase concentration on copper and iron dissolution at room temperature, pH 1 and at a stirring speed of $600 \, min^{-1}$

Time (min)	20% solid		25% solid		33% solid		50% solid	
	X_{Cu} (%)	X_{Fe} (%)	X_{Cu} (%)	X_{Fe} (%)	X_{Cu} (%)	X_{Fe} (%)	X_{Cu} (%)	X_{Fe} (%)
2	36	0.64	36	0.58	48	1.47	34	0.96
5	52	1.28	48	1.18	56	1.56	48	1.40
10	58	1.56	52	1.44	60	1.65	50	1.58
15	60	1.65	54	1.51	62	1.74	52	1.70
30	60	1.74	56	1.65	62	1.90	54	1.88
60	60	2.02	58	1.95	64	2.22	56	2.16
120	60	2.39	60	2.3	64	2.52	58	2.46

Table 6
The effect of the stirring speed on the rate copper and iron leaching at room temperature, pH 1 and a pulp density of 20%

Time (min)	Without stirring		$300 \, min^{-1}$		$600 \, min^{-1}$		$900 \, min^{-1}$	
	X_{Cu} (%)	X_{Fe} (%)	X_{Cu} (%)	X_{Fe} (%)	X_{Cu} (%)	X_{Fe} (%)	X_{Cu} (%)	X_{Fe} (%)
2	28	0.52	32	0.58	36	0.64	36	0.60
5	34	0.84	50	0.92	52	1.28	52	1.10
10	44	1.08	54	1.18	58	1.56	60	1.32
15	50	1.20	58	1.30	60	1.65	60	1.48
30	52	1.32	60	1.52	60	1.84	60	1.62
60	52	1.40	60	1.74	60	2.02	60	1.80
120	52	1.44	60	1.98	60	2.22	60	2.12

ing from +0.212 mm to −0.036 mm under the aforementioned conditions. From the results presented in Fig. 6 it can be concluded that the greatest percentage of the dissolved copper is obtained with smaller fractions. In fraction −0.074 mm, copper dissolution was 58%, whereas in fraction +0.074 mm, it was 4.92%. The highest copper dissolution was achieved with the lowest fraction −0.036 mm and amounted to as much as 74%.

The obtained results are quite logical considering the fact that the smaller the particle size the larger the surface of the mineral in contact with the leach solution, which results in higher copper dissolution rate. Moreover, these results are consistent with mineralogical composition of the raw material presented above. In the coarser fraction range above 74 μm, free grains of copper minerals, mostly covellite, comprise up to 25%, and the rest are quartz–pyrite intergrowths. In the fraction range below 74 μm, free covellite grains comprise 90%, which accounts for considerably higher copper dissolution since almost whole mineral surface is exposed to the leach solution.

The iron dissolution degree per sieve fraction is mostly the same and very low (Fig. 7). Somewhat higher iron dissolution (2.71%) occurs in fraction −74 μm, which cannot be accounted for. It could be caused by a higher content of readily leachable hydroxides and iron sulphates in that particular sieve fraction.
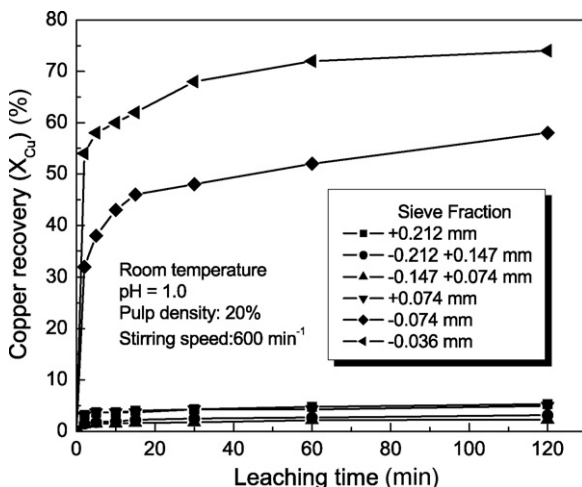
3.5. The effect of iron (III) sulphate concentration

This investigation was carried out by leaching flotation tailings with H_2SO_4 and iron (III) sulphate solutions in which iron (III) concentration was varied in the range of 0.5–10 g/l. The results of the investigation are given in Table 7. The presented results lead us to a conclusion that the presence of Fe^{3+} ions in the sulphate solution has very little effect on copper dissolution. The obtained copper dissolution values are approximately the same and differ by only ±4%.

The obtained results are consistent with the results of the investigation into dissolution of pure covellite conducted by Dutrizac and MacDonalds, and Hirato and coworkers [23–24].
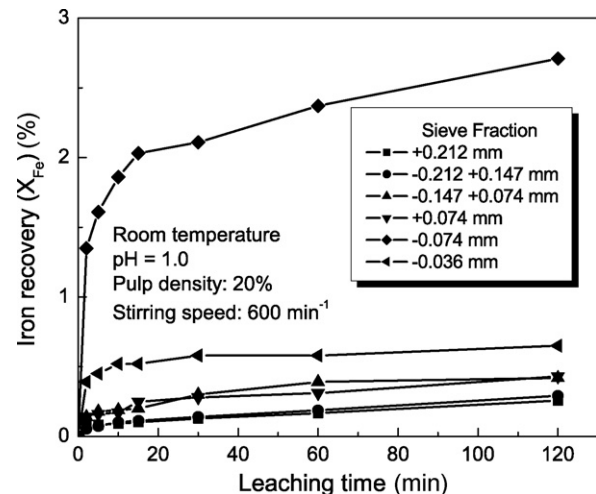

Fig. 7. The effect of particle size on iron leaching recovery as a function of time.

Table 7
The effect of iron (III) sulphate on copper dissolution at room temperature, pH 1, pulp density of 20% and a stirring speed of $600 \, min^{-1}$

Time (min)	X_{Cu} (%)				
	0.5 g/l Fe^{3+}	1 g/l Fe^{3+}	2 g/l Fe^{3+}	5 g/l Fe^{3+}	10 g/l Fe^{3+}
2	52	52	52	56	52
5	56	56	60	60	56
10	60	60	64	64	60
15	64	64	68	68	60
30	64	64	68	68	60
60	64	64	68	68	60
120	64	64	68	68	60

Fig. 6. The effect of particle size on copper leaching recovery as a function of time.

Table 8
The effect of temperature on copper and iron leaching recovery (without the addition of an oxidant) at pH 1, pulp density of 20% and a stirring speed of $600\,min^{-1}$

Time (h)	X_{Cu} (%)	
	Without oxidant	$Fe_2(SO_4)_3$, 5 g/l Fe^{3+}
2	60	68
4	60	68
6	60	72
8	60	76
24	60	76
26	60	80
28	64	84
30	64	88
32	68	88

Table 9
The effect of temperature on copper and iron leaching recovery (without the addition of an oxidant) at pH 1, pulp density of 20% and a stirring speed of $600\,min^{-1}$

Time (min)	20 °C		40 °C		60 °C	
	X_{Cu} (%)	X_{Fe} (%)	X_{Cu} (%)	X_{Fe} (%)	X_{Cu} (%)	X_{Fe} (%)
2	36	0.64	52	1.74	56	2.10
5	52	1.28	56	2.20	60	2.94
10	60	1.56	60	2.57	62	3.30
15	60	1.65	61	2.76	64	3.49
30	60	1.74	62	2.94	68	3.77
60	60	2.02	64	3.40	68	4.23
120	60	2.39	65	3.95	70	5.43

They investigated the effect of Fe^{3+} ions on the dissolution of pure covellite. Based on the obtained results, they found that the rate of reaction

$$CuS + 2Fe^{3+} \rightarrow Cu^{2+} + 2Fe^{2+} + S^{\circ}, \tag{17}$$
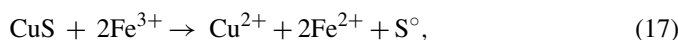
is directly dependent on Fe^{3+} ions for concentrations below 0.28 g/l. They also established that the rate of the reaction is determined by the rate of the reaction on the surface of a mineral, i.e. that it is chemically controlled. Sulphur, which was a product of the reaction, did not form a protective layer around the mineral grain. The results obtained by Dutrizac and MacDonalds, and Hirato and coworkers [23–24] are fully consistent with the results of this study since the most abundant of all sulphide copper minerals in the flotation tailings is covellite.

However, in order to gain a better insight into the effect of $Fe_2(SO_4)_3$ on the dissolution of copper from flotation tailings, two more experiments were carried out under identical conditions but with a prolonged leaching time. The leaching agent used in one of them was sulphuric acid, whereas both sulphuric acid and iron (III) sulphate were used in the other. During the experiment, the pulp was stirred for the first 8 h and the sampling was performed every 2 h. Then, in the next 16 h stirring and sampling were not performed, whereupon the initial procedure was repeated in the next 8 h. The results of the investigation are given in Table 8. It can be seen that throughout the experiment copper recovery was higher when an oxidizing agent (iron (III)) was present in the leach solution. After 32 h of leaching, the achieved percentage recovery of copper was 88%, whereas it was 20% lower when sulphuric acid was used. Given that oxide copper content in a flotation tailings sample is almost 50%, it can be considered that after the dissolution of oxide copper minerals in this prolonged experiment, a considerable part of covellite as a predominant copper mineral was dissolved under the oxidizing influence of ferric ions. Smalley and Davis [16] found that copper recovery is 93% during treatment of copper ore by ferric sulphate leach pilot plant. They used following conditions: mild acidic sulphate solution of iron (III), 28 g/l; temperature, 85 °C and pulp density, 10–15%.

3.6. The effect of temperature

Leaching of the flotation tailings was carried out at temperatures of 20 °C, 40 °C and 60 °C in 0.1 M H_2SO_4 solutions, at a stirring speed of $600\,min^{-1}$ and a pulp density of 20%. In these experiments an electromagnetic stirrer was used with a heating plate enabling temperature regulation. Simultaneously, under the same conditions, the effect of temperature was examined when ferric sulphate was added at a concentration of 5 g/l Fe^{3+} ions. The results are presented in Tables 9 and 10. Evidently copper and iron dissolution increases with increasing temperature.

The data in Table 9 show that leaching with sulphuric acid gave 10% higher copper dissolution values at 60 °C than at 20 °C. It was also observed that iron dissolution was slightly higher (5.43% at 60 °C). Since the achieved dissolution after 32 h at room temperature was 5.24%, it can be assumed that, under the influence of temperature, apart from the dissolution of iron hydroxides and carbonates, partial pyrite oxidation occurred, probably only superficially due to its inertness.

The data from Table 10 indicate that in the presence of an oxidant (5 g/l Fe^{3+} ions), copper recovery from the tailings also increases with increasing temperature and at 60 °C it amounts to 80%, which is 12% higher than at 20 °C. It was also observed that copper dissolution values were 8–10% higher when an oxidant was present in the leach solution. High copper dissolution values of 80% at 60 °C after 2 h and 88% at room temperature after 32 h of leaching, point to the dissolution of a considerable

Table 10
The effect of temperature on copper leaching recovery with the addition of $Fe_2(SO_4)_3$ at a concentration of 5 g/l Fe^{3+} ions, at pH 1, a pulp density of 20% and a stirring speed of $600\,min^{-1}$

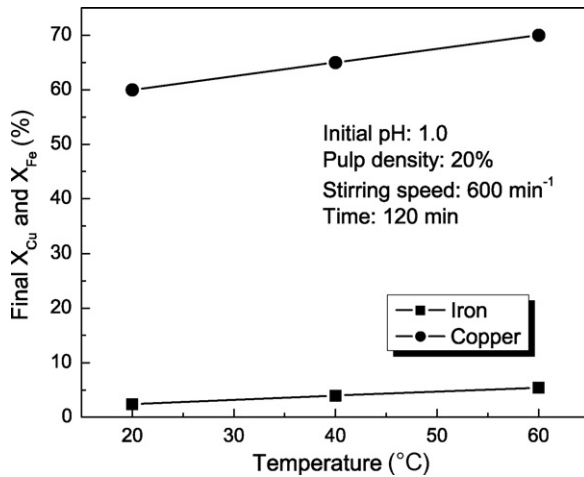| Time (min)	X_{Cu} (%)		
	20 °C	40 °C	60 °C
2	56	56	56
5	60	60	64
10	64	64	68
15	68	68	70
30	68	70	74
60	68	72	76
120	68	72	80

Fig. 8. The effect of temperature on the final percentage of copper and iron leaching recovery.

part of covellite, subsequent to the dissolution of copper oxide minerals.

Considering the observed rise in copper and iron dissolution with increasing temperature and almost linear dependence (Fig. 8) it can be concluded that covellite dissolution rate is dependent on the rate of the chemical reaction on the surface of the mineral.

This conclusion can be supported by the investigations conducted by Thomas and Ingraham [25]. These two researchers investigated the effect of temperature on the dissolution of pure covellite in a 0.1-M H_2SO_4 solution with the addition of iron (III) sulphate the concentration of which was 13 g/l Fe^{3+} ions. Based on the results of this study, they established that covellite dissolution rate is chemically controlled up to a temperature of 80 °C, above which the reaction rate is determined by the rate of diffusion through the solution.

4. The mechanism of copper and iron dissolution

According to the results of laboratory investigations it is possible to postulate a mechanism of dissolution of copper and iron minerals which is schematically presented in Fig. 9.
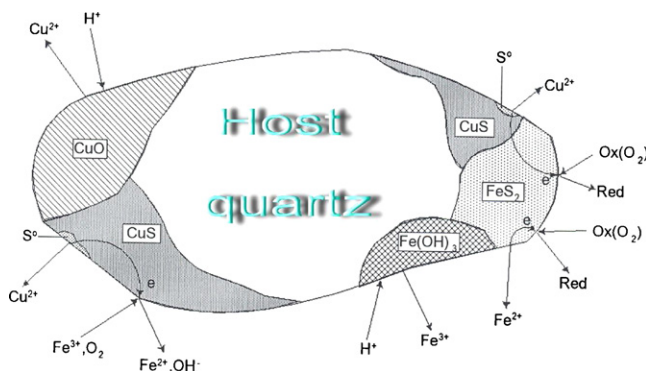

Fig. 9. Schematic representation of a mechanism of dissolution of copper and iron minerals on a flotation tailings particle model.

In leaching flotation tailings first tenorite dissolution occurs since it is the most readily leachable copper mineral with sulphuric acid. Tenorite dissolution is represented by the following reaction:

$$CuO + 2H^+ = Cu^{2+} + H_2O \tag{18}$$

that is, by the following reaction

$$CuO + H_2SO_4 = CuSO_4 + H_2O \tag{19}$$
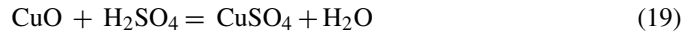
In the next stage, subsequent to the dissolution of oxides, the dissolution of copper sulphides takes place. First, covellite is dissolved as the most abundant copper sulphide in the flotation tailings. Covellite oxidation proceeds according to an electrochemical mechanism (Eqs. (20) and (21)) at the anode parts of the mineral [26]:

- Anode:

$$CuS - 2e^- = Cu^{2+} + S^° \tag{20}$$

whereas iron (III) reduction occurs at the cathode parts
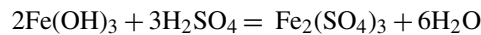
- Cathode:

$$Fe^{3+} + e^- = Fe^{2+} \tag{21}$$

Consequently, covellite dissolution in a sulphuric acid solution and in the presence of iron (III) can be represented by the following summary equation:

$$CuS + 2Fe^{3+} = Cu^{2+} + 2Fe^{2+} + S^°$$

Among iron minerals, hydroxides are dissolved first by the following reaction:

$$2Fe(OH)_3 + 3H_2SO_4 = Fe_2(SO_4)_3 + 6H_2O$$

Finally, the dissolution of pyrite, which is refractory iron sulphide, occurs to a certain extent as well. Pyrite dissolution in a sulphuric acid solution in the presence of iron (III) is represented by reactions (1)–(7) in Section 1.

5. Ecological aspect of the investigation

From the above investigations it can be seen that tap water and consequently atmospheric water can leach out copper from flotation tailings since they contain soluble copper forms. In the course of leaching, copper ions can be transferred to the surrounding soil and underground waters polluting the natural environment. In addition, the soil and the waters in the vicinity of the flotation tailings become more acid as a result of the formation of sulphuric acid due to pyrite oxidation by oxygen (Eqs. (1)–(7)). The increased acidity of the leach solutions can lead to a more intense dissolution of the present sulphide minerals, whereas atmospheric oxygen, which enters the leach solutions by dissolution and diffusion, intensifies the oxidizing action of those solutions resulting in accelerated leaching of minerals and the formation of copper, iron and sulphate ions. The tailings contain a certain amount of arsenic which can be released during

the leaching process contaminating the environment. Furthermore, the investigations carried out in this study have shown that the effect of the stirring speed on the dissolution rate is negligible, which indicates that great quantities of copper, arsenic, iron and sulphates will be formed under stationary conditions, posing a great potential threat to the environment. Our previous investigations have shown that oats grown on a flotation tailings substrate, with the addition of $CaCO_3$ for neutralization purposes and organic fertilizers, absorb copper and arsenic beyond acceptable levels [27]. Consequently, flotation tailings treatment for the purpose of recovering copper would be greatly useful for two reasons. The first reason is economic, since the cost of copper recovery in this process would be lower than the cost of obtaining copper by pyrometallurgical method. The second major reason why flotation tailings treatment should be performed is reducing the uncontrolled contamination of the environment with copper, arsenic and H^+ ions which can be released during the leaching of sulphide minerals.

6. Conclusion

On the basis of the results presented in this study, the following conclusions can be drawn:

- Sulphuric acid concentration has a considerable effect on the copper recovery from flotation tailings. A sharp increase in copper recovery is observed at pH < 3.
- The achieved copper recovery of 12% for 2 h with tap water, points to the possibility of natural dissolution of copper from the tailings due to the presence of copper oxides or copper sulphate in it.
- Iron dissolution was observed only at pH values lower than 1.5 and can be neglected.
- Varying solid-phase concentrations does not have considerable effect on copper or iron dissolutions.
- Stirring speed has no significant effect on copper and iron dissolutions. However, relatively high copper extraction without stirring, points to the presence of readily soluble copper compounds in the tailings.
- The effect of particle size is observed only in smaller fractions. 92% of the total dissolved copper was obtained with fraction $-74\,\mu m$, whereas only 8% of copper was dissolved with fraction $+74\,\mu m$. The highest copper dissolution was achieved with the smallest fraction $-36\,\mu m$, which points to the presence of free copper minerals in the smallest fractions. As far as iron is concerned, 86% of the dissolved iron was obtained with fraction $-74\,\mu m$, and only 14% with fraction $+74\,\mu m$.
- Increasing the leaching temperature from $20\,^\circ C$ to $60\,^\circ C$ results in a linear increase in both copper and iron recovery. At a temperature of $60\,^\circ C$ with the addition of the oxidant, iron (III) sulphate at a concentration of 5 g/l Fe^{3+} ions, the obtained copper recovery was 80% after 2 h. The investigation results show linear dependence of copper dissolution and temperature, as well as chemically controlled dissolution rate of copper minerals.

- A mechanism of dissolution of copper and iron minerals from the tailings has been proposed.
- An average copper leaching recovery of 60% at pH 1 and negligible iron dissolution vales indicate that it is necessary to start processing the flotation tailings as soon as possible with the aim of copper extraction.

Acknowledgements

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