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RESEARCH ON CHEMICAL COMPOSITION OF SECONDARY COPPER ANODES OBTAINED FROM AQUEOUS RESIDUES OF REFINING PROCESS

Purpose. The experimental research on the chemical quantitative composition of the secondary copper anodes. Copper anodes, which are the object of the study, are obtained from a secondary multicomponent product, composed of certain concentration of soluble and insoluble metals, and other various components.

Methodology. To examine the chemical composition of secondary copper anodes, special apparatus, devices, and modern methods are used as well as necessary materials to implement the electrolytic refining process.

Findings. The main results of the presented research are obtained in the field of processing secondary product from which precious metals are recovered. This paper presents the research results on the reuse of the residues of waters of refining processes in order to produce secondary copper anodes with the purpose of precious metal recovery. The quantitative and qualitative composition of the anodes varies, based on the composition of the primary raw materials.

Originality. Experimental studies were conducted in specialized laboratories. The results obtained are novel and original.

Practical value. The research results will be useful in expanding the understanding of the use of pollutants to obtain clean products used in the industry. The proposed approach contributes not only to improving the environmental situation, but is also aimed at sustainable economic development of relevant industries.

Keywords: *secondary copper anodes, waste waters, precious metals, platinum group metals*

Introduction. Copper is widely used in many fields due to its excellent features. In nature, it is most commonly present in the form of its minerals such us sulfides, oxides, and carbonates [1]. Pure copper (Cu) metal is mostly produced from these ores by concentration, smelting, and refining [2]. Production of refined Cu, from both primary and secondary sources, has increased much in recent years along with the progress achieved in technology lines for its production [3]. Reduction of raw reserves of primary mineral resources of many metals, high production costs for the metal extraction and increasing metal prices for gold and silver (PM) and platinum group metals (PGM) in particular are obliging scientific research institutions, academic institutions, and industry to work continuously in treatment and processing of secondary sources of metals such as waste waters residues, slag, slimes, and others [4]. The refining processes of precious metals (PM) and platinum group metals (PGM) generates large volumes of residues, that are composed of a certain concentration level of metals, such as Cu, PM, PGM and other metals [5, 6].

The secondary copper anodes (SCA), which are the object of this study, are obtained from a secondary multicomponent product such as residue of waste waters of refining process, which consists of insoluble compounds of copper (Cu), gold (Au), silver (Ag), platinum (Pt), Palladium (Pd), Iridium (Ir) and other platinum metals. Treatment of these residues is very important; therefore, the further processing showed the possibility to reuse them to produce the copper anodes as a secondary product, Fig. 1.

The use of such anodes in electrolytic refining processes can help to alleviate the extraction of the PM, PGM and other elements, which consist of the SCA. This paper indicates that the aqueous residues of refining processes as a secondary product are basic secondary raw material to obtain the SCA. Recovery of PM and PGM from waste waters is very important for saving of primary resources and protection of environment. This topic emphasizes the unique features required to achieve the good quality of the anodes, as well as better environmental performance and economic effects. Anodes should be measured relative to their weight, body shape and thickness specifications before they are placed in electrolysis cell for refining process. During our work we take into consideration published data of the previous research studies related to the same field.

Cu refining is necessary for impurity removal to achieve the properties desired by the customers. The refining is done in two stages: firstly, anode copper is produced by fire refining in an anode furnace and then it is cast into anodes molds. The commercial anodes usually contained copper with mass content from 98.0 to 99.5 %. They are obtained during the flame refining process, then they are subjected to electrolysis as a final process for pure copper production. The continuous improvement of the pyro-metallurgical refining process for SCA production is necessary in metallurgy; thus, it is very important in the end of the casting process to have an anode with low content of impurities. Due to this the usage of such anodes can enable realization of unproblematic final electrolytic refining (ER) of Cu. Usually, for high quality Cu production, it should undertake several steps before it subsequently undergoes ER processes. The smelted material that will be cast must meet certain requirements such as suitability for casting, capability of removing most of its S and O during the fire-refining process, and it should be released from other impurities contained in molten Cu.

Cu anodes should be of certain quality to satisfy the requirements of subsequent ER. The anodes should feature uniform corrosion, weight, and geometric dimensions (especially thickness), smooth surfaces, minimal edge effects as well as minimal distortion of the body and the lugs. The anode casting process is essential for anode quality, which determines anodic dissolution behavior during electrolytic refining [7]. The production of high-quality cathodes, using modern smelting and converting technology in order to minimize cost production, emissions, and management of impurity control must be properly addressed [8].

The non-commercial Cu anodes, which are the subject of the experimental research, are benefited from two different sources, during the treatments of aqueous water residues gained from refining processes, and as a result of their processing, the SCA are benefited. Such samples are prepared for chemical analysis and their quantity shows their influence in further ER process. These anodes are composed of various contents of different metals and compounds and are analyzed regarding the quantitative chemical composition. During this process the considerable amounts of copper-hydroxide or copper-oxide are obtained as well. Reductive smelting of these filter cakes results in metallic copper, which contains runaway values of silver, gold and especially of PGM, each between

a *b* *c*

Fig. 1. Wastewater residues of refining processes:

a — aqueous residues of PM; b — aqueous residues of PGM; c — filtrate after filtration process

3–1000 ppm. These products are collected, and as a result of their processing, the SCA are produced. All stages of processing were developed using lab scale devices and apparatus. Different ingredients contained in anodes have very strong influence in the electrolysis process, respectively they can cause e.g. passivation of the anodes, that is reflected in whole process up to finishing. Further investigations should enable the utilizing of SCA, which can be inserted into the ER without any restrictions, not depending only on the quality of the raw material used, but attention should be paid to casting parameters, too [7]. Steps of obtaining the secondary copper anode are presented in Fig. 2.

The heterogeneity of SCA composition varies and it is complex and they are different based on their composition, size and their weight. In addition, the composition of anode also depends on the conditions of previous refining processes, characteristics and composition of residues of waste waters. Anodes contain significant amounts of copper, PM, PGM, antimony, arsenic, bismuth, lead, nickel, selenium, silver, and tellurium. The Cu is present largely as Cu_2O and metallic copper. The anodes are characterized with some features such as: physical quality, chemical composition, quantity of the metals that compose anode, application of standard methods of their production and processing, possibility to be used as a source for the PM and PGM, ability to fulfill the technical criteria for final products [5]. Photos of secondary copper anodes are shown in Fig. 3.

The fact that the secondary copper anode is a valuable final product, produced as a result of a large number of technical and technological processes, proves that is not a residue of waste waters, but is very important precious resource in the present experimental research. Thus, an attempt has been made to study and analyze two SCA (A-1 and A-2) related to their composition, Fig. 3.

Experimental research on SCA. This study is focused on experimental research on secondary copper anode samples taken from the corresponding anodes SCA (A-1 and A-2, that

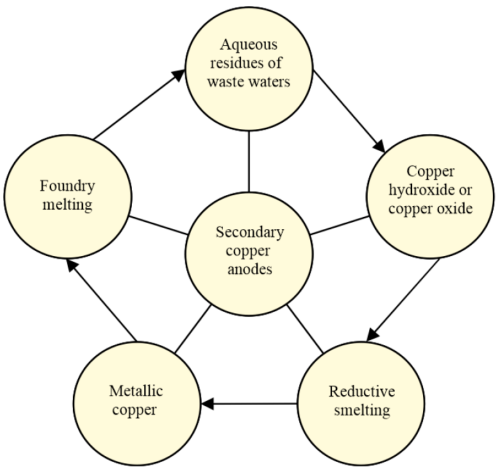
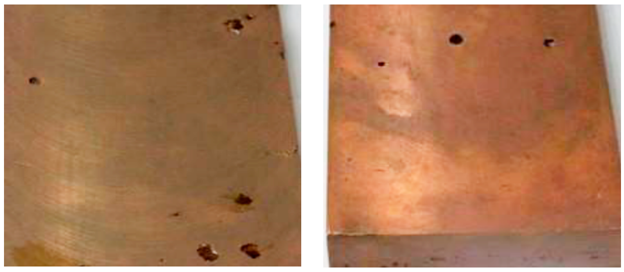


Fig. 2. Steps of obtaining the secondary copper anode



a *b*

Fig. 3. Photos of secondary copper anodes analyzed:

a – SCA-A1; b – SCA-A2

are subject to determinate the quantitative chemical composition of the ingredients contained in them. These chemical analyses are carried out with Spectroscopy device and results achieved are compiled and presented within the paper.

The quantitative chemical composition of Anode-1. The overall quantitative chemical composition analysis of Anode-1 (A-1) is very complex and is shown in Fig. 4. These data identify the presence of several metal impurities in various quantities in A-1. Fig. 5 show the data related only to the PM and PGM contents in A-1.

Based on the results achieved during the experimental research on the anodes A-1, it can be concluded that there is a significant amount of the undesired metals contented in them, due to the fact that they are processed from secondary raw material source. Based on the results achieved during the experi-

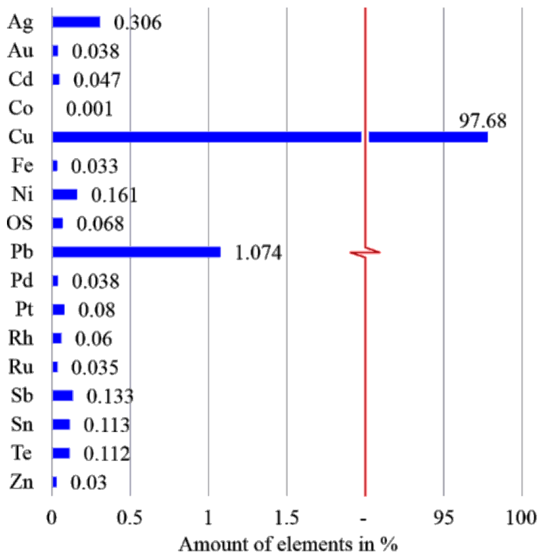


Fig. 4. Element distribution of metals in anode A-1

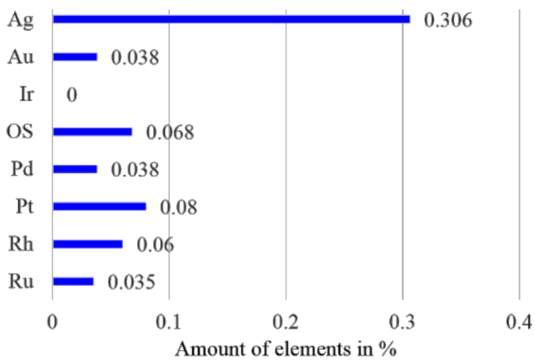


Fig. 5. The amount of precious metals and platinum group metals in A-1

mental research on anodes it is pointed out that these are generally rich in Cu, Pb, Sn, Ni, Zn, Cd, Fe, Sb, Te, Co, and a less amount of PM and PGM.

Based on the above data regarding the A-1 anode presented in Fig. 5, it can be concluded that it is composed of different contents of PM and PGM metals.

Due to the fact that PM and PGM are of economic value in the metal market, this anode can be considered for further investigations for metal extraction, although the low amount of these metals is noticed.

The quantitative chemical composition of Anode-2. The overall quantitative chemical composition analysis of A-2 is very complex and is shown in Fig. 6. Fig. 7 show the data related only to the PM and PGM contents in A-2.

The data given in Fig. 6 identify the fact that the anodes contain high levels of various quantities of impurity metals in different forms, which is an obstacle for further investigation. However, taking into consideration difficulties that are faced during the mining process as for these metals, it is still possible to extract them form this anode. This A-2 is rich in Cu, but it also contains a significant amount of PM and PGM.

Based on the above data regarding the A-1 anode presented in Fig. 7, it can be concluded that it is composed of different contents of Au, Ag and PGM metals.

Due to the fact that these metals are of economic value in the metal market, this anode can be considered for further investigations for metal extraction, although the low amount of these metals is noticed.

The quantitative chemical composition of both anodes A-1 and A-2. The overall quantitative chemical composition analysis of both anodes is very complex and shows that the differences in the composition between two anodes in Fig. 8. The given data prove that the anodes contain high levels of various quantities of metals in different forms.

The investigation shows that anodes are composed of different metals and compounds of various contents, due to the fact that they are processed from different sources. Chemical

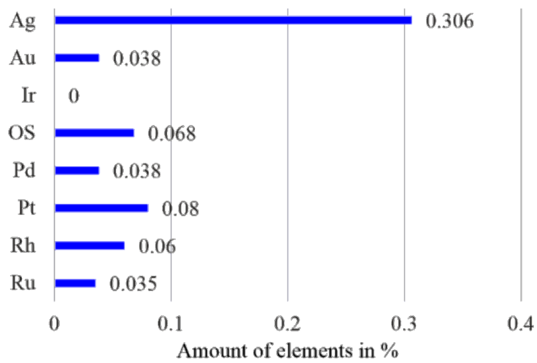


Fig. 6. Element distribution of metals in anode A-2

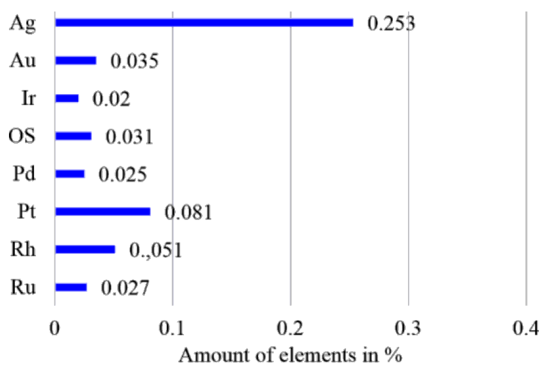


Fig. 7. The amount of precious metals and platinum group metals in A-2

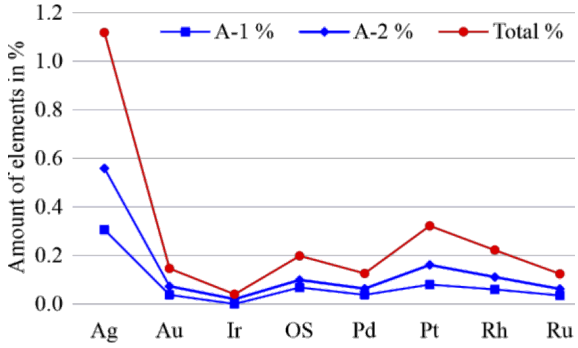


Fig. 8. Contents of precious metals and platinum group metals in A-1 and A-2

analysis of all anodes showed that Cu content was up to the average of 98 % (980 ppm). The average values of other metals content, obtained by analyzing the composite samples prepared from the material from samples taken of SCA 1 and 2, are presented in Figs. 4, 6. The impure anode copper contains both base and noble metals as impurities. Based on the results achieved during the experimental research on anodes, it is pointed out that they are generally rich in Cu, Fe, Pb, Ni, Sn, Ni, Sb, and have a low content of Se, Te, and a less amount of PM and PGM.

Discussion. The chemical composition of the samples of two secondary copper anodes was thoroughly analyzed in order to investigate chemical quantity and quality. During the investigation, the average values of some elements' content in anodes were obtained by analyzing the samples taken from the anodes discussed in the paper, and the results achieved are presented in the tables above. The reported results show varying metal composition and different amounts of elementary elements contained in them. A relatively homogeneous chemical quality was detected in the investigated samples.

The quantitative chemical composition analysis of A-1. The acquired results of the quantitative analysis of anode A-1, are presented in Fig. 4, The measured results indicate that in A-1, the total amount of Cu is 97.768 %, while other metals are present with 2.322 %. Fig. 5 present the data related to the amount of the PM and PGM contained in A-1; the amount of the PM in A-1 is 0.344 %, while PGM are present making 0.281 %.

The quantitative chemical composition analysis of A-2. The acquired results of the quantitative analysis of anode A-2 are presented in Fig. 6. The measured results indicate that in A-2, the total amount of Cu is 96.327 %, while other metals are present with 3.671 %. Fig. 7 present the data related to the amount of the PM and PGM contained in A-2; the amount of the PM present in A-2 is 0.287 %, while PGM make 0.235 %.

The total amount of Precious Metals and PGM in both anodes A-1 and A-2. The total value of the PM in both anodes is 0.631 %, while PGM total value in both anodes is 0.516%. These results are obtained by analyzing the samples taken from both anodes, presented in Fig. 8.

Based on the previous data published, the ingredients of anodes could be divided into three groups.

The first group consists of ingredients with a dissolution potential that is much more negative than a dissolution potential of copper: Ni, Fe, Zn, and Co. During the process, these elements are accumulated in the electrolyte. In the nickel-rich copper anodes, the following oxide phases can be formed: NiO, Cu-Sb-Ni, and Cu-Sn-Ni [9].

The second group consists of ingredients with a dissolution potential that is much more positive than the copper dissolution potential, which prevents their dissolution in the electrolyte, but they directly pass into the anode slime: Au, Ag, Pt, Pd, Se, and Te. This group also includes the insoluble salts such as $PbSO_4$ and $Sn(OH)_2SO_4$, which pass from electrolyte into anode slime.

The third group consists of ingredients with a dissolution potential close to a dissolution potential of copper: As, Sb, and Bi [10]. The anodes investigated are composed of different metals and compounds of various contents, being processed from different sources. Chemical analysis of both anodes showed that Cu average content was up to 98 %.

The impure anode copper contains both base and noble metals as impurities. The noble metals do not dissolve and form anode slimes [11]. The research shows that these anodes are generally rich in Cu and have a low amount of Fe, Pb, Ni, Sn, Ni, Sb, Se, Te, PM and PGM.

This study has indicated that the SCA (secondary copper anodes) are composed of various valuable metals, such are Cu, Au, Ag, Pt, Pd, Ir, and others. These anodes can become a valuable resource for wide use in acquiring precious metals and PGM in the industry. The SCA contains Cu, PMs, PGM and some other recoverable metals such as nickel, selenium and tellurium. Thus, these anodes are suitable for processing through the electrolytic refining process. The scientific research realized during the experimental work regarding the assessments of quality of SCA proved that the anode meets the requirements and its treatment can be continued for further investigation for the recovery of PM and PGM. The results achieved during experimental research can contribute as a model for the support and inspiration for other researchers to continue research in this field [12]. There are several technologies which may be used to recover metals from industrial waste such as pyro-metallurgy, hydrometallurgy, and bio-hydrometallurgy [13].

The decreasing quality of the input materials in copper recycling leads to a higher content of impurities in the anode copper. Therefore, improvement of the pyro-metallurgical refining process is necessary to produce high quality anodes for the copper refining electrolysis. Apart from copper, the raw materials for copper winning contain numerous other elements like nickel, lead, tin, zinc and iron. During the refining procedure of the copper these elements are removed by using different techniques like the selective vaporization and oxidation as well as the refining electrolysis. Nearly all copper which is won by the pyro-metallurgical way (about 85 %) passes through the copper refining electrolysis, even so it is mostly the secondary copper. In the electrolysis, the impure copper is anodically dissolved and crystallized at the cathode without impurities [14].

The main purpose is not only to produce pure copper that is essentially free of harmful impurities but also to separate valuable impurities (e. g. gold and silver) from the anodic copper slime for later recovery [15].

Conclusions. With a good preparation of secondary Cu anode as raw material and its rational use, the process of obtaining metals for which it is intended will be optimized. These anodes represent very valuable materials to the industry and provide a good basis for the extraction of precious metals and platinum group metals. The process of electrolytic refining of the anodes can result in certain benefits considering the amount of anode slime, and its rational utilization will make it possible to recover precious metals and platinum group metals.

The present study is related to the copper secondary copper anodes (SCA), concentration of chemical ingredients, which are the main target of the experimental research-study in regard of elements contained. The paper describes the possibility of the SCA utilization in terms of opportunities for recovery of precious and platinum metals as valuable resources. During the electro refining process of these anodes, anode slime is deposited in bottom of electrolytic cells, which is obtained as secondary by-product and its processing is very useful for gaining abovementioned metals.

Developing new ideas related to the methods for forecasting effects in the environment and economy, based on usage of secondary raw materials, residues of waste waters, their integrated monitoring, which will ensure industrial development and environmental safety of the country, should be the primary task of the scientists in the future.

Compared with other data that are published related to the abovementioned issue, the same definitive general trends for elemental distribution were found in these anodes.

Processing of the secondary sources such as raw materials to recover metals with the high value is beneficial for the metal market, in addition to being a good opportunity of valorization of the industrial mid-product, and through this processing concept it will raise the possibility to reduce the level of environmental pollution and will enable a modern maintenance management of the industrial waste landfills.

In addition to the increase in generation of other metal wastes, especially of metals such as Ni, Zn, Pb, etc. in other industry branches, it can be concluded that Kosovo has challenges in regard how to process further these secondary raw materials with the main aim to obtain final products such as anodes in order to obtain valuable metals, which has direct influence in terms of environmental protection and sustainable economic development of the country in general.

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Дослідження хімічного складу вторинних мідних анодів із водних відходів процесу нафтопереробки

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Мета. Експериментальне дослідження хімічного складу вторинних мідних анодів. Мідні аноди, що є об'єктом дослідження даної роботи, отримані із вторинного багатокомпонентного продукту, який складається з певної концентрації розчинних і нерозчинних металів, а також інших різних компонентів.

Методика. У роботі для дослідження хімічного складу вторинних мідних анодів застосовувалися спеціальні пристрої, прилади, сучасні методики й необхідні матеріали для реалізації процесу електролітичного очищення.

Результати. Основні результати представлених досліджень отримані у сфері переробки вторинного продукту, з якого вилучаються цінні метали. У цій роботі представлені результати досліджень із вторинного використання залишків вод рафінувальних процесів задля отримання вторинних мідних анодів з метою вилучення цінних металів. При цьому кількісний та якісний склад анодів варіюється, виходячи зі складу первинної сировини.

Наукова новизна. Експериментальні дослідження проводились у спеціалізованих лабораторіях. Отримані результати при цьому відрізняються новизною та оригінальністю.

Практична значимість. Результати досліджень будуть корисними у частині розширення уявлення про використання забруднюючих речовин для отримання чистих продуктів, що використовуються у промисловості. Запропонований підхід сприяє не тільки поліпшенню екологічної обстановки, але й спрямований на економічний розвиток відповідних галузей.

Ключові слова: *вторинні мідні аноди, стічні води, дорогоцінні метали, метали платинової групи*

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