REPROCESSING OF THE OLD FLOTATION TAILINGS DEPOSITED ON THE RTB BOR TAILINGS POND - A CASE STUDY

Article Highlights
- Mass of the flotation tailings and valuable metal potential was estimated
- Purification of the flotation tailings for possible using in construction materials industry
- Copper oxide minerals leaching followed by the re-flotation of residual sulphide
- Inlet concentration of copper, iron and sulphur was reduced 3 to 5 times
- Proposed a new flotation tailings purification process

Abstract
Flotation waste, which was produced through seventy years of copper ore processing in RTB Bor, Serbia, is deposited in a flotation tailings pond. In total, almost 26.4 Mt could be considered as available for eventual reprocessing and reuse. Chemical analysis has shown that an average concentration of targeted metals in the tailings is: 0.183% Cu, 0.35 g/t Au and 2.17 g/t Ag. The tailings contain 60 to 70% of SiO₂, 10 to 17% of Al₂O₃ and pyrite 5 to 8%. Flotation tailings reprocessing consisted of acid leaching followed by re-flotation of the leach residue. Leaching of the tailings resulted in leach liquors containing Cu²⁺ ions from 50 to 580 ppm. The average copper removal degree in the leaching stage was 70%. After re-flotation, the total copper removal degree reached 83 to 85%. Sulphur removal degree reached 77%. Sulphur concentration in the treated tailings was reduced almost 5 times compared to the inlet concentration. An equivalent amount of iron was also reduced through the flotation process. Concentration of total copper was reduced 3 times.

Keywords: acid leaching, copper removal, flotation tailings, re-flotation.
ardous components, negatively affect the environment [6-8].

Wherever they are placed, flotation tailings ponds are regarded as an ecological threat to air, soil, and surface or underground water reservoirs. Tailings’ fine particles will be spread around by the wind, dusting the surrounding soil. Traces of heavy metal minerals in the particles, exposed to atmospheric conditions, are spontaneously decomposed and leached out, polluting and acidifying soil by metals and co-occurring sulphuric acid. In the case when flotation tailings are disposed close to populated areas, that represents a serious and highly expensive concern for these communities. On the other hand, in many cases flotations tailings represent valuable waste material, which is often recycled to recover residual metals, mainly heavy and/or precious metals [2,3,8-11]. In some cases, considerably large facilities were installed for flotation tailings reprocessing based on acid leaching, solvent extraction, and electrowinning process (L-SX-EW), such as the ZCCM in Chingola, Zambia, for example, with a capacity of 90,000 t of produced copper per year. This plant could be considered as a bigger one, which reprocessed old copper flotation tailings produced before the First World War, containing copper concentration higher than 1.2%.*

In spite of the L-SX-EW applied on an industrial scale a long time ago, different other approaches in research of reprocessing the flotation tailings, originating from heavy metal sulphide ore processing, have been made during last two decades with the aim of recovering the residual copper as well as associated heavy and precious metals. All the methods are based mainly on chemical- and/or bioleaching and the leach liquor treatment which follows, in rare cases, with re-flotation of the leach residue to concentrate additionally the residual sulphide minerals [8-10,12]. Recently, attention has been paid to the electro-kinetic remediation in those cases when sulphide mineral content was small and the content of precious metals was negligible. In cases like these having rather an ecological than economical approach, the aim was to extract traces of hazardous metals from tailings in order to prevent further surface water and soil pollution caused by acid mine drainage (AMD), flowing out from tailings ponds and to remove heavy metal ions and sulphuric acid from captured water thereafter [13,14].

Not long ago, increased interest has been shown in recycling of the flotation tailings with an intention of utilizing gangue minerals in construction materials production. Eventual previous extraction of heavy metals from the tailings means that it will open a new and wide direction in tailings recycling, which should contribute in lessening a huge mass of tailings now existing in ponds all over the world and to bring about an additional worth to tailings recycling [3,8,10].

A particular advantage of flotation tailings recycling over other natural sources for mining is that tailings consist of fine particles and can be easily used for reprocessing, without any additional comminution, saving in such a way a great amount of energy, regardless of the purpose for which it will be reused. In spite of several attempts that have been carried out recently, concerning the flotation tailings being used for production of either concrete- or mortar-based products [15-18], flotation tailings remain just as important potential source for this purpose, waiting to be processed and implemented on an industrial scale in construction materials industry. So far, tailings have been employed as mine backfill, as filler for surface filling prior to cementation in the construction industry, in cave filling of closed underground mines and restoration of open mining areas, or for some other similar purposes. In some cases, old flotation tailings were uncontrollably exploited, without any pre-treatment, as a low-cost substitution for sand, or as a fine aggregate in road or ground construction, spreading in such a way hazardous minerals across wide areas [16,17].

In this work, the old flotation tailings pond, from the Mining and Smelting Copper Co. Bor, Serbia (RTB Bor), will be considered regarding its copper and precious metals potential, as well as the possibilities of their removal from the tailings by leaching followed by re-flotation of the leach residue in order to reduce their sulphide mineral content, particularly pyrite as a major iron mineral present in the tailings. After completing the leaching and re-flotation, the residual solid waste should be clean enough to be used in the non-metallic industry of building materials. Incorporation of the products, produced in the flotation reprocessing within the existing facilities in RTB Bor and their further utilisation will also be considered.

Balancing and characterisation of the old flotation tailings (OFT)

Mass estimation of the OFT deposits

The flotation concentration plant (colloquially known as the old concentrator) at RTB Bor started working on industrial scale in 1933 and terminated in 2003. During those seventy years of copper ore processing, the flotation plant had disposed a huge
amount of solid waste in the OFT pond. The pond was fragmented by three dams in three parts, internally named as Field I, Field II and Field III. Field I is the smallest and the oldest one. According to measurements carried out in this study, it was found that Field I contained an estimated quantity of around 3.2 Mt. Field II was a newer one and considerably larger, in which almost 23.2 Mt of tailings was accumulated. In total, in these two fields approximately 26.4 Mt of solid waste were disposed that could be considered as available for eventual reprocessing and reuse. Field III contains an unknown amount of flotation waste. This field is covered with a gangue material from the Copper Mine Bor, as well as with ash from the RTB Bor power and heating plant. So far, the Field III can be considered as inaccessible and lost to contemplation in terms of its eventual utilization for any purpose.

In such a long period of seventy years of the flotation plant work, different quality of copper ores (containing different copper minerals with different concentrations of copper), were mined and processed. Flotation tailings of different quality (considering the copper content) were produced during that period, as illustrated by Figure 1.

According to the RTB Bor archive and the published data [19], the average copper content in the processed ores varied from 4%, at the very beginning to 0.6% at the end of the Old Flotation Plant works. Copper content in the flotation tailings had been changing in the same period from 0.5% at the beginning to less than 0.1% at the flotation process ending, depending on the copper ore quality and the flotation process parameters applied at that time.

Characterization of the OFT

In order to perform characterization of the flotation tailings from Fields I and II, sampling was carried out by issuing samples from 19 places in Field I and from 33 places in Field II, according to a previously sketched out net of sampling on the field surface area, as presented in Figure 2, for Field I only.

On site, samples were taken from two depths - from 5 and 10 m depths. In total, 104 samples were taken and packed in plastic bags, each having mass between 50 and 60 kg. From the flattened mass of each sample subsamples were issued by quartering method and used for further characterization and processing.

Physical properties and particle-size distribution

Physical characterization of the tailings was performed by measuring moisture, density, and bulk density, as well as particle-size distribution by means of wet sieve analysis. The moisture of the samples increased significantly with the sampling depth, so going deeper, at depths below 10 m, it became almost like slurry. The increased moisture content could be attri-

![Figure 1. Change of copper percent in processed ore and percent of copper in flotation tailings vs. time [19].](image-url)
buted to a winter period of the tailings sampling. Tailings density and bulk density were both determined by standard methods for each sample. The averaged values for the density were: 2830 to 2880 kg m\(^{-3}\) for Field I, while slightly less for Field II, i.e., 2750 to 2810 kg m\(^{-3}\). Bulk density was in the range of 1700 to 1900 kg m\(^{-3}\) for both fields. Mass estimation was carried out owing to the help of the RTB Bor Mining Geodetics Service, by measuring the tailings volume. Density changed slightly with depth, most probably due to spontaneous segregation of particles and weathering alteration over decades of the tailings being deposited on the fields. Density of the samples from Field II was smaller than in Field I, due to a higher concentration of lighter particles, that will be discussed in the context of the chemical composition of the tailings. Bulk density was smaller in the upper layers due to a smaller compressibility effect in the upper layers.

As copper ore is grinded, reaching 80% of particles size <75 µm before entering the flotation plant, one should expect similar or even finer particles of the tailings due to their chemical alteration with time. Because of that, wet sieving analysis was carried out using only four sieve fractions, as illustrated in Figure 3.

Mineralogical analysis

Qualitative mineralogical analysis has been carried out by preparing samples of mineral grains in plexiglass for microscopic analysis under polarization microscope “JENAPOL-U”, Carl Zeiss-Jena, equipped with Pinnacle System for taking micrographs, for identification of metal and gangue minerals, as presented in Figure 4.

Mineralogical analysis has shown the following mineral composition:

- copper minerals: chalcopyrite, chalcocite, covellite, bornite, malachite, cuprite;
- iron minerals: pyrite, magnetite, pyrrhotite, hematite, limonite;
- other metal minerals: molybdenite and rutile;
- major gangue minerals were quartz and feldspars – mainly as K-feldspars and plagioclases;
- side gangue minerals: amphibolites, pyroxenes, tourmaline and gypsum, while apatite and zircon appear as accessories.

According to the analyses, a fraction of the major gangue minerals in the samples was close to 90%. Considering metal minerals, it was found that pyrite is the most abundant, with an absolute fraction of around 6% in the samples. The major copper mineral is chalcopyrite with an absolute fraction of 0.4%. The second one is cuprite with 0.13%, while the other copper minerals (tenorite, covellite and chalcocite) are present to a lesser extent. Gold and silver grains are associated mostly with pyrite and chalcopyrite, while in a lesser extent (<30%) with quartz grains.

Chemical composition

Chemical analysis of each flotation tailings sample was carried out on the six main constituents: SiO\(_2\), Al\(_2\)O\(_3\), Cu, S, Au and Ag. Since copper exists in the samples in oxide (Cu\(_{\text{ox}}\)) and in sulphide form (Cu\(_s\)), the analyses were made on the oxide as well as on the total copper content. Sulphide copper content Cu\(_s\) was then determined as a difference between total and oxide copper concentration Cu\(_{\text{ox}}\).
The obtained data for each analysed tailings constituent were then averaged and presented in Table 1. Besides chemical composition, the natural pH of each sample was measured, averaged, and added to Table 1.

Table 1. Chemical composition (%) of the flotation tailings - averaged value

<table>
<thead>
<tr>
<th>Constituent</th>
<th>Field I 5 m depth</th>
<th>Field I 10 m depth</th>
<th>Field II 5 m depth</th>
<th>Field II 10 m depth</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu</td>
<td>0.192</td>
<td>0.112</td>
<td>0.106</td>
<td>0.038</td>
</tr>
<tr>
<td>Cu,ox</td>
<td>0.106</td>
<td>0.038</td>
<td>0.113</td>
<td>0.037</td>
</tr>
<tr>
<td>Cu/Cu,ox</td>
<td>1.86</td>
<td>3.37</td>
<td>1.57</td>
<td>4.1</td>
</tr>
<tr>
<td>S</td>
<td>5.11</td>
<td>6.86</td>
<td>7.15</td>
<td>8</td>
</tr>
<tr>
<td>SiO₂</td>
<td>69.3</td>
<td>61.5</td>
<td>65.5</td>
<td>60</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>13.45</td>
<td>14.4</td>
<td>11.3</td>
<td>14.3</td>
</tr>
<tr>
<td>Ag in g/t</td>
<td>1.45</td>
<td>1.49</td>
<td>1.28</td>
<td>1.57</td>
</tr>
<tr>
<td>Au in g/t</td>
<td>0.36</td>
<td>0.21</td>
<td>0.39</td>
<td>0.27</td>
</tr>
<tr>
<td>pH</td>
<td>4.04</td>
<td>6.01</td>
<td>5.77</td>
<td>7.64</td>
</tr>
</tbody>
</table>

Being 20 years older, after richer copper ores had been processed, Field I contains almost a twice higher total and almost triple higher oxide copper concentration than Field II. Moreover, the ratio between the total and oxide copper content - Cu/Cu,ox - is much less for the samples from Field I, which implies a weathering alteration of copper minerals from sulphide to oxide or even to sulphate form.

As already mentioned, major tailings constituents are quartz, with a fraction of around 60 to 70%, as well as alumina, the fraction which was in an interval between 11 and 15%. Field I contains more SiO₂ and Al₂O₃, particularly in the upper layers, partly due to different rock mass excavated at that time and partly due to alteration of the minerals, which contributes to a slightly smaller density in the shallower layers of this field. In total, almost 90% are gangue minerals - SiO₂ and Al₂O₃, while the rest are iron- and then copper minerals. Sulphur originates mostly from pyrite and to a lesser extent from sulphidic copper minerals. The oxidation process of pyrite, its stoichiometry, kinetics, and mechanism, are well described in the relevant literature [1,20-22]. Here will be given a simplified process stoichiometry by the following equations:

\[
2\text{FeS}_2 + 7\text{O}_2 + 2\text{H}_2\text{O} \rightarrow 2\text{Fe}^{3+} + 4\text{SO}_4^{2-} + 4\text{H}^+ \text{, chemical} \tag{1}
\]

\[
2\text{FeS}_2 + 7.5\text{O}_2 + \text{H}_2\text{O} \rightarrow 2\text{Fe}^{3+} + 3\text{SO}_4^{2-} + \text{H}_2\text{SO}_4 \text{, bacterial} \tag{2}
\]

\[
\text{FeS}_2 + 14\text{Fe}^{3+} + 8\text{H}_2\text{O} \rightarrow 15\text{Fe}^{2+} + 2\text{SO}_4^{2-} + 16\text{H}^+ \tag{3}
\]

\[
4\text{Fe}^{2+} + \text{O}_2 + 4\text{H}^+ \rightarrow 4\text{Fe}^{3+} + 2\text{H}_2\text{O} \text{, bacterial} \tag{4}
\]

\[
\text{S}^{2-} + 2\text{O}_2 \rightarrow \text{SO}_4^{2-} \text{, bacterial} \tag{5}
\]

In naturally acidic systems the oxidation of pyrite can be dramatically accelerated by the presence of acidophilic microorganisms, like Acidithiobacillus ferroxidans, or some other type of acidophilic microorganism [20,21], due to direct formation of ferric ions and sulphuric acid as shown by Eq. (2), which acts as an oxidant in further processes. In fact, the role of microorganisms may be twofold: enzymatic and non-enzymatic. In the first case, enzymes produced by microorganisms act catalytically on sulphide minerals.

In the second case microorganisms’ metabolic product is acid, which act on sulphides. In tailings upper layers there are conditions for growing and acting natural aerobic autotrophic microorganisms. Once the sulphuric acid is generated, present heavy metal oxides, carbonates or hydro-carbonates will react with it forming corresponding metal salts. Oxidation of other sulphide minerals existing in the tailings, by a similar mechanism as pyrite or by an electrochemical mechanism, occurs simultaneously forming conditions for their natural leaching by means of atmospheric precipitation containing dissolved oxygen [20]. The overall process is slow, while the ultimate result is a runoff of AMDs, characterized by an elevated acidity and high or modest concentration of metal ions, such as Cu, Zn, Cd, Pb, Ni, As, Mn and others, as well as a considerably high concentration of sulphate anions.

Because of H₂SO₄ formation in excess, lower natural pH was detected in the upper layers of the tailings. Going deeper, pH goes toward neutral and even basic values, meaning that at these depths oxidation of pyrite does not occur yet in a measure that can affect significantly the tailings pH change. Since flotation processes occur usually at pH>9 and tailings flows out at the same pH value, one can assume that even higher pH values than those given in Table 1 could be expected going deeper in the tailing pond.

When it is raining and snowing, leached copper and associated other ions will spontaneously percolate through the tailings bed by gravity towards deeper layers where pH is higher, to be precipitated at a certain depth as copper hydroxide or basic copper sulphate. One can assume that this copper is not lost, just migrated through the tailings towards the bottom, so one can speculate that even an increased metal content could be expected in deeper region than the ones we found in the samples at 5 and 10 m depth of the tailings.
Chalcopyrite showed a good stability against chemical and bacterial leaching and may be considered as an unchanged mineral in the flotation tailings [20,22,23].

**Estimation of valuable metal potential in the OFT**

Based on chemical analysis data, presented in Table 1, as well as the estimated amounts of the OFT, a balance of valuable metals was estimated. As seen from Table 1, copper content differs more than twice between Fields I and II. Looking chronologically, Field I contains older tailings, disposed at the time when richer copper ores were processed, so it is clear (and visible in Figure 1) that the tailings should have a higher copper content. Content of precious metals in Field I could also be attractive for researchers, but also for potential investors, to reuse and reprocess the tailings. Valuable metal potential in the OFT fields, derived according to current prices expressed in USD on the metal market [24], were summarized and given in Table 2. The figures are rounded up.

Estimated value, MUS$, Potential mass in Field II

<table>
<thead>
<tr>
<th>Field Tailings amount Cu</th>
<th>Ag</th>
<th>Au</th>
</tr>
</thead>
<tbody>
<tr>
<td>Potential mass in Field I</td>
<td>2,300,000</td>
<td>8,500</td>
</tr>
<tr>
<td>Estimated value, MUS$</td>
<td>125</td>
<td>59</td>
</tr>
<tr>
<td>Potential mass in Field II</td>
<td>23,200,000</td>
<td>25,000</td>
</tr>
<tr>
<td>Estimated value, MUS$</td>
<td>441</td>
<td>174</td>
</tr>
<tr>
<td>Commercial values, MUS$, Assumed removal degree* is 70% for Cu and 50% for Ag and Au</td>
<td>330</td>
<td>163</td>
</tr>
</tbody>
</table>

*On an industrial scale one should expect lower removal degrees than on the laboratory scale. During this study, the achieved removal degree for copper was > 83%. On industrial scale a rough estimation is 70%. Sulphur removal degree (see Table 3) is > 76%. As silver and gold are mostly attached to sulphide minerals (≈70%), their average removal degree is roughly estimated as 50%.

As it can be seen, the amounts of valuable metals are considerably attractive. The estimated values of the metal content are US$125 M, for the Field I and US$441 M for the Field II. Grand total is US$566 M. Assuming the amount of 70% of copper is recoverable as well as 50% of noble metals [12,25], it comes out that approximately US$163 M for copper, US$11 M for silver, and even US$156 M for gold could be retrieved – or in total, around US$330 M.

It looks as if the sum of approximately US$330 M is attractive enough to consider reprocessing of the tailings, with the aim of removing metals from it. The image of the tailings value becomes much more attractive when taking into consideration the value of micrionized quartz, kaolin, or K-feldspar, separated from each other in an economically viable extent and offered to industry of non-metallic products. This aspect of the OFT potential value will not be considered in this study.

**EXPERIMENTAL**

**Acid leaching of the OFT followed by re-flotation of the solid leach residue - experimental conditions and the procedure**

A series of experiments has been carried out, including acid leaching followed by flotation concentration of the solid leach residue, in order to decrease the amount of non-leachable copper and iron minerals in the tailings. Such separation of metal minerals from non-metallic ones makes the latter suitable to be used either in ceramic, glass, tile, or cement industry, or in the fabrication of various kinds of building and construction materials.

At this stage, only samples from Field I were used in the experiments. The choice was made based on the total copper content in the samples and the ratio between oxide and sulphide copper concentration is given in Table 1.

Ten samples were chosen from a depth of 5 m, which had copper concentration >0.15%, while from a 10 m depth eight samples were used for the leaching experiments, with total copper content >0.2%. The chosen samples were leached by sulphuric acid solution and then, after phase separation and washing the solid leach residue, they were processed by flotation concentration.

Pure H$_2$SO$_4$ and distilled water were used in preparation of the leaching solution. Leaching experiments have been carried out in a batch mode in a glassy reactor equipped with a mechanical stirrer [12], under the following conditions:

- leaching agent was 0.2 mol dm$^3$ H$_2$SO$_4$;
- solid vs. liquid ratio was S:L = 1:2;
- mechanical stirring rate, 300 rpm;
- leaching time, 1 h.

The measured mass of the solid phase was between 600 to 700 g, which is limited by the reactor volume. All the experiments were carried out at ambient temperature, approximately 20 °C.

After completing the leaching, the suspension was filtered and the filtrate was analysed on Cu$^{2+}$. The filter cake was then washed with a predetermined volume of distilled water and subsequently used in the flotation concentration experiments, which were performed in a laboratory flotation cell, under the following conditions:
The filter cake was re-pulped to a desired concentration of solids in suspension (26% of solid phase) and conditioned for 5 min at pH 10.5, adjusted by lime milk. After that, 14 g t⁻¹ of potassium ethyl xanthate (PEX) was added into the suspension, as a collector, to proceed with the flotation for the next 10 min. The flotation process was carried out in two stages (5 min each) by adding 7 g t⁻¹ of PEX at each stage - at the beginning of the process, as well as the same portion of PEX after expiration of the first 5 min. When the flotation experiments were completed, the obtained products - the concentrate of sulphide minerals as overflow and non-floatable gangue minerals as underflow - were sampled and analysed. Detailed procedure of sampling and analysing, as well as the corresponding equipment, is described elsewhere [12,22].

**Table 3. Removal degrees of the main constituents in leaching and flotation step and summarized effect of the tailings purification, where L denotes leaching; F - flotation; L&F - leaching and flotation**

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>% Cu after L&amp;F</th>
<th>% Cu in L</th>
<th>% Cu₂⁺ in L</th>
<th>% Cu₂⁺ after L&amp;F</th>
<th>% S in F</th>
<th>Cu²⁺ in leach solution, g dm⁻³</th>
</tr>
</thead>
<tbody>
<tr>
<td>Samples taken from 5 m depth</td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>1</td>
<td>84</td>
<td>81</td>
<td>95</td>
<td>62</td>
<td>87.4</td>
<td>0.31</td>
</tr>
<tr>
<td>2</td>
<td>83</td>
<td>72</td>
<td>83</td>
<td>50</td>
<td>81</td>
<td>0.49</td>
</tr>
<tr>
<td>3</td>
<td>75</td>
<td>50</td>
<td>56</td>
<td>43</td>
<td>65</td>
<td>0.24</td>
</tr>
<tr>
<td>4</td>
<td>86.4</td>
<td>68</td>
<td>83</td>
<td>70</td>
<td>82</td>
<td>0.51</td>
</tr>
<tr>
<td>5</td>
<td>86.4</td>
<td>77</td>
<td>73</td>
<td>57</td>
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<td>0.53</td>
</tr>
<tr>
<td>6</td>
<td>86.7</td>
<td>73</td>
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<td>8</td>
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<td>46</td>
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<td>84</td>
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<tr>
<td>Average</td>
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<td>68</td>
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<td>77</td>
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<tr>
<td>Samples taken from 10 m depth</td>
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<tr>
<td>1</td>
<td>90.6</td>
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<td>67</td>
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</tbody>
</table>
achieved from shallow OFT layers. Obviously, the removal percentage of total copper does not change significantly and may be considered as constant. It means that only a combination of leaching and re-flotation of the solid leach residue leads to a sufficiently good purification of tailings from copper and iron minerals and from the associated sulphur content.

The quality of the tailings after leaching and re-flotation can be seen in Table 4, in which inlet and outlet concentrations of copper, sulphide iron, and sulphur are given, showing how many times the outlet concentrations are reduced compared to the corresponding inlet ones.

Comparing chemical compositions of the averaged feeding tailings samples with the purified ones, it comes out that sulphur concentration is reduced 4.5-5 times. It means that an equivalent amount of sulphide iron is removed through the flotation process as well. Concentration of oxide copper was almost 2 to 3 times less, comparing to the inlet concentration; the content of copper sulphide is reduced more than 3 times, while the total copper concentration was reduced around 3 times.

The obtained results have shown a satisfactorily high degree of copper, iron, and sulphur removal, making the processed tailings satisfactorily cleaner from sulphide minerals and acceptable to be used in production of various non-metallic products. Slightly higher percentage could be achieved in the leaching step, by adjusting and optimizing leaching conditions, as well as in the flotation step by removing the finest particles of kaolin from the tailings prior to flotation.

**Reasons for re-processing the flotation tailings in RTB Bor on an industrial scale**

As already mentioned, previous studies on the use of flotation tailings from RTB Bor were mostly faced towards recovery of copper and other non-ferrous metals but much less towards recovery of precious metals from them [1,10,25]. Acid leaching does not contribute to the precious metals leaching at all, while the cyanidation process has not been considered here, due to its possible environmentally harmful effect.

As the tailings consists of micronized particles (≈88%, <37 μm); no additional energy for grinding is needed, regardless of where and for what purpose the tailings will be reused. This is a great advantage of the tailings’ utilization over a new mine opening to explore natural minerals - sand or kaolin, for example. Considering that specific energy consumption for ore crushing and grinding to achieve particle size fraction 70%, <75 μm, is approximately 15 kWh/t [26], you may assume that in the RTB Bor flotation tailings pond more than \(400 \times 10^6\) kWh of energy is accumulated. Highly developed surface of the flotation tailings and its chemical composition makes it ready for leaching. The remaining sulphide iron minerals, as well as precious metals, which are mainly attached to pyrite and chalcopyrite and less to quartz, could be recovered from the leach residue during the re-flotation process. These two consecutive processes (leaching and re-flotation) would provide an appropriately clean tailings residue for non-metallic industry.

Several studies have been made in the past with the aim of finding a solution of recovering valuable metals from the tailings in an economically sustainable way [1,19,25]. The basic problem in these studies is handling a huge mass of tailings during its reprocessing, to remove relatively small amounts of valuable metals from the processed tailings. Under current consideration, it is worthy emphasizing that RTB Bor possesses, besides very large mass of tailings as a starting material, several other advantages, the use of which may contribute to a better economy of the tailings processing, as well as to an environmental issue, which is illustrated by Figure 5 and will be more closely elaborated in the text below:

- Within RTB Bor there are several acidic effluents flowing out from the tank-house, containing a few thousand tons of waste H\(_2\)SO\(_4\) and a couple of hundred tons of copper, now going to the wastewater neutralization plant, which could be used in the leaching process [27,29].

- There are several springs of mine waters nearby the RTB, slightly acidic with the pH≈3.5, originating from the open pits and the underground cop-

Table 4. Average concentrations of copper, iron and sulphur before and after tailings processing

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Cu, in</th>
<th>Cu, out</th>
<th>Cu(_{\text{ox}},) in</th>
<th>Cu(_{\text{ox}},) out</th>
<th>Cu, in</th>
<th>Cu, out</th>
<th>S, in</th>
<th>S, out</th>
<th>Fe(_{\text{s}},) in</th>
<th>Fe(_{\text{s}},) out</th>
</tr>
</thead>
<tbody>
<tr>
<td>Conc., %</td>
<td>0.217</td>
<td>0.068</td>
<td>0.117</td>
<td>0.0376</td>
<td>0.1</td>
<td>0.031</td>
<td>5.41</td>
<td>1.2</td>
<td>4.72</td>
<td>1.04</td>
</tr>
<tr>
<td>In/out ratio</td>
<td>3.2</td>
<td>3.1</td>
<td>3.2</td>
<td>3.2</td>
<td>4.5</td>
<td>4.5</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Samples taken from 5 m depth</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

| Conc., %  | 0.274  | 0.096   | 0.088          | 0.049          | 0.175  | 0.048   | 9.71 | 1.96  | 8.48          | 1.74          |
| In/out ratio | 2.85   | 1.8     | 3.6            | 5              |        | 4.9     |      |       |               |               |
| Samples taken from 10 m depth |
per mine in an amount of 4.2 Mm$^3$ year$^{-1}$, containing more than 400 t year$^{-1}$ of copper and a corresponding amount of iron and zinc ions [25,27]. These mine waters could be captured and collected to serve for the preparation of an acid leaching solution:

- There is a sulphuric acid plant, based on the SO$_2$ gas from the copper smelter off-gases, which provides cheaper sulphuric acid that will be consumed in the tailings leaching process.

- There is a capacity in the existing flotation plant with related facilities in which the leach residue could be re-processed.

- There is a capacity in the flash smelting furnace of the RTB copper smelter plant to accept and process the produced pyritic concentrate together with the main furnace charge.

- Moreover, there is complete infrastructure (roads, electricity, technical water and others), which could significantly reduce the potential investment costs of the tailings leaching and re-flotation and the leach liquor treatment facilities.

On the other hand, products obtained through the tailings reprocessing could be incorporated into the existing process technology of copper production, as follows:

- After leaching and phase separation, the leach residue would be re-processed in the flotation plant to remove the remaining sulphide minerals of copper and iron and precious metals associated with them.

- Pyritic concentrate, produced by the re-flotation of tailings, contains an elevated concentration of sulphur and could be charged as a fuel into the copper smelter.

- Leach liquor could be processed to produce either metallic copper or copper-based compounds.

- Other metal ions, could also be separated and concentrated from the leach liquor and converted into commercial products or environmentally friendly and chemically stable mixtures to be safely discarded, as indicated in Figure 5.

- Separation of kaolin and quartz from purified tailings results in obtaining a mixture of these two components that cannot be separated any further and could be used for backfilling in the abandoned RTB mines.

The algorithm presented in Figure 5, illustrates the waste- and by-products currently produced in RTB Bor, which could be used in reprocessing of the flotation tailings, as well as those which could be produced from these sources.

As seen, all the by-products could be incorporated in the flotation tailings reprocessing, contributing significantly to the process itself, but also to a better use of the effluents which would reduce the existing costs of their current purification prior to discharging into the Bor and Krivelj River - tributaries of the Timok River. That will be a great step in improving their water quality, which now is at a very low level and represents a permanent threat, firstly to the Timok as a boundary river between Serbia and Bulgaria and consequently to a lower course of the Danube, as an international river [28-30].

**Proposed process for the flotation tailings treatment**

Removal of copper minerals from the OFT, firstly from Field I and, possibly afterwards, from Field...
II, by leaching and re-flotation of the leach residue could be used in tailings purification from residual heavy metal minerals, to be further used as a raw material in ceramic and glass industry, or for some other non-metallic materials production that could be implemented in the construction industry, which was the main aim of this study.

As the leach liquors have low concentration of copper ions to be directly treated by solvent extraction, the basic idea of its further processing could be an insertion of the ion exchange operation as a pre-separation and concentration step in which copper ions will be removed from the leach solution and adsorbed on the ion exchange resin. In the stripping operation of the loaded resin, copper ions will be concentrated in the stripping solution - eluate. Treatment of the eluate can occur towards further separation of Cu$^{2+}$ from the other strange ions co-adsorbed with copper, Fe$^{2+}$/Fe$^{3+}$, before all. Through the solvent extraction and stripping step, by using an extractant highly selective against Cu$^{2+}$, only copper ions will be separated and concentrated, through this operation, resulting in a solution that fulfils all requirements for the copper electrowinning process [31]. In the third step, the electrowinning will be carried out to obtain metal copper as the main final product.

Flow-sheet presented in Figure 6 describes a possible tailings purification process technology (left side of the sketch) and ion exchange-solvent extraction-electrowinning (IX-SX-EW) process technology, presented schematically on the right side, for the leach liquor treatment. The tailings purification process comprises tailings excavation and mixing with the leaching agent in a leaching tank. The leaching agent consists of a mixture of acidic effluents, AMDs and mine waters, collected in a pond and acidified to a predetermined pH value by concentrated H$_2$SO$_4$. After leaching, phases are separated by filtration. The leach residue is transported to the flotation plant and the leach liquor to the IX-SX-EW plant. Pyritic concentrate, containing also copper minerals in a lesser extent, will be filtrated and dried to be sent to the existing copper smelter. Purified gangue minerals from the down-flow after dewatering are ready for further processing in non-metal industry. The flow-sheet, given in Figure 6, is simplified in a sense that

*Figure 5. Schematic presentation of waste- and by-products existing in RTB Bor and products that could potentially be produced from the flotation tailings.*
only main unit operations and processes are presented. Supplementary operations and processes relating to additional leach liquor treatment after ion exchange, as well as the treatment of water streams appear in cake washing after filtration operation are not presented in Figure 6.

CONCLUSIONS

Flotation waste, produced through 70 years of copper ore processing in RTB Bor, Serbia, is deposited in the flotation tailings pond. In total, 26.4 Mt could be considered as available for eventual reprocessing. The average concentration of targeted metals in the tailings is: 0.183% Cu, 0.35 g/t Au and 2.17 g/t Ag. Copper content consisted from oxide and sulphide minerals. The tailings contain 60 to 70% of SiO₂, 10 to 17% of Al₂O₃ and pyrite 5 to 8%. The tailings contain 60 to 70% of Cu²⁺ from 40 to 580 ppm. Average copper iron sulphide minerals from the tailings. Leach residue was performed to remove copper and first stage, while in the second step re-flotation of the applied - acid leaching to reduce oxide copper as a metal potential of tailings was estimated to be worth US$330 M.

A two-staged process of tailings purification was applied - acid leaching to reduce oxide copper as a first stage, while in the second step re-flotation of the leach residue was performed to remove copper and iron sulphide minerals from the tailings.

Leaching of the tailings resulted in leach liquors containing Cu²⁺ from 40 to 580 ppm. Average copper removal degree in the leaching stage was 70%. After re-flotation, the total copper removal degree reached 83 to 85%. Sulphur removal degree reached 77%. Sulphur concentration in the treated tailings was reduced almost 5 times, while the concentration of total copper was reduced 3 times.

Acknowledgement

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REFERENCES

[19] Z. Mitrović, R. Jovanović, Seventy Five Years of the RTB Flotation Concentrators, RTB Bor and Megatrend University, Bor, 2007, p. 266 (in Serbian)
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NAUČNI RAD

REPROCESIRANJE FLOTACIJSKE JALOVINE DEPONOVANE NA STAROM FLOTACIJSKOM JALOVIŠTU RTB BOR - STUDIJA SLUČAJA

Flotacijska jalovina, proizvedena tokom 70 godina prerade rude bakra u RTB Bor - Srbija, deponovana je na Starom flotacijskom jalovištu. Skoro 26,4 Mt ovog materijala se može smatrati dostupnim za eventualnu preradu i ponovnu upotrebu. Hemijska analiza je pokazala da je prosečna koncentracija bakra i plemenitih metala u jalovini: 0,183% Cu, 0,35 g/t Au i 2,17 g/t Ag. Jalovina sadrži oko 60 do 70% SiO₂, kao i 10 do 17% Al₂O₃ i 5 do 8% pirita. Prerada flotacijske jalovine sastojala se od luženja sumporne kiseline i ponovnim flotiranjem ostatka luženja. Luženje jalovine rezultiralo je dobijanjem lužnih rastvora sa sadržajem Cu²⁺ od 50 do 580 ppm. Prosečan stepen uklanjanja bakra u fazi luženja iznosio je 70%. Nakon ponovnog flotiranja, postignut je ukupan stepen uklanjanja bakra od 83 do 85%. Stepen uklanjanja sumpora je iznosio 77%. Koncentracija sumpora u tretiranoj jalovini snižena je za oko 5 puta, u poređenju sa ulaznom koncentracijom. Ekvivalentna količina gvožđa je takođe uklonjena procesom flotacije. Koncentracija ukupnog bakra (oksidnog i sulfidnog) snižena je 3 puta.

Ključne reči: kiselinsko luženje, uklanjanje bakra, flotacijska jalovina, ponovno flotiranje.