SUSTAINABILITY OF COPPER SLAG PROCESSING FROM NEW FLASH COPPER SMELTER IN RTB BOR

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Abstract: The reconstruction of metallurgical copper production in RTB Bor, replacement of roasting-reverb process with flash smelting technology, is justified both from the ecological aspect as well as from economic aspect. By modernization of the Bor smelter, emissions of sulphur dioxide, dust, arsenic, lead and other pollutants in waste smelter gas streams are drastically reduced and brought under the law set emission limit values (ELV). Increasing the efficiency of metal in the new Bor smelter by 93 to 98 percent will contribute to the economic profit of the company, and one of the essential phase that RTB Bor will lead to higher metallurgical efficiency, and thus to greater profits, represents the processing of copper slag by flotation.

Keywords: flash smelting, copper slag, recycling, flotation, RTB Bor

Introduction

RTB Bor (Rudarsko-topioničarski basen Bor), as an integrated copper mining and metallurgy company, is located in Bor, Serbia. A century ago the town of Bor had been just a small village. With the discovery of copper ore and its exploitation since 1903, the village has turned into an industrial and urban centre in north-eastern Serbia.

The RTB Bor has a long tradition in copper and precious metals production. The industrial activities in this area started with the mining exploitation of copper ore in the beginning of the 20th century. Nowadays, the RTB Bor involves all the copper industrial activities starting from the ore exploitation, flotation processing and pyrometallurgical process of copper concentrates. Flotation process was introduced due to the decreasing copper grades in ore and started in 1930s (Markovic, 2012) The first smelting line was put into operation in 1961.
For more than 100 years, RTB has been excavating more than 40 million tons per annum of copper ore and overburden at open pits Bor (closed), Veliki Krivelj (its largest site) and Cerovo, the underground mine Jama, the Smelter and copper slag processing plant, which are located in and around Bor, plus the Majdanpek mine and flotation processing plant located some 80 km northeast of Bor.

The copper ore treatment process in RTB Bor produces significant amounts of mine waste material such as: mining waste, flotation tailing and copper slag (Stanojlovic et al., 2014). Mine waste can be defined as waste materials that result from the ore exploration, mineral and pyrometallurgical processing. It is estimated that about $1.2 \times 10^9$ tons of mining waste, $0.9 \times 10^9$ tons of flotation tailings and $18 \times 10^6$ tons of copper slag have been stored on the dumps and flotation tailings ponds, which is located in the vicinity of the towns of Bor and Majdanpek, making a boundary between the urban and the industrial zone (Fig. 1).

Figure 1. The macrolocation of Bor and the RTB Bor

A century long mining activities and copper production have left 11,000 tons of mine waste per citizen of Bor (Sokolovic et al., 2007). According to the Markovic (2012), areas affected by mine wastes disposals are over 2.84 million m$^2$. The total copper mining activities in Bor has degraded over 25,000 ha of agricultural land. This represents about 60% of agricultural land in the municipality of Bor (Markovic, 2012). Due to the emission of wastewater out of the flotation tailings pond, 2,500 ha of land were destroyed.

The pollution of waters are the most significant consequences of mining, which is biologically almost completely destroyed, with significant
concentrations of heavy metals. The amount of wastewater is estimated about 9 million m$^3$. The wastewater flows directly without treatment into the Krivelj and Bor rivers and through them to the river Timok and finally, to the river Danube as the final recipient.

Smelting of copper ore with sulfur dioxide emissions have led to air pollution, soil acidification, destruction of vegetation and erosion (Markovic, 2012).

**Rtb Bor Copper Smelter**

**Old Copper Smelter**

**Bor Copper Smelter** has a tradition in the production of copper longer than a century. Bor smelting plant started operating in 1906. Modern production of copper in Bor by melting copper ore started in 1936. Since 1961, it used the reverberatory furnaces for smelting. The second smelting line was put into operation in 1971. The total capacity of the smelter was 600.000 tons of concentrate per year.

The pyrometallurgical production of copper consisted of roasting in FS batch reactors, smelting in the reverberatory furnaces, mate converting in standard PS converters, anode refining of blister copper to anode material and casting. Off gas that was generated in the process of roasting and converting was transported to the sulphuric acid plant. Other gases were discharged through the stack into the atmosphere (EIA Study, 2010). Also, the old Bor Smelter was operating at a low concentrate throughput of 40.000-50.000 tons per year compared to the projected capacity of 125.000 tons per year.

The pyrometallurgical production of copper, using smelting technology in the reverberatory furnaces, was economically unjustified and environmentally unacceptable. Low recovery of copper, low energy efficiency, i.e. high energy consumption, high operating costs, as well as low recovery of sulphur (50% to 60%) and emissions of hazardous substances into the environment made it inefficient (EIA Study, 2010).

The main disadvantages of smelting technology in the reverberator furnaces is the main reason for their replacement and introduction of autogenic technology.

**New Flash Copper Smelter**

In 2010, it began the construction of a new flash copper smelter with a projected capacity of 400.000 tons of concentrate per year. The modernization of copper smelter includes replacement of the old roaster/ reverberator furnace with more efficient autogenous flash smelting process.

The pyrometallurgical copper extraction in the new copper smelter from sulfide concentrate consist of concentrate drying, autogenous smelting in a
flash smelting furnace (FSF) and matte converting process in a Pierce-Smith converter (PSC). The products of copper sulfide concentrate smelting in the FSF are (i) molten sulfide matte (62% Cu), (ii) molten oxide slag (1.4% Cu) and (iii) off-gas (32.3% SO₂). In order to increase process efficiency and reduce environmental impact, the New Copper Smelter include more efficient treatment of off-gas and its further processing in a sulfuric acid plant (SAP). The FSF off-gas is treated in the waste heat boiler (WHB) and the electrostatic precipitator (ESP) (Ivsic-Bajceta et al., 2013). The new flash copper smelter will produce about 80,000 tpa of fine copper.

A block diagram of the new flash copper smelting process after the reconstruction is shown in Figure 2 (Ivsic-Bajceta et al., 2013).

![Figure 2. Block diagram of the new flash copper smelting process](image)

Comparison of roasting-reverb process to Outotec flash smelting process is given in table 1.

<table>
<thead>
<tr>
<th>ROASTING-REVERB PROCESS</th>
<th>FLASH SMELTING PROCESS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Matte grade to PC converting is 40 % Cu.</td>
<td>Matte grade to PC converting is 60 % Cu.</td>
</tr>
<tr>
<td>Requires 2 hot PS converters to capacity of 80,000 t/y copper in anodes.</td>
<td>Requires 1 hot PS converters to capacity of 80,000 t/y copper in anodes.</td>
</tr>
<tr>
<td>Requires 0.15 t coal/t conc. or 90 kg fuel oil/7 conc. in smelting.</td>
<td>Nearly autogenous smelting (6 kg fuel oil/t conc.)</td>
</tr>
<tr>
<td>Process off-gas amount 50,000 Nm³/h (7.5 % SO₂) + 120,000 Nm³/h (1 % SO₂)</td>
<td>Process off-gas amount 38,000 Nm³/h (24.8 % SO₂).</td>
</tr>
<tr>
<td>PS converter slag fed molten into the reverb furnaces and reverb slag with about 0.8 % Cu.</td>
<td>FSF and PS converter slag are slow cooled, crushed, grinding, floated, filtered, dried and fed back to FSF.</td>
</tr>
</tbody>
</table>
The advantages of applying flash smelting process are (EIA Study, 2010):

**Environmental Benefits**

Air quality of the local area has been significantly affected through the history of smelting operations of RTB Bor over the last century. The modernization of the existing smelter and acid plant will contribute significantly in further improving the ambient air quality of the Bor area.

By modernization of the smelter at Bor, emissions of sulphur dioxide, dust, arsenic, lead and other pollutants in waste smelter gas streams are drastically reduced and brought under the law set emission limit values (ELV).

**Minimal unit operating cost**

Flash Smelting technology is very flexible. New autogenic smelting unit should ensure better efficiency regarding metal production and decrease in unit operating costs.

The introduction of new modern Outotec flash smelting technologies in the metallurgical production in Bor Copper Smelter should provide:

- Technological recovery of metal up to 98%,
- Efficiency of sulphur collection from SO$_2$ gas above maximum and fulfilling all environmental standards,
- Maximum technologically justified energy efficiency and
- Low operating costs.

**Copper Slag**

Copper slag, which is produced during pyrometallurgical production of copper, contains a significant amount of Cu together with trace amounts of other heavy metals.

According to Gorai et al. (2003), about 2,2 tons of copper slag is generated for every ton of copper production. Approximately 24,6 million tons of copper slag is generated each year from world copper production (Gorai et al., 2003). It is usually disposed in uncovered dumps in the vicinity of a copper smelter plant. Dumping or disposal of such large amounts of copper slag can cause environmental problems.


Recovery and recycling of the valuable metals and other useful materials from the industrial wastes are becoming extremely important to the society, industry and environment. During the past two decades attempts have been made by several investigators and copper producing units all over the world to investigate a various processes for metal recovering and the possible utilization of copper slag.
Also, copper slag can be utilized to make the products like cement, fill, ballast, abrasive, aggregate, roofing granules, glass, tiles etc. (Shen and Forsberg, 2003).

**Copper Slag Processing**

Recycling today’s copper slag is similarly possible. Recovery of metals from the copper slags and utilisation of the copper slags are important not only for saving metal resources, but also for protecting the environment (Shen and Forsberg, 2003).

By applying mineral processing technologies, such as crushing, grinding, magnetic separation, eddy current separation, flotation and so on, leaching or roasting, it is possible to recover metals such as Fe, Cr, Cu, Al, Pb, Zn, Co, Ni, Nb, Ta, Au, and Ag etc. from the copper slags. (Shen and Forsberg, 2003). Some of these methods were briefly reviewed by Gorai et al. (2003).

Flotation is an important technology to recover copper from copper slag. There are a few industrial flotation facilities for treatment of copper slag, such as: Magma Copper San Manual facility, USA, Altonorte Flotation Plant, Chile, Outokumpu facility, Finland, Mount Isa Mines, Australia, Aurubus, Bulgaria, Black Sea Copper Works, Samsun, Turkey and Copper Mine Bor, Serbia (Stanojlovic and Sokolovic, 2014).

**Copper Slag Processing In Rtb Bor**

**Copper Slag Processing From Old Copper Smelter**

Since the beginning of copper smelter operations in Bor, the first half of the twentieth century, when the first smelter started operating in 1906, it is estimated that about 18 million tons of copper slag have been historically dumped and disposed (Stanojlovic and Sokolovic, 2014). Copper slag dump was located in the industrial area of Copper Mine Bor, near the smelter and covered an area of 10 ha.

Historical copper slag, which’s formed in different period of copper smelting in Bor contained considerable amounts of copper and other valuable metals with average content of copper from 0,6 to 0,8%.

The efficient recovery of metals from slag, difficult to treat complex secondary ores, requires integrated effort from the mining industry, researchers, field engineers and plant designers and also new technologies and combination of them. The similar effort for possibile reprocessing of copper slag is provided by Copper Mine Bor.

The Copper Mine Bor started production in 2001, treating copper slag by flotation, after crushing and grinding (Stanojlovic et al., 2014). Slag processing capacity was 900.000 tons per year during the 2002-2006 period. The average feeds was about 0,7 % Cu with a significant amounts of sulphide
and oxide copper minerals. Precious metals was also presents in the copper slag (0.40 g/t Au, 7.57 g/t Ag).

Our previous studies showed that low metal recovery of copper (31.66 %), gold (22.99 %) and silver (22.10 %) was achieved in the Bor flotation plant. The average content of copper, gold and silver in the produced copper concentrate were about 11.22 %, 2.71 g/t and 20.18 g/t, respectively (Stanojlovic et al., 2002).

Based on the achieved results that can be concluded that the flotation of copper slag was relatively inefficient, recoveries rarely being above 30 %, so that the flotation tailings contain between 0.3 and 0.4 % copper, of which 0.1-0.2 % was a oxide minerals (Stanojlovic et al., 2002).

Since 2006 began intensive exploitation of copper slag, which further treatment is carried out in flotation in Bor, and by 2015 most of the slag is excavated and processed.

Latest research by Stanojlovic et al., (2008) showed that valorization of copper and other metals from copper smelting slag of the Bor mine by flotation, leaching and magnetic separation can be produced without residue, so called “wastefree technology” (Stanojlovic et al., 2008; Stanojlovic and Sokolovic, 2011).

**Copper Slag Processing From New Flash Copper Smelter**

The beginning of work of reconstructed Smelting plants in the first half of 2015, brought the end of the classic processing of copper slag. However, exploitation of the remaining amount of copper slag, which is not processed by conventional flotation method will be used as an abrasive material (Zikic et al., 2015).

The reconstruction of Smelter and construction of new sulfuric acid plant includes an technological line for processing of smelting slag to achieve maximum metallurgical recovery of 98.5% for obtaining blister copper. For this purpose, it uses existing flotation line (mill section B) for copper slag processing in the Bor flotation plant.

The projected capacity of the copper slag processing is 340,000 tons per year with an average copper content of about 2 %. This amount of copper slag will be obtained from 290.360 tons/ year from the Flash process technology with copper content of 1.4 % and 49.640 tons/year from PS converter with copper content of 6 % (Sokolovic et al., 2015).

Material bilans of flash furnace and converter slags is given in Table 2.
Table 2. Material of slag from "Flash" furnaces and PS converter

<table>
<thead>
<tr>
<th>Slag</th>
<th>Amount</th>
<th>Cu</th>
<th>Fe</th>
<th>SiO$_2$</th>
<th>S</th>
<th>Zn</th>
<th>Pb</th>
<th>As</th>
<th>Sb</th>
</tr>
</thead>
<tbody>
<tr>
<td>FSF</td>
<td>729.8 t/d</td>
<td>1.4%</td>
<td>42.5%</td>
<td>29.0%</td>
<td>1.2%</td>
<td>0.5%</td>
<td>0.07%</td>
<td>0.04%</td>
<td>0.01%</td>
</tr>
<tr>
<td>PS</td>
<td>111.9 t/d</td>
<td>6.0%</td>
<td>48.6%</td>
<td>24.0%</td>
<td>1.0%</td>
<td>0.8%</td>
<td>0.62%</td>
<td>0.07%</td>
<td>0.01%</td>
</tr>
</tbody>
</table>

The process of treating smelting slag includes: slow cooling, crushing, grinding and flotation. After the cooling process is obtained by copper slag with maximum grain size 150 mm, wherein an average copper content of 2 % and which can be further treated with flotation process. Projected yield of copper from the smelter slag is 84 %, a required quality concentrate based on copper content in the concentrate was 30 %.

Technological scheme of the smelting slag processing is shown in Figure 3.

![Figure 3. Technological scheme of the smelting slag processing in RTB Bor](image)

The slag from the copper smelter is crushed initially with the 1927 model Symons 5½-foot “oldie” and then with a new Metso HP200 cone crusher running in close circuit with a Metso CVB screen. The controlled – screened product from the crushing plant is fed to the grinding circuit. Fine classification in hydrocyclones comes after grinding.
The novelty in the production of copper with significant advantages over the existing equipment used in the flotation plants in Bor, Krivelj and Majdanpek represents a vertical mill in the processing of copper smelting slag. Since May 2015, Metso’s Vertimill VTM400 vertical grinding mill significantly enhances RTB Bor’s recovery of copper slag reprocessing.

**Industrial Results of Copper Slag Processing From New Flash Copper Smelter**

Compared to the projected and installed technological scheme, there have been certain changes in the copper slag process, as follows:

- grain size of the feed in the grinding process is GGK 6 mm,
- grinding process running in the two stage grinding with ball mill and vertical mill.

After two stage of the grinding to 68.54% - 38 microns (projected feed size is 80 %–40 microns), the copper slag is conditioned with NaIPX 500 g/t and Dow-froth D250 12 g/t before being fed to the flotation process. The flotation rougher concentrate contains 10.33% of copper and then cleaning in the three stages of the flotation process to obtain projected quality of the final concentrate. Obtained copper recovery in the rougher flotation is 73.85%.

Our latest studies show that two-stage wet grinding in close circuit with a hydrocyclones are a critical point of the copper slag processing. The classification of complex slag is relatively inefficient. The efficiency in the both hydrocyclones are 42.06% and 37.07%. A circulating loads are about 150% in the primary and about 400% in the second stage of the grinding-classification process. Obviously, the particles have a great probability to going with underflow. The underflows are 61.72% and 80.24% of the total feed. These products of the hydrocyclone contains significant mass of the liberated copper particles, with average copper content about 2.4%.

Valorization of copper from hydrocyclone underflow by flash flotation cell may cause significant improvement in flotation process and as well as the whole process of copper slag processing.

Based on predicted mathematical data of the flotation results, with techno-economic point of view, obtained flotation results on the second hydrocyclone underflow (sand) are very satisfactory, taking into account the grain size and characteristics of the hydrocyclone underflow. Predicted mass yield, copper recovery and concentrate quality are 9.7%, 44.71% and 10.33%, respectively.

Technological improvements in the existing industrial processing of copper slag with additional flotation on the second hydrocyclone underflow (sand) will enable a higher total copper recovery as well as decrease energy consumption than achieved in the current Bor flotation plant.
Conclusion

Due to its complexity and heterogeneity, copper slag, in relation to the copper ore, is very different, both in terms of physical and chemical characteristics. In an effort to solve future copper slag processing, these obviously differences cause different conceptions and optimization of technological schemes and technological parameters in Bor flotation plant. By optimizing, starting with the exploitation and transportation, crushing and screening, grinding and classification, flotation process and reagent regime, the introduction of new technological solutions and application of new flotation reagents, can be achieved significant improvement of the processing efficiency of these valuable waste materials.

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