Research of Laws Pyrite-Bearing Slag Flotation of Copper Melting in Water used Change Settings

I. V. Shadrunova¹, M. N. Sabanova², N. N. Orekhova³, A.I. Petrova*⁴

The work was supported by the Ministry of Education of the Russian Federation, the Agreement №14.604.21.0128 (unique identifier RFMEFI60414X0128 project)

¹Institute of Problems of Comprehensive Exploration of Subsoils of Russian Academy of Sciences, Moscow, Russia
²Sibay branch of JSC “Uchaly Mining and Processing Enterprise”, Sibay, Republic of Bashkortostan, Russia
³Mining Engineering and Transport Institute, Nosov Magnitogorsk State Technical University, Magnitogorsk, Russia
⁴Institute of Problems of Comprehensive Exploration of Subsoils of Russian Academy of Sciences, Moscow, Russia

*Corresponding Author

Abstract: The article presents the results of studies of the effect of conditioning method of circulating water in the flotation of refractory copper slag in Ural region. The mineralogical characteristics of slag are given, the slag feature, which de-termines the efficiency of the flotation to extract copper from the slag not in the alkaline environment, as it is usual-ly in enterprises, but in the slightly acidic and neutral pH range of the environment is disclosed. The influence of the method of water conditioning and of the concentration of metal ions in the prepared water on the performance of flotation is found.

Keywords: copper smelting slag, flotation, conditioning-tion, copper recovery

1. Introduction

Rebellious copper slags are involved in the processing at concentrating plants of the Southern Urals, in addition to pyrite copper and copper-zinc ores. Flotation technology is a universal method of enrichment of natural raw materials (minerals) and man-made (mining and metallurgical waste) origin. It contains non-ferrous metals, and allows you to extract copper from free-milling crystallized copper slag aggregates [1, 2]. Flotation copper ground to 0.074 mm class minutes slag is carried out on the circulating water in an alkaline medium created lime [3]. Extracting copper flotation of refractory bad- devitrified lag does not exceed 45-60% on average from the dump and 76% of the converter (working) on Mednogorsky copper and sulfur plant [2]. Mass fraction of copper in the resulting foam products do not reach the minimum value conditioned for copper concentrate, which is a consequence of the low selectivity of the process (Table 1).

Table 1: Technological parameters of the processing of copper slag in the conditions of the processing plant Sibai branch of Ural mining and metallurgical company (UMMC)

<table>
<thead>
<tr>
<th>Period processing, year</th>
<th>Slagname</th>
<th>Original content,%</th>
<th>Product</th>
<th>Content, %</th>
<th>Extraction,%</th>
</tr>
</thead>
<tbody>
<tr>
<td>2010</td>
<td>returnslag</td>
<td>1.81-3.29</td>
<td>2.83-3.7</td>
<td>Milltailing</td>
<td>0.56-0.8</td>
</tr>
<tr>
<td>2011</td>
<td>waste slag</td>
<td>0.49-0.54</td>
<td>2.6-3.0</td>
<td>Heading</td>
<td>4.0-5.52</td>
</tr>
</tbody>
</table>

Improving tasks copper recovery and the selectivity of the separation process of man-made mineral formations refractory slag remain valid up to the present time [4-6,8]. It should be noted that the production of copper concentrate from the slag is the not the primary objective concentrator. This process allows you to get an additional metal-to-metal processing by current volumes of ore. The study of the influence of the main parameters of the circulating water at the concentrator the slag flotation indicators technologically important. Influence of methods of water conditioning for effective flotation of pyrite slag copper and copper-zinc ores should be subjected to the study. Slag copper different companies differ significantly from each other [1,2]. Typing copper slag Ural region has allowed to identify three main technological type of slag: fayalite-ferrite, ferrite-fayalite-magnetite and fayalite-magnetite-pyrite [2,4]. Mednogorsky copper slag referred to by typing fayalite-magnetite-pyrite type (third type). Our previous studies [2,4,7,8] that consists of copper slag, slag glass, fayalite, magnetite, pyrite, iron oxide, alumina, silica and silicates of calcium and iron, as well as exudates bornite solution inclusions pyrite oxides of lead and iron. The content of the sulfide phase is on average 7%. Bornite represented 0.5%, and the rest - pyrite. Copper is a metal alloy, αsrCu therein ranges from 1.40% to...
85.08%. Copper is found in pyrite and pyrrhotite as an impurity (up to 3.23%) and oxide phases (magnetite, ferrite) and fayalite sodium aluminosilicate. The main copper phases are chalcocite-bornite solid solution (αsrCu - 73.15%), bornite (αsrCu - 56.09%), sulfide Fe-Cu solid solution (αsrCu - 54.91%), sulfide Fe-Cu-of Zn solid solution (αsrCu - 16.83%).

The results showed that the depleted slag and working one company could be attributed to one variety of raw materials. Quality of raw materials will be the only difference for component. The main feature of the copper slag ITCs - the presence of cuprous pyrite, with metallic copper pyrite enclosed in a capsule (Figure 1).

![Complex sulphide splice - "copper-bearing pyrite globule": in the center of pyrite grains is metallic copper bead size of 3 microns.](image1)

Flotation of copper slag in a closed water concentrator is not described in the literature, but is of considerable practical interest. Involvement in the flotation process is not involved in the maelstrom of process water has environmental and economic importance. The water deficit conditions in ore-processing plant of the Southern Urals.

2. Methods of the Research

To determine the influence of parameters of the circulating water in the floatability of copper slag Mednogorsky copper-sulphur combine (MCSC):

- Analyzed the performance of its processing in the ore-processing plant conditions for six months;
- Floatability studied depending on the pH of the process water and the use of mining and processing enterprises of various origins in vitro;
- The change of slag zeta potential as a function of pH.

Crushing process raw samples was carried out in preparation for flotation of copper slag (figure 2). Crushing of samples was conducted in a ball mill in controlling mineral intergrowths disclosure 70-73% copper content in the class minus 0.044 mm 95% under a microscope Polan 312. Flotation tests were carried out on the mechanical laboratory flotation machine 240FL. They used a collector (butyl potassium xanthate) and a foaming agent (floatation oil T-92). The concept includes a main flotation, flotation control, two recleaning main operations of concentrate flotation. The solids content was 28% in the primary flotation operation.

![Lump of whole copper ore size 100 mm*70mm*42mm](image2)

Flotation was carried out on the actual circulating water-processing factory, conditioned water back to fixed values of pH and process waters enterprise. Fixed pH conditioned circulating water was achieved in several ways:

- Reagent preparation, which consisted of air conditioning circulating water when applying reagents to predetermined pH values. The initial pH of the circulating water averaged 11.0 -11.5. High alkaline pH environment created 12-13 fed 10% milk of lime in water, low alkaline medium 8-10, neutral and slightly acidic pH 4 to supply certain volumes of 10% sulfuric acid solution.
- Aeration preparing oxygen in the air, which was forced aeration of recycled water in operating flotation chamber with forced air at a rate of 0.08 l / s. for 1 - 8 hours.
- Mixing process water mining and processing enterprise in various ratios;
- The combined preparation, which includes several successive stages:
  - Stage 1 - preparation of aeration of recycled water to a pH of 8-8.5;
  - Stage 2 - prepared by mixing circulating water with underspoil water in a certain ratio;
  - Stage 3 - the supply of reagents into the mixing water to the specified pH values.

The study of flotation of copper slag was carried out on the technical water, circulating water, underspoil water, mine water and stormwater drainage. The chemical composition of process water is presented in Table 2.
Table 2: Results of the monitoring of the chemical composition of the process water Sibai branch of Ural mining and metallurgical company (UMMC) for 2011-2013

<table>
<thead>
<tr>
<th>No.</th>
<th>Defined indicators</th>
<th>Values of indicators for water</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Circulating</td>
</tr>
<tr>
<td>1</td>
<td>pH</td>
<td>10.5-12.5</td>
</tr>
<tr>
<td>2</td>
<td>The content of free CaO, mg / dm³</td>
<td>100,9-902.9</td>
</tr>
<tr>
<td>3</td>
<td>Total hardness, mmol-equiv / dm³</td>
<td>32-118</td>
</tr>
<tr>
<td>4</td>
<td>Dissolved matter, mg / dm³</td>
<td>3256-5221</td>
</tr>
<tr>
<td>5</td>
<td>Sulphates, mg / dm³</td>
<td>917-1322</td>
</tr>
<tr>
<td>6</td>
<td>Chlorides, mg / dm³</td>
<td>165-800</td>
</tr>
<tr>
<td>7</td>
<td>Copper, mg / dm³</td>
<td>0.01-0.08</td>
</tr>
<tr>
<td>8</td>
<td>Zinc, mg / dm³</td>
<td>0.08-0.3</td>
</tr>
<tr>
<td>9</td>
<td>Iron, mg / dm³</td>
<td>0.02-1.2</td>
</tr>
<tr>
<td>10</td>
<td>Manganese, mg / dm³</td>
<td>0.01-0.05</td>
</tr>
<tr>
<td>11</td>
<td>Calcium, mEq / dm³</td>
<td>28-97</td>
</tr>
<tr>
<td>12</td>
<td>Magnesium, mmol-eq / dm³</td>
<td>4-21</td>
</tr>
</tbody>
</table>

The pulp with a solids content of 20% was prepared using actual enterprise circulating water and recycled water, conditioned to a predetermined pH values in the powdered dry in the slag of cup attritor to a content-class minus 0.044 mm 100%. Measurements of the zeta potential of slag was conducted on electro acoustic spectrometer Dispersion DT-310 (made in USA). The actual particle size distribution of the samples was determined by a laser diffraction analyzer of Sympatec GmbH (Germany) QUXEL system for wet dispersion, which allows you to analyze particles in suspensions and emulsions in size from 0.001 to 3.5 mm.

3. Results and Discussion

A comparison of daily full monitoring parameters of copper slag flotation (pulp density, the grinding, the alkalinity of the pulp, the pH of the circulating water, the consumption of reagents) revealed a significant correlation between the indicators of enrichment of copper slag alkalinity of the pulp and the pH of the circulating water in the conditions of the processing plant to the performance of flotation (extract and the mass fraction of copper products). Increasing the pH of the circulating water and the flotation pulp alkalinity leads to an increase in copper loss with flotation tailings with all things being equal, the process of processing mode. The increase in the collector flow at high alkaline pH increases the yield of the foam product, reduces the quality of copper concentrate. Losses copper flotation tailings remain at the same level at the same time. Experimental tests of flotation of copper slag third type [2, 4, 7, and 8] showed that the pH range of effective extraction of copper 5.0-7.5, and maximum values obtained at pH 5.5 (Figure 3) that is probably due to the presence of pyrite in the cuprous slag.

The apparent correlation is observed between the change of slag flotation and zeta potential (Fig. 3.4). Changes in zeta potential of the copper slag was analyzed in the medium at different pH values. It was found that finely ground slag of the third type manifests itself as unstable system in a strongly alkaline medium circulating water. The average zeta potential of the slag particles is close to zero. The process is non-selective flocculation of particles, which entails a reduction in the selectivity of the flotation process. Introduction acidifiers (10% sulfuric acid solution or underspoil water with a pH of 2.5-5.5) leads to a sharp increase (surge) of the negative charge of the particles. This is achieved in a weakly acidic medium 6.5-5.5 rN, (Figure 4).

The process is deflocculated particles. The system goes into a stable state. The greatest contribution is made by the ζ - potential of fayalite in total curve ζ-potential of the particles of copper slag. Maximum recovery of copper slag particles occurs in peptizationfayalite in this case can be assumed. Flocculation copper technogenic mineral phases associated
with pyrite (to the isoelectric state of the surface of pyrite aims at reducing the pH below 6 [9]). Change the ζ-potential fayalite surface (for measurement conditions with a reduction in the pH of the slurry acidification) probably contributes to desorption from the surface of the Ca²⁺ ions adsorbed fayalite of recycled water.

Slag peptization confirmed by studying slag deposition rate as a function of pH in the pH of maximum recovery of copper.

Experiment on precipitation of finely divided slag in water showed that at pH 14 the precipitation suspension is 10 mm/sec. reducing the pH of the slurry to a pH of 8 units reduces the deposition rate is five times longer and is 2 mm/sec. The deposition rate slows down further in a neutral medium at pH 7, the suspension becomes stable in a weakly acidic medium at pH 6.5 -5.5. The shift to more acidic pH region increases the rate of deposition of the larger particles, but the thinnest flakes remain in suspension, creating a high turbidity of the liquid column.

The result of the influence of pH on the extraction of copper in the concentrate is reproduced in the flotation of copper slag third type of process waters at different (Table 4).

This is reflected in the fact that the maximum recovery obtained using underspoil water having a pH of 5.5.

| Table 4: Results extraction of copper from the slag flotation in the various process waters |
|---|---|---|---|---|---|
| Slag | Circulating (pH 11.0) | Technical (pH 7.9) | Underspoil (pH 5.5) | Mine (pH 7.8) | Stormwater drainage (pH 7.9) |
| Extraction of copper in the copper concentrate,% | 70% | 66% | 74% | 62% | 60% |

The results are worse on technical, mine water and stormwater drainage than using recycled water. Type flotation froth varies depending on the slag flotation type III water. Flotation froth loaded on technical water, but is not expressed froth layer and resembles film (Figure 5). The floating forth on the circulating water - a lush, but not downloaded (Figure 6). The flotation foam in an acidic medium is loaded, medium-grained, and soft (Figure 7).

Industrial, circulating and underspoil water are significantly different not only for pH, but also in their content of copper, zinc, iron, sulfate and hardness. The study of the effect of changes in the values of certain parameters in the white water in the flotation of copper slag third type with equal pH = 11.0 we carried out. The experimental results presented in Figure 8.

---

**Figure 5:** The flotation foam, process water

**Figure 6:** The flotation froth circulating water

**Figure 7:** The floating froth underspoil water
During the experiment, it is determined that increasing the concentration of copper ions and 0.04 to 3.78 mg / dm$^3$ leads to increased copper recovery at 3% overbased circulating water at pH = 11. The subsequent increase in the copper ion concentration leads to a lower yield and extraction of copper concentrate to copper therefrom that is accompanied by breach visually frothing and froth folding. Increasing the concentration of zinc ions and 0.032 to 576 mg / dm$^3$ and the ion-Lez from 0.22 to 134 mg / dm$^3$overbased circulating water at pH 11 does not affect the recovery of copper in the copper concentrate. Increased total hardness from 30 to 89 reduces the copper extraction from 75 to 64%.

The study of the possibility of reducing the pH of aeration, based on the need to reduce the pH of the circulating water to the flotation of copper slag third type. The largest decline reached 12 hours of aeration from 12 to 7.5 pH Copper recovery during flotation aerated using recycled water result increased relative to the initial circulating water at 2.2%.

Conditioning circulating water conducted in different ways to achieve a pH of 7.5. Focusing on achievable aeration pH of the circulating water and based on changes in the quality of conditioned water requirements are not to the detriment of the primary flotation processing plant raw materials (copper pyrite and copper-zinc ores). The results of the effect of acidification on the flotation reagent water are shown in Figure 9.

Results showed that the most effective acidification with sulfuric acid (an increase of 3.2% recovery) and iron sulfate (II) (5.1% increase in extraction). Recovering copper reduction can be explained by a too high concentration of copper ions using a copper sulfate (II). The result is shown in Figure 4 (a).

Water conditioning mixing should be focused on increasing the copper concentration to 3-4 mg / dm$^3$, the total hardness reduction and lowering the pH to 7.5. This result can be achieved by the combined conditioning (Table 5):

Stage 1 - preparation of aeration of recycled water to a pH of 8-8.5 (to lower reagent consumption - acidifier);

Stage 2 - prepared by mixing water with reverse aerated underspoil water in a specific ratio to reduce the consumption of acidifying agent and increasing the concentration of copper;

Stage 3 - the supply of sulfuric acid prepared in the first two stages of the water to a predetermined pH.

Experimental verification confirmed the benefit of the combined method of water conditioning for flotation (Fig 10).

It is noted that the use of acidic water conditioning underspoil reverse speeds by a combined flotation process scheme 20-30% [2.8], and reduces the consumption of...
reagents increases the extraction of copper in the product to 10%.

4. Conclusions

Recycled water processing factory, processing pyritic copper and copper-zinc ores, the most cheaply and affordable aqueous phase, which can be used in the flotation of slag today. It is necessary for the conditioning of water pH indicators, the concentration of copper, the stiffness to improve copper recovery at the flotation pyrite-bearing slag processing of copper smelting. Water conditioning mixing should be focused on increasing the copper concentration to 3-4 mg / dm³, reducing total hardness and lowering the pH to 7.5. This results without significant investment in water treatment can be achieved by the combined conditioning, which includes aeration preparation of recycled water to a pH of 8-8.5, prepared by mixing the aerated circulating water with underspoil water at a certain ratio, caused the necessary concentration of copper ions in the water, finishing the set up of acid pH with sulfuric acid. Another result of the use of the combined method of conditioning the circulating water is the involvement of a water circulation concentrator underspoil waters, which have a negative impact on the environment. This will reduce the environmental load and minimize damage to the company at the expense of environmental penalties.

References