COPPER MINERALS FLOTATION IN FLOTATION PLANT OF THE "RUDNIK" MINE

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Abstract: A unique technology of direct selective flotation is in use in flotation plant of the "Rudnik" mine in order to obtain selective lead, copper and zinc concentrates. Technological process is very sensitive to so-called "selectivity" because loss of individual metals through selective concentrates is present. Copper minerals flotation cycle is especially sensitive to selectivity and sometimes there is a higher content of lead and zinc minerals present in copper concentrate which is penalized. In this paper laboratory research results of lowering galena and zinc content in copper concentrate possibility due to extended time of cleaning are shown. All experiments were carried out on copper concentrate samples taken from the "Rudnik" flotation plant. Copper concentrate mineralogical analysis were carried out before flotation experiments.

Keywords: selective flotation; copper minerals; penalized elements;

1 INTRODUCTION

Research results, presented in this paper, shows determination of lowering main harmful (lead and zinc) elements content possibility in copper concentrate. Contents of lead and zinc, in examination copper concentrate, were 4.4-4.86% of Pb and 5.3-9.3% of Zn.

Each smelter requires different copper concentrate quality in term of impurities content limitations. Typical limitations of impurities content in copper concentrate and penalties for exceeding content are shown in Table 1. (Friedberg & Robinson, 2015; Weidenbach et al., 2016)

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Table 1: Typical impurities content limitations in copper concentrate

<table>
<thead>
<tr>
<th>Element</th>
<th>Penalty limit [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Arsenic</td>
<td>0.2</td>
</tr>
<tr>
<td>Higher Arsenic</td>
<td>&gt;1</td>
</tr>
<tr>
<td>Antimony</td>
<td>0.05</td>
</tr>
<tr>
<td>Bismuth</td>
<td>0.02</td>
</tr>
<tr>
<td>Cadmium</td>
<td>0.03</td>
</tr>
<tr>
<td>Fluorine</td>
<td>0.03</td>
</tr>
<tr>
<td>Lead</td>
<td>1</td>
</tr>
<tr>
<td>Mercury</td>
<td>0.0005</td>
</tr>
<tr>
<td>Nickel + Cobalt</td>
<td>0.5</td>
</tr>
<tr>
<td>Selenium</td>
<td>0.03</td>
</tr>
<tr>
<td>Zinc</td>
<td>3</td>
</tr>
</tbody>
</table>

Impurities content (lead and zinc) in examined copper concentrate is 3-4 times higher than limitation showed in Table 1. Content of other impurities present in examined copper concentrate is below penalty limits.

Flotation is used to selectively separate particles (minerals) based on their surface properties which were modified by flotation reagents. (Leppinen et al., 1998; Bulatovic, 2007; Long et al., 2014; Bournival et al., 2014; Chen et al., 2019; Ran et al., 2019; Zanin et al., 2019).

Researches were focused on the flotation selectivity increase during copper concentrate cleaning stage in flotation plant of the "Rudnik" mine. Microscopic analysis of harmful elements appearance in copper concentrate was the basis for further researches.

Procedures and research results of content and distribution of lead, copper and zinc by size fractions in copper concentrate are shown. Also, mineralogical (microscopic) analysis of copper concentrate by size fractions results are shown.

Cleaning copper concentrate experiments were carried out after the above-mentioned examinations. Those experiments had a goal to determine possibility of better results achievement by application of one additional copper concentrate cleaning stage in the industrial flotation plant. Influence of cleaning time duration and pulp density on concentrate quality were examined, without use of flotation reagents except for frothing reagents and pH regulators. Comments on all obtained results, conclusions and used literature are shown at the end of paper.
2 SAMPLE AND RESEARCH METHODS

All researches, shown in this paper, were carried out on composite copper concentrate sample from flotation plant of the "Rudnik" mine.

2.1 Particle size distribution determination procedure

Based on the fact that copper concentrate contains particles which are all below 100 µm, particle size distribution is determined by wet sieving on Tyler sieve series. Sieve openings were 0.074 mm and 0.038 mm. Particles below 0.038 mm were treated by sedimentation method (Beaker decantation). Mass measurement was performed after drying, and examination results are presented in Table 2 and graphically (Fig. 1).

2.1.1 Beaker decantation metod

“Beaker decantation” is the most commonly used method to determine particle size distribution and size fractions extraction of particles size below 38 µm. (Tomanec, 2000)

Determination of particles settling rate by Stokes law is necessary for this method:

\[ v_o = 545(\gamma - 1)d^2 \]  

Where:

\[ v_o \] – settling rate, [mm/s]
\[ \gamma \] – mineral density, [t/m³]
\[ d \] - particle size [mm]

Settling time of certain size fraction (d) is determined by formula:

\[ t = H/v_o\times 1.05 \]  

Where:

\[ t \] – settling time, [t/m³]
\[ v_o \] – mineral settling rate, [mm/s]
\[ H \] - suspension height [mm]

Copper concentrate was analyzed according to galena density (\( \gamma = 7.6 \) t/m³), by calculating the equivalent diameter and two size fractions were produced: 0.018 mm (18 µm) and 0.009 mm (9 µm).

2.2 DETERMINATION OF METALS AND MINERALS DISTRIBUTION BY SIZE FRACTIONS

Rational analysis was performed on the base of obtained size fractions metal content, in fact, by recalculating metals content to minerals with assumption that all of copper is bonded to chalcopyrite, lead to galena and zinc to sphalerite. (Tomanec at al., 2012, 2013)
2.3 Microscopic analysis

Microscopic analysis was performed on copper concentrate samples with the aim to determine harmful (penalizing) minerals appearance by size fractions.

2.4 Copper concentrate flotation experiments

Flotation experiments in function of extended cleaning time of copper concentrate were carried out, according to research goal. Determination possibility of achievement better copper concentrate quality due to extended cleaning time was the goal of the research.

Flotation experiments of cleaning copper concentrate were carried out by the following conditions: in function of cleaning time (1.2 and 3 min) with solid-in-pulp concentration of 14%: This laboratory researches were carried out on laboratory flotation machine "DENVER" with flotation cell volume of 2.8 dm³, (14% S); in this cell conditioning at 1200 r/min and flotation at 1500 r/min were performed; Lime was used as pH regulator and dorthfroth - 250 as frother; Flotation concentrates were filtered and dried.

3 RESULTS AND DISCUSSION

3.1 Particle size distribution

Particle size distribution was determined by wet sieving to a +38 µm fractions and -38 µm fractions by “Beaker decantation” method.

Particle size distribution of chalcopyrite concentrate is shown in Table 2 and Fig. 1.

<table>
<thead>
<tr>
<th>Table 2</th>
<th>Particle size distribution of chalcopyrite concentrate</th>
</tr>
</thead>
<tbody>
<tr>
<td>Size fraction [mm]</td>
<td>Wt,%</td>
</tr>
<tr>
<td>-0.104+0.074</td>
<td>12.52</td>
</tr>
<tr>
<td>-0.074+0.038</td>
<td>57.50</td>
</tr>
<tr>
<td>-0.038+0.018</td>
<td>4.31</td>
</tr>
<tr>
<td>-0.018+0.009</td>
<td>16.43</td>
</tr>
<tr>
<td>-0.009+0.000</td>
<td>9.24</td>
</tr>
<tr>
<td>$\sum$</td>
<td>100.00</td>
</tr>
</tbody>
</table>
Based on particle size distribution analysis it can be concluded that copper concentrate is relatively finely milled (87.48% of -0.074 mm fraction). Chalcopyrite concentrate \(d_{95}\) is approximately 0.082 mm and \(d_{50}\) is approximately 0.05 mm. Content of -0.009 mm fraction, which have poor flotation properties, is 9.24%.

### 3.2 Mineral distribution by size fractions

Determination of mineral distribution by size fractions was carried out on copper concentrate by size fraction extraction, metals and minerals distribution analysis and by microscopic mineral appearance analysis.

#### 3.2.1 Mineral distribution by size fractions results discussion

Examined copper concentrate from flotation plant of the "Rudnik" mine contained 24% of copper, 5.5% of zinc and 4.5% of lead. By copper content this is a high-quality concentrate. However, there is high content of penalty elements (lead and zinc) in copper concentrate. Microscopic analysis gave the following results, shown in Table 2.
<table>
<thead>
<tr>
<th>Size fraction, [mm]</th>
<th>Wt, %</th>
<th>Cu, %</th>
<th>CuFeS$_2$, %</th>
<th>R CuFeS$_2$, %</th>
<th>Zn, %</th>
<th>ZnS, %</th>
<th>R ZnS, %</th>
<th>Pb, %</th>
<th>PbS, %</th>
<th>R PbS, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>-0.104+0.074</td>
<td>12.52</td>
<td>15.21</td>
<td>43.96</td>
<td>7.95</td>
<td>6.04</td>
<td>9.00</td>
<td>13.64</td>
<td>6.65</td>
<td>7.68</td>
<td>18.72</td>
</tr>
<tr>
<td>-0.074+0.038</td>
<td>57.50</td>
<td>24.78</td>
<td>71.62</td>
<td>59.49</td>
<td>5.48</td>
<td>8.17</td>
<td>56.85</td>
<td>3.45</td>
<td>3.98</td>
<td>44.56</td>
</tr>
<tr>
<td>-0.038+0.018</td>
<td>4.31</td>
<td>19.78</td>
<td>57.17</td>
<td>3.56</td>
<td>4.77</td>
<td>7.11</td>
<td>3.71</td>
<td>2.82</td>
<td>3.26</td>
<td>2.74</td>
</tr>
<tr>
<td>-0.018+0.009</td>
<td>16.43</td>
<td>27.21</td>
<td>78.64</td>
<td>18.67</td>
<td>6.18</td>
<td>9.21</td>
<td>18.32</td>
<td>3.87</td>
<td>4.47</td>
<td>14.30</td>
</tr>
<tr>
<td>-0.009+0.000</td>
<td>9.24</td>
<td>26.78</td>
<td>77.40</td>
<td>10.33</td>
<td>4.49</td>
<td>6.69</td>
<td>7.48</td>
<td>9.47</td>
<td>10.94</td>
<td>19.68</td>
</tr>
</tbody>
</table>

**Metals and minerals distribution in –0.104+0.074 mm fraction of copper concentrate**

This size fraction-weight ratio, relative to 100% copper concentrate, is 12.52%. Metals content in this fraction is 6.04% of Zn, 15.21% of Cu and 6.65% of Pb. Mineral distribution in this fraction is 13.64% of ZnS, 7.95% of CuFeS$_2$ and 18.72% of PbS. Sphalerite content in this fraction is slightly higher relative to comprehensive copper concentrate. Also, galena content is 7.68%, i.e. 2.55% higher than in concentrate. Chalcopyrite content is 43.96%, i.e. 26% lower than in concentrate.

Microscopic analysis of polished specimen determined that in this fraction mostly intergrowth particles are present, i.e. poly-mineral crystal aggregates made of mostly idiomorphic quartz, pyrrhotite, sphalerite and small amount of galena. This size fraction is optimal for flotation process and very small amount of free galena and sphalerite particles is present. (George et al., 2004; Gontijo et al., 2007; Ata & Jameson, 2013; Cveticanin, 2017; Kohmuench et al., 2018; Maknosa et al., 2018; Jameson & Emer, 2019) This galena and sphalerite particles could not be liberated without additional milling of ore. Due to complex structural-textural characteristic of one part of the ore, poly-mineral intergrowth particles are present in the milled ore and it could not be expected that at the optimum particles size fraction for flotation the presence of intergrowth particles could be avoided. (Tomanec, 2011)

**Metals and minerals distribution in –0.074+0.038 mm fraction of copper concentrate**

This size fraction-weight ratio is high, 57.5%. Metal content in this fraction is 5.48% of Zn, 24.78% of Cu and 3.45% of Pb. Mineral distribution in this fraction is 56.85% of ZnS, 59.49% of CuFeS$_2$ and 44.56% of PbS. Minerals distribution follows high weight ratio of this size fraction. Content of harmful minerals is 8.17% of ZnS and 3.98% of
PbS. This size fraction is optimal for selective copper minerals flotation process. (George et al., 2004; Gontijo et al., 2007; Ata & Jameson, 2013; Cveticanin, 2017; Kohmuench et al., 2018; Maknosa et al., 2018; Jameson & Emer, 2019)

In this size fraction chalcopyrite is appearing in mostly liberated particles form. In comparison with -0,104+0,074 mm fraction chalcopyrite has significantly higher liberation degree. Besides liberated chalcopyrite particles there is appearance of liberated pyrrhotite particles. Also, in this size fraction pyrrhotite appears in intergrowth particles with sphalerite. Minerals ratio in this intergrowth particles is approximately equal. Galena rarely occurs. Estimated amount of liberated galena and sphalerite particles is approximately 15-18%. With that in mind, it can be estimated that one additional stage of copper concentrate cleaning can lower content of unwanted minerals in final concentrate, which would improve the quality of the concentrate.

**Metals and minerals distribution in –0,038+0,018 mm fraction of copper concentrate**

This size fraction-weight ratio is low 4,31%, thus participation of this fraction in metals and minerals distribution is insignificant. This size fraction is suitable for flotation process.

**Metals and minerals distribution in –0,018+0,009 mm fraction of copper concentrate**

This size fraction-weight ratio is 16,43%. Metals content in this fraction is 6,18% of Zn, 27,21% of Cu and 3,87% of Pb. Minerals distribution in this fraction is 18,32% of marmatite and 14.3% of galena.

Microscopic examination results of this size fraction are similar to –0,038+0,018 mm fraction. A very high content of liberated chalcopyrite particles is present. Also, significant content of sphalerite particles with 5-12% of chalcopyrite droplet intrusions. The presence of galena is very small.

In this size fraction all minerals particles are mostly liberated, and the particles size is still suitable for flotation. Based on that, it can be expected to determinate conditions for removing a part of unwanted minerals with additional cleaning stage of copper concentrate.

**Metals and minerals distribution in –0,009+0,0 mm fraction of copper concentrate**

This size fraction contains small size particles which demand more complex flotation conditions. Also, lower process selectivity can be expected. (George et al., 2004; Gontijo et al., 2007; Ata & Jameson, 2013; Cveticanin, 2017; Kohmuench et al., 2018; Maknosa et al., 2018; Jameson & Emer, 2019) Microscopic mineral identification is more
complex. This size fraction has poor flotation rate in industrial flotation plants, thus the lowest content of this fraction in milled ore i.e. flotation pulp is desirable. This size fraction-weight ratio is 9.24% in copper concentrate. In this size fraction mineral content is 6.69% of sphalerite and approximately 11% of galena. Mineral distribution is approximately 7.5% of sphalerite and almost 20% of galena. This high difference in mineral distribution is due to galena extreme weariness, which easily converts into small particle sizes, which demands longer flotation time.

A high content of liberated chalcopyrite particles and significant amount of liberated galena particles are present. Present intergrowth particles were composed only of chalcopyrite and sphalerite.

### 3.3 Copper concentrate cleaning

Researches of copper concentrate quality improvement possibility were carried out in laboratory conditions by applying one additional stage of concentrate cleaning. Experiments were carried out in function of cleaning duration time with solid-in-pulp concentration of 14%.

**Exp. 1** \( t=1\text{min.} \)
- 0.5 kg concentrate (14 %S)
- 0.5 g CaO
- pH=10
- 3 g/t D-250

**Exp. 2** \( t=2\text{min.} \)
- 0.5 kg concentrate (14 %S)
- 0.4 g CaO
- pH=9.3
- 3 g/t D-250

**Exp. 3** \( t=3\text{min.} \)
- 0.5 kg concentrate (14 %S)
- 0.5 g CaO
- pH=9.1
- 3 g/t D-250

Chemical analysis results of flotation products are presented in Tables 3, 4 and 5, as metals balance. Metals recovery is calculated based on 100% recovery in starting copper
concentrate sample (Copper average recovery in this flotation plant produced concentrate is approximately 64%).

Table 3 Exp. 1 Conc./Cu Metal balance

<table>
<thead>
<tr>
<th>Products</th>
<th>Wt,%</th>
<th>Pb,%</th>
<th>Zn,%</th>
<th>Cu,%</th>
<th>R_Pb %</th>
<th>R_Zn %</th>
<th>R_Cu %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rough conc./Cu</td>
<td>100,00</td>
<td>4,86</td>
<td>5,31</td>
<td>27,03</td>
<td>100,00</td>
<td>100,00</td>
<td>100,00</td>
</tr>
<tr>
<td>Cleaned conc./Cu</td>
<td>13,46</td>
<td>2,65</td>
<td>9,69</td>
<td>29,04</td>
<td>7,34</td>
<td>24,56</td>
<td>14,46</td>
</tr>
<tr>
<td>Middling conc./Cu</td>
<td>86,54</td>
<td>5,20</td>
<td>4,63</td>
<td>26,72</td>
<td>72,66</td>
<td>75,44</td>
<td>85,54</td>
</tr>
</tbody>
</table>

Table 4 Exp. 2 Conc./Cu Metal balance

<table>
<thead>
<tr>
<th>Products</th>
<th>Wt,%</th>
<th>Pb,%</th>
<th>Zn,%</th>
<th>Cu,%</th>
<th>R_Pb %</th>
<th>R_Zn %</th>
<th>R_Cu %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rough conc./Cu</td>
<td>100,00</td>
<td>4,79</td>
<td>9,34</td>
<td>26,87</td>
<td>100,00</td>
<td>100,00</td>
<td>100,00</td>
</tr>
<tr>
<td>Cleaned conc./Cu</td>
<td>29,19</td>
<td>2,33</td>
<td>6,46</td>
<td>30,66</td>
<td>14,21</td>
<td>20,19</td>
<td>33,31</td>
</tr>
<tr>
<td>Middling conc./Cu</td>
<td>70,81</td>
<td>5,80</td>
<td>10,53</td>
<td>25,31</td>
<td>85,79</td>
<td>79,81</td>
<td>66,69</td>
</tr>
</tbody>
</table>

Table 5 Exp. 3 Conc./Cu Metal balance

<table>
<thead>
<tr>
<th>Products</th>
<th>Wt,%</th>
<th>Pb,%</th>
<th>Zn,%</th>
<th>Cu,%</th>
<th>R_Pb %</th>
<th>R_Zn %</th>
<th>R_Cu %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rough conc./Cu</td>
<td>100,00</td>
<td>4,63</td>
<td>7,36</td>
<td>26,53</td>
<td>100,00</td>
<td>100,00</td>
<td>100,00</td>
</tr>
<tr>
<td>Cleaned conc./Cu</td>
<td>44,94</td>
<td>2,41</td>
<td>6,74</td>
<td>30,81</td>
<td>23,40</td>
<td>41,17</td>
<td>52,20</td>
</tr>
<tr>
<td>Middling conc./Cu</td>
<td>55,06</td>
<td>6,44</td>
<td>7,86</td>
<td>23,03</td>
<td>76,60</td>
<td>58,83</td>
<td>47,80</td>
</tr>
</tbody>
</table>

Based on results obtained in this copper minerals flotation experiments the following can be concluded:

An increase in copper content from 27,03% to 29,04% of Cu in copper concentrate was achieved during concentrate cleaning in period of t=1 min. Lead content was decreased from 4,86% to 2,65% of Pb and zinc content was increased from 5,31% to 9,69% of Zn. Also, copper recovery in concentrate was 14,46% of Cu, zinc recovery was 24,56% of Zn and lead recovery was 7,34% of Pb.
By increasing the cleaning time to $t=2$ min an increase of copper content from 29.04% to 30.66% of Cu in copper concentrate was achieved. Lead content was decreased to 2.33% of Pb and zinc content was decreased to 6.46% of Zn. Copper recovery in concentrate was 33.31% of Cu, zinc recovery was 20.19% of Zn and lead recovery was 14.21% of Pb.

By increasing the cleaning time to $t=3$ min a insignificant increase of copper content in concentrate to 30.81% of Cu was achieved. Lead content was decreased to 2.41% of Pb and zinc content was decreased from 7.36% to 6.74% of Zn. Copper recovery in concentrate was 52.20% of Cu, zinc recovery was 41.17% of Zn and lead recovery was 23.40% of Pb.

These results are graphically presented in Fig. 2.

**Figure 2** Metals content in Cleaned conc./Cu

## 4 CONCLUSION

Based on presented results the following can be concluded:

- Copper concentrate is composed of relatively small particles size, $d_{95}$ is approximately 0.082 mm and $d_{50}$ is approximately 0.05 mm. Size fraction $-0.009$ mm participation in copper concentrate is 9% by weight, and this size fraction has poorly flotation properties.
- According to metal and mineral distribution by size fraction in copper concentrate, in $-0.009+0$ mm fraction chalcopyrite (CuFeS$_2$) recovery is
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approximately 10%, sphalerite (ZnS) recovery is approximately 7.5% and galena (PbS) recovery is approximately 20%.

- The highest mineral recovery in copper concentrate is recorded in -0.074+0.038 mm fraction, approximately 60% of CuFeS₂, approximately 57% of ZnS and approximately 44.5% of PbS. As assumed, the highest minerals recovery in copper concentrate is in -0.074+0.038 mm fraction, because this fraction is the most suitable for industrial scale flotation. Mineralogical analysis results show that harmful elements in copper concentrate (galena and sphalerite) are present in form of intergrowth particles with chalcopyrite, tailings minerals and each other. Liberated particles are also present, especially galena, which indicates a possibility of copper concentrate quality rising by removing those harmful minerals particles.

Research results showed that by applying one additional stage of copper concentrate cleaning (Rough/Cu), in duration of t=2 min, quality of copper concentrate can be improved, especially in terms of lowering content of harmful penalizing elements in copper concentrate: from 4.5% to approximately 2.5% of galena and from approximately 7% to 6% or less of zinc.

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