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New insights into recovery of copper and gold from old flotation tailings from Bor, Serbia

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Abstract: Mining and processing tailings often contain significant amounts of valuable metals, that can represent valuable sources of secondary raw materials. Especially this is case in early-stage operations, in which the head grades were higher, and the tailings were higher grade. These tailings can also present a substantial risk to the environment. Serbia has copper deposits which have been exploited since ancient times, and these operations have generated large amounts of mineral processing tailings. The main objective of this study is to show how valuables can be recovered from chemically and mineralogically challenging tailings. After detailed chemical and mineralogical characterization, the laboratory scale flotation tests focused on evaluating the effect of particle size, different types of collectors, pH, and pulp potential. Based on the test work, copper and gold can be recovered effectively into pyrite concentrate.

Keywords: copper, gold, mineralogy, tailings, flotation, value recovery, modelling

1. Introduction

Efficient processing of tailings, i.e., mine waste, is crucial to eliminate environmental risks often connected with tailings ponds. Tailings also represent a valuable source of secondary raw materials, which has been earlier neglected as an opportunity, but now seen globally .as potentially exploitable and cost saving raw material sources, since they consist of already mined and comminuted minerals [1-5].

The present research is a part of the European Institute of Innovation and Technology (EIT) funded RIS-CuRE project, which aims at zero waste extraction of valuable metals from the old Bor tailings containing copper and gold. Serbia has copper deposits that have been exploited since ancient times, and date back to 4500 B.C. These operations have generated large amounts of mineral processing tailings. The Bor copper mine located in the eastern part of Serbia started exploiting the high grade, 17% Cu, copper ores in 1903 [6] the open-pit mining started in 1912 and continued until 1986 with decreasing copper grades [7].

During these mining operations, approximately 700 Mt of waste rocks and tailings were disposed In the Bor Valley [8]. The dumped tailings are extremely acid, with pH values ranging between 2 and 4.25 [9], which is mainly due to the decomposition of abundant pyrite, that has led to acid generation [10-11].

These acid conditions facilitate the mobility and bioavailability of toxic heavy metals. the soil surrounding the old flotation tailings pond is contaminated with metallic elements, with particularly high values obtained for iron, copper, and arsenic concentrations [12-13]. Overall, a century of mining has left its mark on the Bor area landscapes being one of the most polluted places in Serbia [7].

In the case of a tailings dam failure there is the potential for a significant portion of the toxic material to run directly to the Borska River and onward to the Danube River, with enormous environmental consequences to the entire region [9, 14].

Reprocessing of tailings can enable reduction of the acid generation and following release of metals to waterways and soils by removing pyrite with simultaneous recovery of valuables. Several studies have been conducted at laboratory scale to recover copper and gold from the Bor tailings by acid leaching [8, 15], acid leaching followed by flotation of leaching residue [16] leading to copper and sulfur recoveries of 70% and 77%, correspondingly. Conić et al. [15] concluded, that the most efficient technology for copper recovery from the old flotation tailings of the Bor copper mine was leaching with biogenic lixiviant. Falagán et al. [2] reached copper recoveries of over 90% by bioleaching.

Markovic et al [9] and Han et al. [17] used flotation to recover valuables from the Bor tailings. Markovic et al [9] achieved flotation recovery of copper over 97% and pyrite recovery over 87%. Copper and pyrite grades in bulk concentrate were 1.34% and 42.74%, correspondingly. Recoveries of gold and silver were above 60%.

2. Materials and Methods

The old Bor flotation tailings have been disposed in the Bor River valley from 1933 to 1987 into two tailings ponds, that covers an area of approximately 1.6 km² and consists of 27 million tons of tailings with an average copper and gold contents in the range of 0.2-0.3% Cu and 0.3- 0.6ppm Au, correspondingly [18].

About 230 kg of tailings was sampled from six drill holes and delivered to Metso Outotec Research Center, Pori, Finland for characterization and beneficiation test work. The received sample was homogenized and divided into subsamples. Particle size d_{80} and d_{50} were 132 µm and 36 µm, by sieve analysis, correspondingly.

2.1. Chemical composition of tailings

The chemical analysis of metals in solids was conducted using Inductive Coupled Plasma Optical Emission Spectrometry (ICP-OES, Thermo Scientific iCAP 6000) after total dissolution. The total carbon and sulfur concentrations were determined by a combustion method (Eltra CS-2000). The gold content was determined Inductive Coupled Plasma Mass Spectrometry (ICP-MS, Thermo Scientific iCAP Q).

In addition, the copper contents were determined according to the four-stage sequential copper phase assay procedure described by Young [19] and further developed by Metso Outotec. This procedure enables the quantification of different copper sulphates, oxides, secondary copper sulfides, and primary copper sulfides by using the element-tomineral conversion (EMC) method, [20-21], included in the HSC Chemistry® 10 software [22].

2.2. Mineral composition of tailings

The main minerals and their modes of occurrence were first studied per size fraction by optical microscopy (Zeiss Axio Imager M2m) and X-ray diffraction (PAnalytical Aeris). Scanning electron microscopy and liberation measurements were performed by using a field emission scanning electron microscope (JEOL JSM 7000F) equipped with an Oxford Instruments energy-dispersive spectrometer (X-Max 80) coupled with AZtec Mineral liberation measurement software.

2.3. Grinding tests

Grinding test was performed by using mild steel laboratory ball mill (215mm height x 205 mm diameter) using 27 mm (3.3kg) and 19 mm (8.7kg) balls with 65% solid density with the grinding times of 5, 10, 20, 40, 80, and 105 minutes.

2.4. Flotation test work

Bor flotation test work was carried out by using a laboratory type Outotec GTK Lab Cell flotation machine. GTK flotation lab cell is equipped with adjustable external water feed pump for adjusting constant pulp level. Froth is recovered by automatic froth scraper system. The flotation and grindability test work were carried out with Pori tap water. The pH of the slurry was measured as 3.5.

Makeup water was added during the flotation tests to obtain constant pulp level in the flotation cell. Bor rougher flotation tests were carried out by 35% solid ratio using 1 kg and 2 kg feeds in 2- and 4-liters flotation cell, respectively. The air flow was set to 3 l/min throughout the flotation test. Moreover, air was fed in 15-20 seconds delayed for the purpose of building froth. Once the froth reaches the discharge lip, the flotation time and froth scraper were started. An impeller rotational speed was selected to achieve a suitable pulp suspension in the flotation cell. Impeller rotational speed of 1300 rpm and 1500 rpm were used in 2 L and 4 L respectively. Rougher flotation concentrates were collected at 2, 6, 14, 22, and 30 minutes, to determine the flotation kinetics (Figure 1).



Figure 1. Flow sheet for kinetic rougher flotation test, RC1-6 refers to rougher concentrates 1 to 6.

3. Results

3.1. Chemical and mineral composition

Based on the assays, the received old Bor tailings sample contains 0.24% copper, 7.7% iron, 7% sulfur and 0.41ppm gold and 2.2ppm silver. Almost 60% of the samples total copper is carried by water and acid soluble copper minerals.

The mineralogy of the old Bor tailings is complex due to the subsequent alteration of main primary sulfides and occurrence of subsequent water and acid soluble copper minerals. Copper in the old Bor tailings is carried mainly by secondary water and acid soluble, chalcanthite -type minerals (57.5%) and by relicts of primary chalcopyrite (16.6%), enargite (16.3%) and covellite (9.6%).

3.2. Flotation test work

To recover both copper minerals and pyrite into concentrate, 24 flotation tests with Bor tailings were carried out at low pH of 9.75- 9.85. In the base case, sodium iso-butyl xanthate (SiBX) was the main collector and polypropylene glycol methyl ether (Dow froth 250) was the main frother. Moreover, the dissolved copper can be precipitated by adjusting pH and Eh and floated into concentrate in presence of SiBX collector. The reagent dosage were 140g/t and 80g/t, correspondingly and particle size distribution (P₈₀) was 26µm.

3.2.1. Effect of particle size on bulk flotation

The purpose was to determinate the optimum particle size distribution for bulk flotation stage. Different grinding times were applied to produce particle size distribution (P₈₀) from 50 μ m down to 13.4 μ m, were applied in presence of SIBX and Dow froth 250. The highest copper grade, 0.49% Cu, was achieved when P₈₀ was 50 μ m. Although with finer P₈₀ of particle size was 26 μ m, highest copper recovery of 93% was obtained, but the concentrate grade, 0.46% Cu, remained slightly lower. The lowest copper recovery (78%) and grade (0.25% Cu) to bulk concentrate was obtained without grinding at 132 μ m (P₈₀). Decreasing the particle size of the feed improved both recovery and grade as the degree of liberation of sulfides increased (Figure 2).



Figure 2. Effect on particle size distribution to flotation performance a) copper grade versus copper recovery and b) bulk copper recovery and grade by P₈₀.

3.2.2. Effect of different promoters on bulk flotation

Thiocarbamate and dithiophosphates are one of the most important collectors enabling robust flotation performance especially for oxidized copper minerals like Bor tailings. Therefore, Solvay's 3418A (Sodium di-isobutyl-dithiophosphinate) and XD 5002 (alkyl thiocarbamate) were tested to reach better flotation performance.

According to the copper recoveries and grades, overall flotation kinetics are almost identical for both collectors. The usage of different types of collectors didn't improve the flotation performance as well as selectivity (Figure 3).



Figure 3. Effect of different promoters on bulk flotation performance a) copper grade versus copper recovery and b) copper recovery against mass pull

3.2.3. Effect of pulp potential

In the presence of oxidized minerals, sulfurizing agents such as sodium sulfide (Na₂S) and sodium hydrosulfide (Na₅H) are one of the best effective way to increase recovery of oxidized minerals. Heavily oxidized sulfide minerals mineral surface can be transformed to the hydrophobic surface by flotation modifiers such as Na₅H. Therefore, Na₅H make such oxidized minerals more floatable in presence of xanthate or thiol collectors [23]. Copper phase of Bor tailings mostly consist of oxide type minerals. In case of sulfurizing method, pulp potential need to be adjusted precisely to avoid excessive dosages. Therefore, different pulp potentials were adjusted using by NaSH.

By reducing the pulp potential using by NaSH, flotation rate increased, but it also effected to copper grade and recovery negatively. Also, decreasing the pulp potential below -150 mV (Pt-Ag/AgCl) by NaSH, the selectivity of flotation against gangue minerals decreased (Figure 4).



Figure 4. Effect of pulp potential on bulk flotation performance a) copper grade versus copper recovery and b) copper recovery against mass pull

3.2.4. Effect of Na₂SiO₃ on cleaner stages

The best bulk flotation test conditions were used to produce material for cleaner kinetic tests (Figure 5). In the cleaner tests, all reagents were added as stage wise to avoid excessive dosages and obtain proper kinetic trends. According to the results, addition of 250g/t Na₂SiO₃ (Zeopol 30) didn't improve the copper grades in first cleaner concentrate. Based on the results, there is no dramatic effect of Na₂SiO₃ in first cleaner stage. Moreover, sulfidation also decreased the selectivity of flotation process (Figure 6).



Figure 5. Flow sheet for kinetic cleaner flotation tests.



Figure 6. Effect of Na₂SiO₃ on cleaner flotation performance a) copper recovery versus copper grade and b) copper recovery against mass pull

3.2.5. Flowsheet simulation

Simulation was carried out on developed preliminary flowsheet including rougher, scavenger, and two bulk cleaner stages by HSC Chemistry ® 10 software [22] to determine final copper and pyrite recovery in continuous process.

Mass balances were calculated including grades and recoveries for each mineral in each stream. HSC Sim Model fit® -tool [22] was used for mass balance, middle stream calculation and Klimpel flotation model for batch flotation to calculate kinetic parameters such as maximum recovery (R_{max}) and flotation rate constant (k_{max}). The Klimpel model (Equation 1), R_{max} showing the highest possible recovery for each mineral and the k of rectangular distribution showing how fast each mineral is floated.

$$R = R_{max} \left\{ 1 - \frac{1}{kt} [1 - e^{-kt}] \right\}$$
(1)

where, t is the cumulative residence time and $R_{max} \leq 1$.

HSC model fit draws kinetic curves for each mineral and define values for k_{max} and R_{max} . These values were then used for flotation modelling. A 100 tph plant capacity was selected and carried out continuous simulation using by R_{max} and k_{inf} constants with rectangular distribution method.

According the simulation results, 50,7% S pyrite (sulfur) concentrate can be produced at 85% recovery. Additionally, the pyrite concentrate contains 1.65% Cu and 9 ppm Au with the recovery of 48% and 80%, respectively (Figure 7).



Figure 7. Simulated flowsheet with copper and sulfur grades and recoveries

Discussion and conclusions

The main objective of the test work carried out by Metso Outotec was to show how valuables can be recovered from chemically and mineralogically challenging tailings. The Bor tailings contain 0.24% copper, 0.41ppm gold and 2.2ppm silver. Based on detailed chemical and mineralogical characterization, the main sulfide in the tailings is pyrite with accessory chalcopyrite, enargite, covellite and chalcanthite. Half of the total copper content is water and acid soluble.

In the laboratory scale flotation tests, the focus is on evaluating the effect of particle size, different types of collectors, pH, and pulp potential on achieved grades and recoveries. The dissolution of copper can be prevented by adjusting pH and Eh.

Based on the test work conducted, both copper and gold can be recovered effectively into pyrite concentrate. Finally, 85% of sulfur and 80% of copper were recovered in into concentrate. The recoveries for gold and silver were 49% and 84%, correspondingly. The final concentrate contained 50.7% sulfur, 1.65% copper and 9 ppm gold.

Reprocessing of old mine tailings can be both economic and environmentally friendly solution by recovering a substantial amount of copper, gold, and sulfur into concentrate, that can be utilized in smelting as a source of energy or fed to sulfuric acid plants, and at the same time reducing the environmental impact caused by acid mine drainage. **Author Contributions:** Conceptualization, J.L., A.L. and E.Ö.; methodology, E.Ö and A.L.; resources, J.S.; writing—original draft preparation, J.L.; writing—review and editing, E.Ö, A.L, and J.S.; supervision, J.S.; All authors have read and agreed to the published version of the manuscript

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