1. OUTOKUMPU COPPER PRODUCTION

Outokumpu is one of the few copper producers refining copper concentrates all the way to semi-products. Production involves flash smelting of the concentrates, converting, anode casting, and electrolytic refining. About 70% of the copper concentrate comes from the company’s own mines.

The Outokumpu flash smelting process was invented in the late 1940s at Harjavalta smelter. The main advantages of this process are flexibility, low energy consumption, and high recovery of sulphur. After converting and refining in an anode furnace the copper is cast to anodes by automatic weighing and casting equipment.

Electrolytic refining is carried out using the periodic reversed current (PRC) technique at the Pori Works (Fig. 1). Capacity of the tankhouse is 55,000 t/a cathodes. High grade cathodes are produced and impurities in the anodes are recovered. The copper cathodes are used for making several kinds of semi-finished products, e.g. tubes, bars, sheets, wire and rod. Especially high quality is demanded of the cathodes because production includes high conductivity oxygen free copper for electrical purposes.

Figure 1. Flowsheet of Pori Refinery
2. IMPURITY CONTROL IN TANKHOUSE

2.1. Anode Composition

Most of the impurities are introduced to the tankhouse in the anodes. Because of the variety of concentrates and different intermediate products or residues from other plants of the company the impurity level of Outokumpu anodes has greatly increased in recent years and the variations in anode analysis are large (Table 1).

Table 1 - Anode analysis at Outokumpu Pori Refinery (based on weekly averages 1981)

<table>
<thead>
<tr>
<th></th>
<th>minimum</th>
<th>average</th>
<th>maximum</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni</td>
<td>0,3</td>
<td>0,6</td>
<td>0,9</td>
</tr>
<tr>
<td>Pb</td>
<td>350</td>
<td>580</td>
<td>1030</td>
</tr>
<tr>
<td>Ag</td>
<td>510</td>
<td>810</td>
<td>1340</td>
</tr>
<tr>
<td>As</td>
<td>880</td>
<td>1830</td>
<td>3630</td>
</tr>
<tr>
<td>Sb</td>
<td>170</td>
<td>350</td>
<td>630</td>
</tr>
<tr>
<td>Bi</td>
<td>50</td>
<td>100</td>
<td>260</td>
</tr>
</tbody>
</table>

Impurities in the anodes either dissolve in the electrolyte where they tend to accumulate (Ni, Fe, Zn, As, Sb, Bi) or they stay undissolved and form the anode slime which sinks to the bottom of the electrolyte cells (NiO, Pb, precious metals, Se, Te, Sn).

2.2. Insoluble Components

The primary anode slime contains the following main components:

- metallic copper
- nickel oxide
- lead sulphate
- precious metals (Au, Ag, Pt, Pd)
- selenium and tellurium (mainly as copper and silver selenides vs. tellurides)
- anode mould paint, e.g. BaSO₄

The slime is first fed to a leaching reactor where copper is dissolved by air oxidation at 80°C. The reaction time is limited to 2-3 hours to avoid the dissolution of tellurium. The slime is then filtered. The amount of "copper free slime" is 5-8 kg/t anodes dissolved and has the following approximate analysis:

<p>| | |</p>
<table>
<thead>
<tr>
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<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni</td>
<td>25-35%</td>
</tr>
<tr>
<td>Cu</td>
<td>4-7 %</td>
</tr>
<tr>
<td>Pb</td>
<td>7-8 %</td>
</tr>
<tr>
<td>Ag</td>
<td>10-13%</td>
</tr>
<tr>
<td>Au</td>
<td>0.4%</td>
</tr>
<tr>
<td>Se</td>
<td>3-4 %</td>
</tr>
<tr>
<td>Te</td>
<td>1.5-2 %</td>
</tr>
</tbody>
</table>

This slime is then treated with concentrated sulphuric acid at 180°C, whereby NiO becomes NiSO₄, which is removed by
washing with water. After filtration the slime is roasted with sulphuric acid to remove and recover selenium. The slime is then further treated to recover the precious metals.

The slime settles well in the cells and there is no cathode contamination. In addition the solid content of the electrolyte can be reduced by using two polishing filters.

2.3. Soluble Components

For producing high grade cathodes the electrolyte composition is a crucial factor. The build-up of impurities dissolving from anodes must be controlled by treatment of the electrolyte.

The solubilities of the main components in the present conditions are approximately:

<table>
<thead>
<tr>
<th>Component</th>
<th>Solubility</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni</td>
<td>70%</td>
</tr>
<tr>
<td>As</td>
<td>90%</td>
</tr>
<tr>
<td>Sb</td>
<td>40%</td>
</tr>
<tr>
<td>Bi</td>
<td>40%</td>
</tr>
</tbody>
</table>

These vary according to anode composition.

Accepted impurity levels in the electrolyte are:

<table>
<thead>
<tr>
<th>Component</th>
<th>Level</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni</td>
<td>15 g/l</td>
</tr>
<tr>
<td>As</td>
<td>10 g/l</td>
</tr>
<tr>
<td>Sb</td>
<td>0.4 g/l</td>
</tr>
<tr>
<td>Bi</td>
<td>0.15 g/l</td>
</tr>
</tbody>
</table>

If the Ni, Sb or Bi content of the electrolyte is higher the probability of cathode contamination is increased. Arsenic is not critical in this respect.

2.4. Nickel Control

For nickel removal electrolyte is bled-off through decopperizing cells and evaporated. The amount of electrolyte treated is:

\[
\frac{\text{Ni dissolved}}{\text{Ni in electrolyte}} = \frac{0.7}{15} = 0.0473 \text{ m}^3/\text{t Cu}
\]

The total amount of solution treated in decopperizing and evaporation is 0.38 m\(^3\)/t Cu, because the NiSO\(_4\) solution from slime treatment is mixed with the electrolyte bleed-off.

Decopperizing cells are arranged in three stages in series (Fig.2). In the first and the second stage there are 5+5 cells in parallel. Then electrolyte flows through them.
copper concentration is reduced to 8 g/l. In the third stage (10 cells) electrolyte is circulated until copper concentration 0.5 g/l is reached, then the solution is fed into the evaporator.

Figure 2 - Flowsheet of Decopperizing and Evaporation

Normal Cu-starting sheets, 31 per cell, are used as cathodes and lead sheets as anodes. Cathodes are changed once a week. Compact cathodes are pulled from the first and the second stage, where current density is 180 A/m². In the third stage deposition is powder, Cu-As-sludge, falling on the bottom of the cells. Current density is varied between 180-50 A/m² according to copper concentration in solution.

The evaporator is submerged combustion type fuelled with heavy oil. The temperature of the solution is kept at 143°C which corresponds to 70% acid strength. Nickel and other bivalent metals such as iron and zinc, crystallize as metal sulphates. Acid and nickel sulphate are separated by a thickener and a pan filter. Acid is returned to the tank house. Crude nickel sulphate is purified chemically and sold out as nickel sulphate hexahydrate mainly for plating purposes.

Submerged combustion evaporator has the following special features:
- good thermal efficiency
- high crystallization temperature which gives large, easily filtered crystals
- high operating efficiency
- flexible in feed rate and concentration
2.5. Arsenic Control

In the third stage of decopperizing when the copper concentration is low enough arsenic starts to be deposited on the cathode surface as copperarsenic, Cu_3As, and finally as elemental arsenic. If the potential of hydrogen discharge is exceeded, highly poisonous arsine AsH_3-gas is produced. The phenomenon can be explained with Fig. 3 which shows cathodic current density - potential curves in solutions containing various contents of copper, 5 g/l As and 250 g/l H_2SO_4. When applied current density is under the limiting current density of copper and copper arsenide deposition, only these ions are discharged at the cathode, but if the current density exceeds the limiting current density the overpotential of the electrode rises into the hydrogen evolution area and consequently arsine evolution starts immediately.

Figure 3 - Cathodic Current Density-Potential Curve

The limiting current density depends on the diffusion of dischargable ions onto the cathode surface and so the factors affecting its magnitude are:
- copper and arsenic concentrations in solution
- agitation of flow rate of solution
- temperature of solution
- viscosity of solution

The increase of concentration, agitation and temperature and the decrease of viscosity increase the limiting current density. The actual limiting current density increases steadily with durations of electrolyte, because actual cathode surface area is increased by powder deposits on the
In order to avoid arsine evolution the copper concentration of the circulating solution is analyzed continuously by an Outokumpu Courier 30 On-stream Analyzer (Fig. 4). Using an arsine detector in off-gas duct current vs. Cu-concentration curves in different conditions are determined experimentally and these values are recorded on the minicomputer. The minicomputer receives actual copper concentration from Courier 30 analyzer and adjusts the current of the rectifier according to the present values. Figure 5 shows an example of the experimentally determined curve showing the range of arsine evolution.

**Figure 5 - Limits of Arsenic Evolution**

- Arsenic concentration: 6-38/1
- Flow rate: 3 m³/h/CELL
- Temperature: 45°C
- Cathode age: 1 d

![Graph showing arsenic concentration vs. current density](image-url)
The proportion of current discharging arsenic increases with decreasing copper concentration, in the other hand because the current must be decreased with decreasing copper concentration in order to avoid arsine production, the maximum rate of arsenic removal is reached at about 2 g/l copper concentration. At that range about 50% of the current is used by arsenic deposition (Fig. 6). This is very sensitive for flow rate variations. 

For safety reasons all cells are hooded and properly ventilated. The reactifier is automatically switched off if ventilation stops. Handling of Cu-As-sludge containing an average 30% As is designed to be as dust free as possible. Solids are separated by centrifuge and dropped directly into plastic sacks, which are transported to the smelter or sold.

**Figure 6 - Rate of Arsenic Removal vs. Copper Concentration**

![Graph showing the rate of arsenic removal vs. copper concentration](image)

Antimony and bismuth dissolved into the electrolyte are codeposit with arsenic in the decopperizing cells. The volume of bleed-off is determined by nickel. So if in anodes the proportion of antimony and/or bismuth is increased compared with nickel, the antimony and/or bismuth content of electrolyte exceed accepted limits. The ratios can be estimated from solubilities and accepted electrolyte concentration as follows:

\[
\begin{align*}
0.7 \times \text{Ni in anode} &= 0.4 \times \text{Bi in anode} ; \text{Bi} = 0.018 \times \text{Ni} \\
0.7 \times \text{Ni in anode} &= 0.4 \times \text{Sb in anode} ; \text{Sb} = 0.048 \times \text{Ni}
\end{align*}
\]

If Bi > 0.018 x Ni and/or Sb > 0.048 x Ni more Bi, and/or Sb go into the electrolyte than is recovered and, the feed to the decopperizing cells should be increased more than is...
necessary for nickel. This is expensive and at high rate of bleed-off copper balance of tankhouse electrolyte is destroyed. For these reasons Outokumpu has developed methods to precipitate antimony and bismuth directly from the electrolyte.

Bismuth can be precipitated (4) by adding barium carbonate to a side stream of the electrolyte (Fig. 7). At 70°C and during one hour retention time in a mixing reactor, 80-90% of bismuth content is co-precipitated with BaSO₄ formed. About 50 kg BaCO₃ is needed to remove 1 kg bismuth. After filtration the electrolyte is returned back to the electrolyte circulation.

Antimony is only slightly affected during BaCO₃-precipitation, less than 10% is removed. A more efficient method for antimony removal, which also removes bismuth simultaneously, is based on precipitation as arsenates. Electrolyte is normally supersaturated (3) by antimony and bismuth, which can be dangerous for cathode quality, if antimony and bismuth arsenates start precipitating in the electrolytic cells, for example because of locally reduced temperature. When supersaturated electrolyte is fed to a mixing reactor where favourable precipitation conditions exist, it is possible to achieve about 100-200 mg/l Sb and 50-100 mg/l Bi reductions in concentrations depending on degrees of supersaturation and reactor conditions. The pulp density and quality of arsenates in the reactor are dominating factors affecting the precipitation.

Figure 7 - Precipitation of Bismuth

![Figure 7 - Precipitation of Bismuth](image-url)
3. SUMMARY

Mining of poorer and more complex ores, the increase of the amount concentrates purchased, and the internal circulation of residues from nickel, cobalt and zinc plants have increased the amount of impurities in Outokumpu copper circuit. Research and development work has been carried out both with regarding to smelter operation and chemical treatment at the refinery.

At the Outokumpu copper refinery in Pori nickel is removed by a submerged combustion evaporator from decopperizing solution and the nickel is recovered as chemically purified NiSO₄·6H₂O. The decopperizing section is rebuilt to give better efficiency and improved safety. For removal of antimony and bismuth two different precipitation methods have been developed. Anode slime is processed to recover selenium, gold, silver and platinum.

With this new process development the flexibility of the refinery is greatly improved. A large variation in anode composition can be tolerated for production of copper cathodes of high grade quality.

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