Processes of Extraction of Non-Ferrous and Precious Metals from Alternative Sources of Raw Materials

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Abstract. The presence of precious metals in electronic waste such as gold, silver, platinum and palladium, as well as non-ferrous metals (copper, nickel, zinc, tin, etc.) make it attractive for recycling. In industry, both hydrometallurgical and pyrometallurgical methods are used to extract valuable metals from electronic waste. Universal method for processing of electronic scrap waste does not exist nowadays.

1. Introduction

The increase in demand for electronic equipment based on the development of technology. The service lifetime of existing electronic equipments is reduced, which leads to an increase in waste electronic equipment. The growth in electronic waste is growing and accelerating every year. At present, around 20 to 25 million tons of electronic waste are generated worldwide per year, where the great ratio of them from Europe, United States and Asia. Over the past 20 years, China and Latin America have become producers of a significant amount of electronic waste [1]. The mass of electronic scrap in Russia is about 1.5 million tons per year, and no more than 10% is recycled from them. The resulting waste, on the one hand, causes great harm to the environment, on the other hand, they represent the most valuable resources, surpassing natural sources in the content of useful components. All this creates prerequisites for the development in Russia and in the world of large-scale production of secondary metals [2].

Electronic waste is classified as hazardous materials, as there are components in household and industrial electrical apparatus such as batteries, capacitors, cathode ray tubes, etc. Electronic waste may consist of a large number of components of various sizes, shapes and chemical composition. Some of them contain hazardous metals, including mercury, lead, and cadmium.

The presence of precious metals in electronic waste such as gold, silver, platinum and palladium, as well as non-ferrous metals (copper, nickel, zinc, tin, etc.) make it attractive for recycling. In industry, both hydrometallurgical and pyrometallurgical methods are used to extract valuable metals from electronic waste. Universal method for processing of electronic scrap waste does not exist nowadays. The technologies used may have a number of advantages and disadvantages.

Electronic waste is a complex mixture of ferrous, non-ferrous, precious metals on plastic and ceramic bases. Printed circuit boards are one of the most important components of electronic equipment, on which most valuable metals are concentrated, but most of the toxic components are also concentrated in printed circuit boards.

Printed circuit boards are found in electrical and electronic devices (TVs, computers, mobile phones and laptops). As a rule, printed circuit boards consist of 40% of metals, 30% of plastics and 30% of ceramics [3]. To make them conductive, printed circuit boards are coated with metals (tin, silver or copper). There are two types of printed circuit boards that are used in mobile phones and personal computers. The first type of printed circuit boards is made of multilayered fiberglass coated with copper. Such printed circuit boards are used for small electronic equipment, such as mobile phones. The other type is made of monolayer fiberglass, cellulose paper or phenolic material, which is also coated with a layer of copper and is used for larger devices, such as computers and televisions. Polymers and industrial...
plastics are major components of printed circuit boards. These polymers contain polyethylene, polypropylene, epoxy resins and polyesters [1].

The printed circuit boards contain a large number of small components, so sampling for analyzing the composition of the printed circuit boards is difficult due to the heterogeneous and complex nature of the materials. As a rule, to analyze the composition of printed circuit boards, they are crushed to smaller sizes (less than 1-2 mm), and various methods are used to separate components, including electromagnetic separation, electrolytic dissolving, etc [4]. In [5] investigated the composition of waste printed circuit boards from mobile phones and personal computers. Pretreatment included crushing and then separation by magnetic and electrostatic methods. Chemical analysis was performed using dissolution in aqua regia. The analysis of the composition was performed using atomic emission spectroscopy. The results showed that the printed circuit boards of mobile phones had a higher (34.5%) copper content compared to personal computers boards (20%).

Electronic waste contains a wide range of elements, some of them are valuable, some of them are toxic or hazardous, and some of them are a combination of both. The valuable metals such as, gold, silver, platinum, palladium, copper, aluminum, nickel, tin, zinc, iron, etc. The toxic or dangerous metals, but the most interest are the following metals: mercury, beryllium, indium, lead, cadmium, arsenic, antimony, etc. The printed circuit boards also include: bromine, fluorine, chlorine, plastics, organic liquids, etc. When disposing of such electronic wastes without proper treatment, there is a high risk of environmental damage. The disposal of electronic waste underground has many disadvantages, including pollution of groundwater and soil, as well as the loss of a potential source of valuable metals.

Table 1 shows examples of the material composition of various equipment, as well as printed circuit boards from personal computers, cell phones and TVs. These figures are only indicative figures derived from specific samples, they may also vary within the same type of equipment, but the order of magnitude will be similar.

| Component content, (g/t) | Fe (%) | Al (%) | Cu (%) | Plastic (%) | Ag (g/t) | Au (g/t) | Pd (g/t) |
|-------------------------|-------|-------|-------|-------------|---------|---------|---------|
| TVs                     | 28%   | 10%   | 10%   | 28%         | 280     | 20      | 10      |
| Printed circuit boards  | 7%    | 5%    | 20%   | 23%         | 1000    | 250     | 110     |
| Cell phones             | 5%    | 1%    | 13%   | 56%         | 1380    | 350     | 210     |
| Audio equipment         | 23%   | 1%    | 21%   | 47%         | 150     | 10      | 4       |
| Dvd players             | 62%   | 2%    | 5%    | 24%         | 115     | 15      | 4       |

For printed circuit boards, cell phones, precious metals make up more than 80% of the cost, for TV cards and DVD players, they make up just over 40% [6].

It should be noted that in the development of technologies for the processing of electronic scrap it is necessary to pay attention to the separation of toxic and hazardous components, as well as to minimize the loss of precious metals, which may adversely affect the economic performance of the process.

Most of the electronic waste is dumped, about 20% is burned [7]. In the last decade, many countries have developed legislation on electronic waste management. In some countries, laws have emerged that cannot be placed electronic waste underground or burn it in incinerators without isolating hazardous materials.

In addition, the export of electronic waste to underdeveloped countries is not allowed according to the international regulations. Underground disposal, burning in the air, and acid leaching adversely affect the environment, polluting drinking water and the atmosphere [8]. Therefore, the recycling of electronic waste is important in terms of minimizing pollution and resources management.

Recycling electronic waste to extract valuable components is important in terms of energy savings. Table 2 shows [7] six basic materials, the use or extraction of these materials from electronic
scrap provides significant energy savings compared to the energy conservation which is required for their primary production from raw materials.

Table 2. Energy savings during the recycling of some components compared to the energy consumption in their primary production [9, 10].

| №  | Component    | Energy savings (%) |
|----|--------------|--------------------|
| 1  | Aluminum     | 95                 |
| 2  | Copper       | 85                 |
| 3  | Iron and steel | 74             |
| 4  | Tin          | 65                 |
| 5  | Zinc         | 60                 |
| 6  | Plastic      | >80                |

Moreover, the processing of electronic waste will reduce the burden on the mining industry in terms of ore mining for the primary production of metals. Consequently, this can help in solving problems with the extraction of metals, which exist in low concentrations in the ore of raw materials and their extraction is accompanied by a significant energy consumption. In fact, electronic waste is a rich source of precious and non-ferrous metals in comparison with crude ores. The amount of gold extracted from one ton of electronic waste in the processing of personal computers is greater than in the processing of 17 tons of gold ore. In some cases, recovery of precious and non-ferrous metals from electronic scrap is easier than from their ore [11].

2. Theoretical basis

Technological scheme of processing scrap of electronic industry can be represented as follows (Fig. 1). Raw materials coming from enterprises are sent for preliminary disassembly. At this stage, components containing precious metals are extracted from electronic computers and other electronic equipment. The enriched material is sent to smelt, as a result of that anodes are obtained, containing non-ferrous and precious metals.

Experience in the processing of secondary raw materials containing precious metals, by the largest national and international enterprises, allows us to conclude that the main steps can be: preparation of secondary raw materials (enrichment), burning and electrolysis.

When processing electronic waste, one of the main operations is burning. The main problem at the stage of pyrometallurgical processing is a large amount of plastics and other organic materials, their burning produces a significant amount of gases containing harmful components.

3. Experimental

From the above scheme, it can be seen that after the enrichment of the electronic scrap, the concentrate should be smelted to the anodes. As a result of smelting of the magnetic fraction, alloys with a high content of iron, nickel and cobalt can be obtained, and copper-zinc alloys can be obtained as a result of smelting of the non-magnetic fraction.

3.1. Smelting concentrate to anodes and the effect of tungsten on the extraction of precious metals

When smelting in an induction furnace of an iron-nickel concentrate, it was found that refractory tungsten, when oxidized, goes into slag. At the same time, analyzes of thin cross-sectional polished microscopic sections by Tescan TS 5130 MM microscope showed that tungsten collects gold (Fig. 2), which leads to its loss in accounting. During the smelting process, it was found that refractory tungsten deposited on the surface of a graphite crucible, carrying gold along with it.
In Figure 2 it can be seen that platinum and palladium are evenly distributed, meanwhile some individual large areas with a high concentration of silver can be observed. Gold is evenly distributed in phases, but at the point of high concentration of tungsten, the gold content is maximum, and in this case tungsten is considered to be a collecting agent for gold.

This effect can be avoided if you get rid of tungsten by oxidizing it and converting it to slag. Then precious metals collected in tungsten will remain in the copper alloy.

The density of tungsten is almost close to gold – 19.3 g/cm³, and the ionic radii differ twice, in this case it is possible to collect one metal into another. Tungsten at ordinary temperature is resistant to hydrochloric, sulfuric, nitric and hydrofluoric acids of all concentrations, as well as aqua regia. When heated to 80-100°C, the metal is resistant to hydrofluoric acid, very weakly interacting with hydrochloric and sulfuric acids. Slightly more noticeable, it interacts with nitric acid and aqua regia. In a mixture of hydrofluoric and nitric acids, as well as hydrogen peroxide, tungsten dissolves. This creates significant difficulties in the processing of electrolysis sludge, since non-oxidized tungsten is completely converted into the sludge, and its content in individual deliveries of electronic scrap exceeds the content of precious metals.

In the system of tungsten-iron these compounds are formed: W₆Fe₂, Fe₂W. The mutual solubility of the components in the solid state is insignificant; the interaction between tungsten and cobalt has a similar nature [12].

3.2. The effect of silicon on the process of electrochemical dissolution of anodes

On the basis of the St. Petersburg Mining University, smelting was carried out to anodes of electronic waste in the furnace "Tamman". 2 anodes from the magnetic fraction and 2 anodes from the nonmagnetic fraction were obtained.

The first anode was smelted from the magnetic fraction in a graphite crucible without any additives; during the smelting of the second anode, quartz sand (SiO₂) and potassium nitrate (KNO₃) were added.

A similar operation was performed in the smelting of the anodes from the non-magnetic fraction, followed by the production of anodes 3 and 4.
Studies of the obtained anodes were carried out by using a TESCAN VEGA 3 Sem scanning electron microscope and gave the following results on the composition of the anodes subjected to electrolytic dissolution in a laboratory setup (Table 3, 4).

Based on the data from Tables 3 and 4, it was concluded that silicon was recovered to its elementary state during smelting, or it is present in the anode as an oxide.

The anodes were subjected to electrochemical dissolution in a 1 mol/l solution of NiSO₄·7H₂O with the addition of H₂SO₄ with concentration 30 g/l. At a temperature of 25°C and a cathode current density of 230 A/m². We used an iron cathode and bath potential – 6 V.

As a second electrolyte, a 1 mol/l of CuSO₄·5H₂O was used with the addition of H₂SO₄ with concentration 30 g/l. The electrolyte temperature is 25°C, with copper cathode and cathode current density is 230 A/m². The bath potential – 6 V.

The result of this experiment was a decrease in the current density during dissolution of the obtained anodes, which was described in detail in previous works [12-16].

![Figure 2. The results of smelting iron-nickel concentrate](image-url)
precipitate, followed by their isolation from the solution. It is proposed to carry out an operation to convert these compounds into a frothy product for complete extraction. The method under study involves the transfer of metal compounds into a hydrophobic precipitate, followed by their isolation from the solution. Collecting agent, used as a precipitator, significantly increases the concentration in the resulting product, which will undergo separation.

After this treatment of the solutions, two kinds of cakes are obtained: nickel cake (up to 96% nickel in the cake) and copper cake, which can be recycled or sent to the consumer. The following reactions which take place in the electrolyte:

\[
\text{NiSO}_4 + H_2O + \text{CaO} = \text{CaSO}_4(s) + \text{Ni(OH)}_2(s) \quad (1)
\]
\[
\text{CuSO}_4 + H_2O + \text{CaO} = \text{CaSO}_4(s) + \text{Cu(OH)}_2(s) \quad (2)
\]

3.3. Recycling solutions

Electrolyte solutions obtained after the electrolysis process are enriched in nickel in the case of dissolving Ni-Co-Fe anodes in a nickel electrolyte and copper in dissolving Cu-Zn anodes in a copper electrolyte. There is a need to process or purify such solutions from impurities or salt excess of non-ferrous metals.

And one of the ways is to converted copper and nickel salts into the hydroxide form, by the addition of calcium oxide, as a result of the following reactions which take place in the electrolyte:

After the treatment of the solutions, two kinds of cakes are obtained: nickel cake (up to 96% nickel in the cake) and copper cake, which can be recycled or sent to the consumer. The following reaction is associated with the use of naphthenic acids for the subsequent extraction separation from a solution of copper and nickel. The low solubility of these acids in water, the possibility of their isolating them from waste of oil treatment and, as a result, the comparative cheapness determine the feasibility of using this reagent in the processing of metallurgical solutions. Naphthenic acids form complex compounds with a specific metal ion at a certain pH. This enables the selective isolation of metals from solutions.

In the future, it is possible to carry out the process of reextraction, obtaining a pure naphthenic acid and an aqueous solution of the salt of the corresponding cation. It is possible to use this method with significant concentrations of metal ions in solutions. But it may be that the concentrations of valuable components will be small for standard extraction operations.

If it is impossible to electrochemically extract gold or other metals from poor solutions, it is proposed to carry out an operation to convert these compounds into a frothy product for complete extraction. The method under study involves the transfer of metal compounds into a hydrophobic precipitate, followed by their isolation from the solution. Collecting agent, used as a precipitator, significantly increases the concentration in the resulting product, which will undergo separation. Equipment for this technology is standard laboratory or industrial equipment not required by special regulatory systems. High performance of this process allows its application in any industries. Such devices can be used to clean recycled industrial water. Such devices can be used to clean circulating industrial water. Foam apparatus – a turbo-aerator, constructional design of which provides the formation of an air (foam) layer with the lowest hydraulic resistance. The device is a vertical container with square cross section. The tank is divided into two zones: the upper chamber (expansion), designed to froth breakage and the lower (mixing) chamber. In a turbo aerator, the gas moves through a layer of foam that forms on the grid where the fluid is supplied, when the air is blown from below or when an
air stream hits the surface of the liquid. This device is simple in design and quite effective. In this reactor, happens process of concentration.

Furthermore, in the presence of other cations in the solution, there is the prospect of selective extraction of metals from poor solutions adjusting just some of the process parameters such as temperature or pH value.

4. Conclusions

Based on the obtained data, it can be concluded that during the smelting of concentrates, the obtained anodes contain impurities that can affect the extraction of precious metals. Such impurities should be removed as much as possible at the smelting stage, before the hydrometallurgical processing stage. To these impurities include primarily tungsten, lead, tin.

Some impurities may have a beneficial effect on the electrochemical dissolution of the anodes. Silicon can be used as an impurity with which it is possible to regulate and control the process of electrochemical dissolution. The presence of silicon can reduce the dissolution potential of the anode, which leads to a reduction in power consumption, or allows you to increase the current density to accelerate the process of electrolytic dissolution, if necessary. Furthermore, the silicon additive allows to avoid the passivation process of the electrochemical dissolution of the alloy in sulfuric acid electrolyte.

Recycling solutions is an important ring in a technological chain. In addition, using the proposed options for processing solutions, it is possible not only to make the technology for processing electronic scrap closed loop, but also to be more profitable from an economic point of view, as well as more environmentally friendly. The proposed methods allow working not only with solutions containing a large amount of non-ferrous and precious metals, but also with poor solutions, which the metal content does not exceed 40 mg/m³.

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