

Cost-Effective Technology of Selenium Extraction from Copper Production Waste and Intermediate Products: A Review

Khojiev Sh.T.¹, Saidova M.S.¹, Khotamqulov V.X.¹, Saidqulov A.G.¹

¹Tashkent State Technical University, Tashkent, Uzbekistan

E-mail: hojiyevshohruh@yandex.ru

Abstract—Selenium and tellurium are used as vulcanizers and accelerators to improve the elasticity and increase the durability of rubber. Their use is constantly expanding in the chemical and pharmaceutical industries for catalysts for oxidation, hydrogenation, dehydrogenation, and halogenation. Selenium and tellurium increase the resistance of lubricating oils against oxidation. selenides and tellurides of a number of transition metals are components of antifriction coatings and materials. They are part of disinfectants, insecticides, fungicides and herbicides. Selenium and tellurium do not form independent deposits, they are found as an impurity in the ores of other metals. The behavior of selenium and tellurium and their compounds during ore dressing is characterized by a low degree of conversion into concentrates. So, with selective flotation, the extraction into copper concentrates is 10-25%; zinc 5-10%, lead 20-35%, nickel and molybdenum 0.5-5% of the content of selenium and tellurium in the ore. Most of the selenium and tellurium remains in the enrichment tailings and pyrite concentrates. In the process of metallurgical processing of sulfide ores and concentrates (copper, nickel, zinc, lead), gold-bearing ores and pyrite concentrates, selenium and tellurium are distributed and accumulated in waste and semi-products of enterprises: in dusts of agglomeration processes, smelting and roasting of concentrates non-ferrous metals, sludge from electrolytic refining of copper, nickel, in sludge and sludge from sulfuric acid production, waste from lead refining, etc. The main source of selenium and tellurium is anode sludge from electrolytic refining of blister copper. Selenium and tellurium are extracted from the sludge along with the extraction of copper, gold and silver from it. Another important source of selenium and tellurium is the sludge of sulfuric acid and pulp and paper production, which contains 3-42% Se and 0.2-14% Te. Waste and semi-products of lead production are processed in increasing quantities, extracting selenium and tellurium.

Keywords— metallurgy, selenium, anode sludge, copper production, oxidation, leaching.

1. Introduction

Selenium [Greek Selene - Moon (named as an analogue of the previously discovered tellurium), Lat. Selenium], Se – A chemical element belonging to group VI of Mendeleev's periodic system. Serial number 34, atomic mass 78.96. There are 6 stable isotopes in nature: ⁷⁴Se(0.87%), ⁷⁶Se(9.02%), ⁷⁷Se(7.58%), ⁷⁸Se(23.52%), ⁸⁰Se(49.82%), ⁸²Se(9.19%). Of the 16 radioactive isotopes, only ⁷⁵Se (T_{1/2}=121 days) is of practical importance. Selene Ya. Berselius discovered in 1817 [1-6].

Distribution in nature. Selenium makes up 5·10⁻⁶ % by mass of the Earth's crust. Its important minerals include silver, lead, mercury and copper selenides AgSe - naumanite, PbSe - claustalite, HgSe - timanite, Cu₂Se - berselianite, Hg(Se, S) - onofrite and the equivalent salt of selenic acid CuSeO₃·2H₂O - chalcomyenite enters.

Characteristics. Selenium is a dark gray substance with a brown tint. has several modifications. The most stable of them under normal conditions is gray Selenium in the crystalline state. Melting point 217°C, boiling point 685°C, density 4.81 g/cm³. The most remarkable feature of selenium is that its electrical conductivity changes dramatically when exposed to light. Selenium belongs to non-metals; according to its chemical properties, it is similar to sulfur, but its activity is lower than that of sulfur. Selenium in its compounds is mainly -2, +2, +4 and +6 valence. Selenium is extracted from the "muds" of sulfuric acid and cellulose papers, and from the

sludge that sinks to the bottom of the electrolyzer during copper electrolysis [7-12].

Usage. Selenium is used in semiconductor technology, production of red and yellow glass, metallurgy, chemistry, pharmaceutical and rubber industry. The compounds are poisonous. Most living tissue contains 0.01 to 1 mg/kg of Selenium [13-15].

2. Selenium production technology from anode sludge of copper production

Sulphide copper ores contain a certain amount of rare metals such as gold and silver and rare metals such as selenium and tellurium [16-19].

During the processing of these ores, most of the rare metals are collected in the slurries resulting from the electrolytic refining of copper. In addition to the gold and silver in the ore, the gold and silver in the flux added to the copper smelting process are also collected in the slurries.

Addition to gold and silver, the slime contains a large amount of selenium and tellurium [20].

The amount of anode sludge formation (output) depends on the purity of the anode copper and is 0.4-1% of the average anode weight (mass).

The chemical composition of the sludge from the electrolytic refining of copper anodes is shown in Table 1.

Table 1. Chemical composition of the anode sludge, %

Substance	Quantity %	Substance	Quantity %
Copper	1-80	Lead	1-25
Silver	1-45	Nickel	0.2-10
Gold	0.2-1.5	Iron	0.2-2
Selenium	2-15	Sulfur	2-10
Tellurium	0.1-8	Quartz	0.5-15
Arsenic	0.5-10	Alumina	0.5-1.5
Antimony	0.2-15	Cobalt	0.02-0.1
Bismuth	0.2-1		

Copper is present in the slurry in the form of a powdery metal formed by the transition of monovalent copper ions to divalent ions during electrolysis:

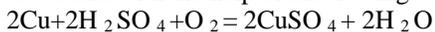


In addition, copper slag contains scrap, Cu_2O , Cu_2S , Cu_2Se , Cu_2Te , CuAgSe . Rare metals are present in the slurry in the form of copper-silver-gold alloy, selenide and telluride (Ag_2Se , CuAgSe , Ag_2Te , $(\text{Au,Ag})\text{Te}_2$). Lead is present in the slurry in sulfate, arsenate, and antimonate forms. Nickel in the slurry is in the form of complex compounds with sulfate and copper and antimony: $3\text{Cu}_2\text{O} \cdot 4\text{NiO} \cdot \text{Sb}_2\text{O}_5$, arsenic (arsenic) and antimony are shown in the following compounds in the slurry: $\text{As}_2\text{O}_3 \cdot \text{Sb}_2\text{O}_5$ – “floating slurry” and $\text{As}_2\text{O}_5 \cdot \text{Sb}_2\text{O}_3$.

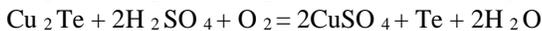
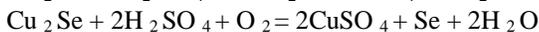
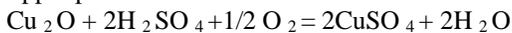
Technological schemes of processing copper electrolytic slurries include the following processes [21]:

- 1) decoppering of sludge;
- 2) oxidation of chalcogenides by thermal treatment;
- 3) getting selenium and tellurium;
- 4) melting the burnt slag into gold alloy.

The decoppering process begins with separating the large fraction from the slurry and sending it to the anodes for remelting. In the next step, copper is selectively dissolved with a 10-15% sulfuric acid solution. This process is carried out at 80-95 °C and with the help of air blowing.



Together with metallic copper, the following compounds of copper pass into the solution:



As a result of decoppering, the amount of copper in the slurry decreases to 1-3%.

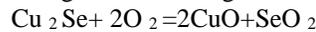
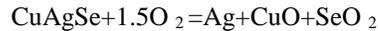
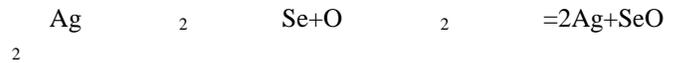
The resulting sulfuric acid copper solutions are sent to the copper electrorefining plant. The decoppered slurry is sent to extract Se and Te.

As a result of decoppering, the amount of copper in the slurry decreases to 1-3%.

The process after decoppering is oxidation of chalcogenites. Oxidation can be done in three ways:

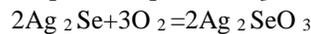
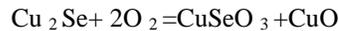
- Oxidizing burn;
- Sulphating incineration
- Baking soda.

annealing is carried out at a temperature of 700-780 °C. Selenides are oxidized by oxygen in the air during combustion:

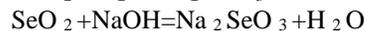
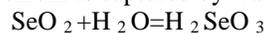


The resulting SeO_2 (selenium dioxide) has a high vapor pressure (100 kPa - 315 °C), and it passes into the gas phase. The rate of transition of selenium to the gas phase is 95-97 %.

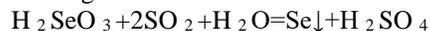
In the process of heating the slurry, selenium changes to the state of involatile copper and silver selenites of selenium at low temperatures, and as a result, part of the selenium remains in the coal:



Oxidizing incineration of sludge is carried out in shaft and multi-bottom furnaces. Incineration gases containing SeO_2 are sent to an aqueous treatment system, and in this process selenium is captured by water or an alkaline solution:



The resulting solution is acidified with HCl acid and the selenium in the solution is precipitated in the elemental state with SO_2 gas:



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