Anode Slime Gained During Electrolysis Process of Secondary Copper Anodes

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ABSTRACT: *The aim of this research is to get a better understanding of the electrolytic refining process in order to yield the anode slime. Three types of secondary copper anodes are electro refined in an electrolytic system, where the electrolyte is an acid of copper sulphate solution. As a result of the electro-refining process the anode slime has been gained as secondary product. The experimental research analysis of anode slime composition is done by two methods: X-Ray Fluorescent (XRF) method which is realized with the help of Thermoscientic Nitro XL 3t device and as second method X-Rays Diffractometry (XRD) is used, which is realized with the help of D8 Advance Bruker AXS equipment. The anode slime introduces a multi-component secondary product of electrolytic refining process of metals composed of insoluble components of Cu, Au, Ag, Pt, Pd, Ir, etc. The composition of the anode slimes varies according to the composition of the anodes. The qualitative preparation of raw material – anode slime of secondary Cu and its rational utilization will result in the optimization of the process of gaining metals for which it is dedicated. This study has shown that the anode slime contains gold, silver and platinum group of metals and these metals can be recovered.*

KEYWORDS: *Anode slime; Copper; Gold; Silver; PGM; Electro refining.*

INTRODUCTION

Electrolytic refining of metals is a suitable and unique process considering the level of energy consumption, refining at low temperature and is the most commonly used method to refine metals from impurities and to produce highly pure metals. Electrolytic refining of copper production has considerably increased within the last years, from both primary and secondary raw material sources, as a result of the progress achieved in copper production technologies [1].

Electrolytic refining is the least expensive way to purify metals because it is so selective in terms of what it produces. In other words, it produces a pure metal in just

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one step, saving time and money. This is a very actual topic for scientific research in technical sciences in general, especially in metallurgy. The paper relies on the abundant sources from the literature on this field and in experimental research of electrolytic refining process of secondary copper anodes as raw material in order to gain anode slime.

EXPERIMENTAL SECTION

Researches of the electrolytic refining process of Secondary copper anodes

The main topics of this experimental research work are:

- the electrolytic refining process of secondary copper anodes, and

- analyzing of the anodes behaviors' during the process.

Electrolytic refining experimental researches were performed in laboratory scaled electrolytic cells where secondary copper anodes are refined by electrolytic way. This process depends on various factors such as composition of anodes, cathodes, electrolyte and its circulation, current density, temperature, additives, distance between electrodes, geometry of electrodes, etc. The experiment is performed with three different types of secondary copper anodes as the main raw material [4].

Apparatus, Devices, and Materials

This experimental research is supported by numerous apparatus, devices, and materials in order to finalize the copper electrolytic refining process. A key device for fulfillment of the electrolytic refining process consists of main devices such as:

electrochemical cell (PVC-acryl glass), secondary copper anodes, stainless cathodes (AISI-316), DC current, electrolyte (Acidic copper solution), glass heat exchangers, peristaltic pump circulated the electrolyte, dosage pump and reservoir for electrolyte recirculation, conductor wire between the anode and cathode(Cu OFHC) additives (Thiourea and gelatin) etc.[4]

Characteristics of the Secondary Copper Anodes

Secondary Cu anodes that are refined by electrolysis process are benefited from the aqueous residues of refining process. Three types of Cu anodes are taken from the refinery regarding their composition, size, and weight. The photos of the anodes are given in Fig. 1.

Fig. 1: Secondary copper anodes.

Table1: Results of the quantitative analyses of anodes.

Metals(%)	A-1(%)	A-2(%)	A 3 (%)	Total (%)
Au	0.0964	0.0526	0.0138	0.1628
Ag	0.2758	0.1965	0.0873	0.5596
Pt	0.0567	0.0499	0.0965	0.2031
Pd	0	0	0.0015	0.0015
Ir	0.7138	0.5743	0.0407	1.3288
Rh	0.0227	0.0121	0.0027	0.0375
Ru	0.0091	0	0.0029	0.012

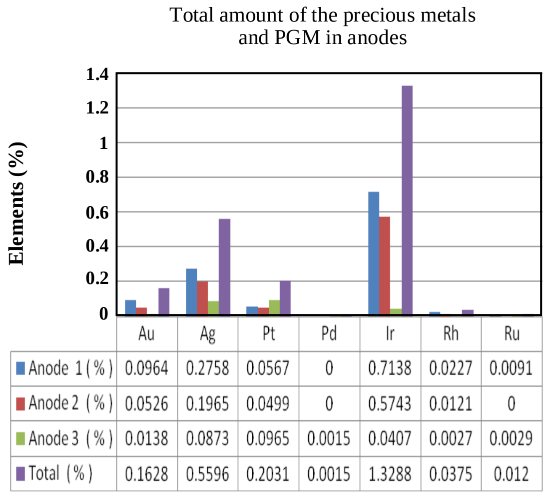


Fig. 2: Contents of precious metals and PGM in secondary copper anodes.

The Contents of Precious Metals and Platinum group of Metals in Anodes

The below table results show that the composition of the secondary anodes which are subject to electrolytic refining process differs from the composition of the primary Cu anode and as a result of it, the value of precious metals and PGM is lower. However, starting from the basic principle that these metals have economic value in the market, it is reasonable to work towards the refining of anodes and finding the methods for the extraction of these metals from anodes. Based on the quantitative analyses of the three anodes the presence of the precious metals was identified and PGM has shown in Table1 and through the diagram Fig. 2.

The given data shows that the anodes contain high levels of various quantities of impurities in different forms and these will behave differently during electrolysis.

Conditions and parameters of the electrolytic refining process

The experimental researches of secondary copper electrolytic refining were performed conform to the conditions and parameters that are required to develop proper refining process and some of them are listed below:

- Electrolyte contains 40 g Cu^{2+}/l, 170 g H_2SO_4/l and 157 g $CuSO_4$ $5H_2O$g/L,

- Electrolyte temperature is kept constant at the desired value of 60-65˚C,

- Applied current density of 0.27 mA/m^2 and applied voltage of 0.05 V volts is required to develop the process, and deliver the required power,

- Rate of electrolyte circulation is 75–80 ml/min and 160-180 rot /min of dosage pump,

- Anode-cathode spacing is 25 mm,

- Anode and cathode polarizations are measured with the help of electrolytic copper wires,

- Cathode edges are rounded off to prevent dendrite growth.

Three above-mentioned anodes (positively charged electrode) and 4 copper cathodes (negatively charged electrode) are housed in the electrolytic cell. These electrodes are dipped into an electrolyte solution of the made up $CuSO_4$-H_2SO_4-H_2O. In this cell, applied voltage of 0.05 V and current density of 0.27 mA cause a reaction to occur and non-spontaneous process starts to commence see Fig. 3.

This initiates the movement of ions in the electrolyte towards the electrodes. Positive ions move towards the negative electrode (cathode) and negative ions move towards the positive electrode (anode) [4]. At the anode, chemical reaction occurs and impure metal from

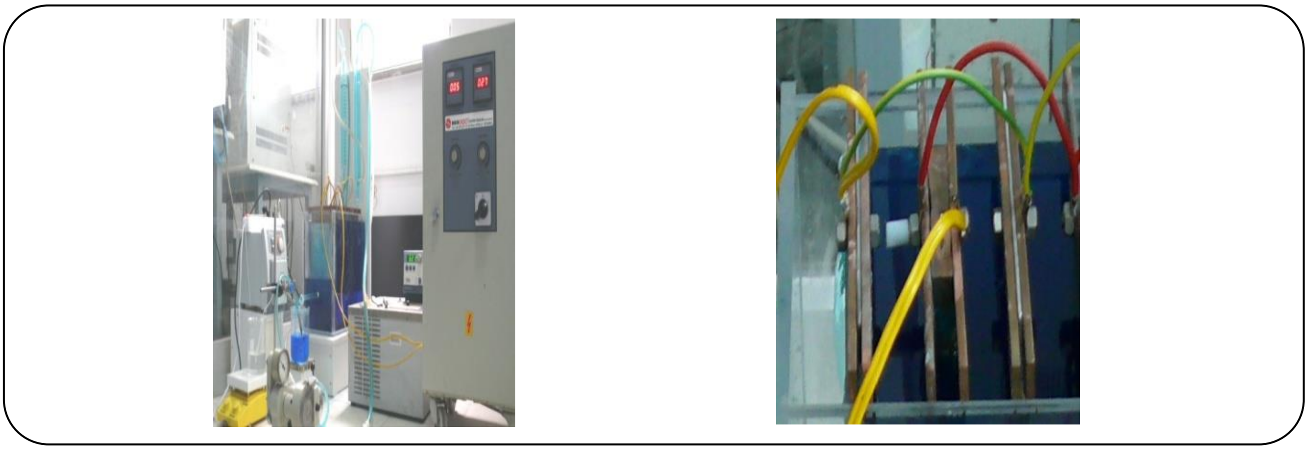


***Fig. 3:** Electrolytic refining process apparatus.*

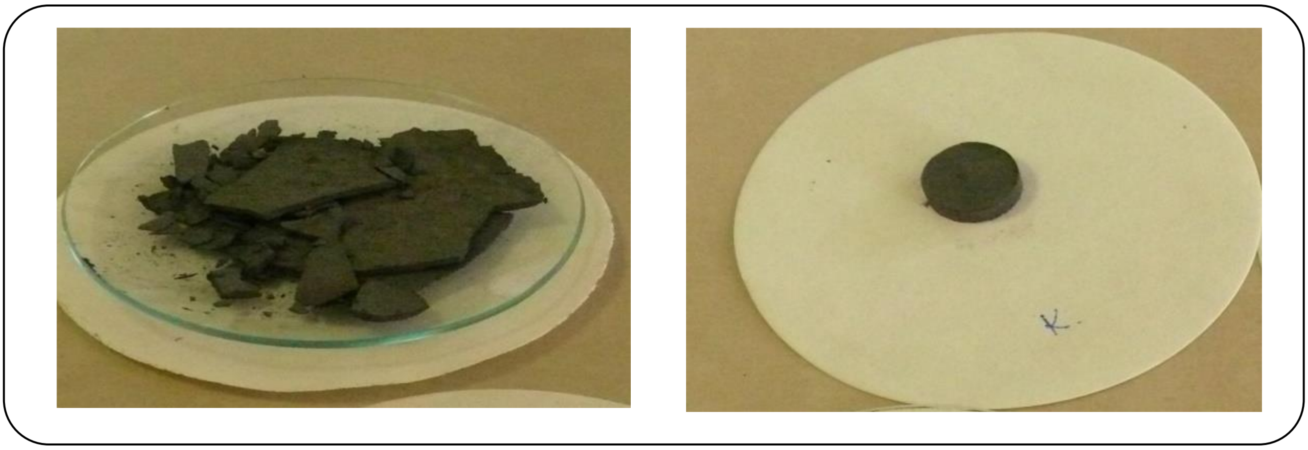


***Fig. 4:** Samples of the anode slime.*

the anode gradually passes into the electrolyte solution and pure metal from the solution gets deposited on the cathode. Copper(II) ions migrate through the electrolyte to the cathode. At the cathode, copper metal plates out but less noble constituents such as arsenic and zinc remain in solution [2] . The reactions are:

At the anode: $Cu(s) \rightarrow Cu2^{+}(aq) + 2e^{-}$

At the cathode: $Cu^{2+}(aq) + 2e^{-} \rightarrow Cu(s)$

Anode impurities such as Au, Ag, and other precious metals, as well as Pb, Se, and Te, are settled at the bottom of cell below the anode known as anode slime, or dissolve in the solution [4]. At the end of the refining cycle, the cell is emptied and anode slime is collected and processed for further processing and analysis.

Characteristcs of the Anode Slime

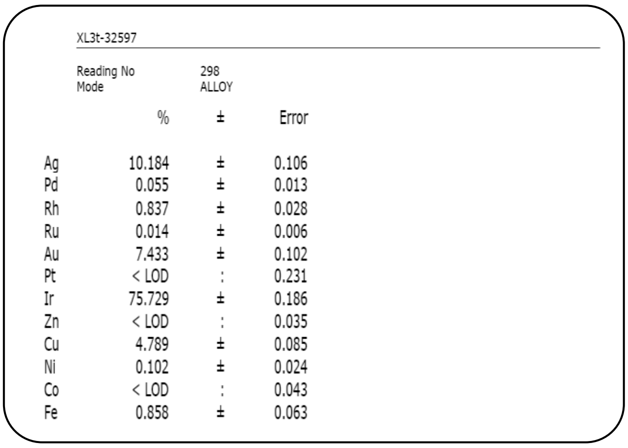
During the experimental research, substantial quantities of insoluble components of the anode as secondary products generate the anode slime. Anode slimes are collected from the bottom of the electrolytic cells during the refining of copper [5]. The anode slime is the unsoluble portion of the anode and as fine material falls to the bottom of the cell. These slimes contain significant quantities of gold and silver as well as variable amounts of Cu, Ni, Pb, As, Sb, Bi, Te and platinum group metals [2,3]. Before the leaching, the decoppered anode slime was washed several times, filtered and then dried at laboratory in the respective types of equipment. Samples of the dried anode slime are given in Fig. 4.

XRD and XRF Anode Slime Analyses

The characterization of the representative sample of anode slime composition was carried out by two methods: X-Ray Fluorescent (XRF) method and as second method X--Rays Diffractometry (XRD) is used which is realized with the help of D8 Advance Bruker AXS equipment [4].

Table 2: Anode slime analyse by XRF.

Contents	%	Tol . ±
Ag	10.184	0.106
Au	7.433	0.102
Pd	0.055	0.013
Rh	0.837	0.028
Ru	0.014	0.006
Ir	75.729	0.186
Cu	4.789	0.085
Ni	0.102	0.024
Fe	0.858	0.063



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	%	±	Error
Ag	10.184	±	0.106
Pd	0.055	±	0.013
Rh	0.837	±	0.028
Ru	0.014	±	0.006
Au	7.433	±	0.102
Pt	< LOD	:	0.231
Ir	75.729	±	0.186
Zn	< LOD	:	0.035
Cu	4.789	±	0.085
Ni	0.102	±	0.024
Co	< LOD	:	0.043
Fe	0.858	±	0.063

Fig. 5: Printed certificate of anode slime analyzed by XRF.

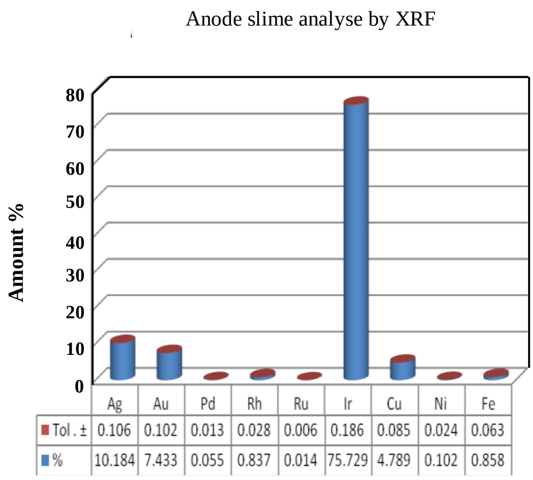

Fig. 6: Diagram of the anode slime composition by XRF methods.

Anode Slime Analyses by XRF (Fluorescent X-Rays)

The characterization of the representative sample of anode slime was carried out using XRF techniques which are realized with the help of the Thermoscientic Nitro XL 3t device. Amount of 4g anode slime sample is analyzed by fluorescent X-rays method, in order to determine the number of elements composing the sample. The analysis result is presented through the printed certificate Fig. 5, Table 2 and through the diagram Fig. 6.

XRF composition analyzes show the significant amount of copper, silver, iridium, gold platinum group of metals, etc., which are present in anode slime. Results of XRF analysis through the wavelength dispersive XRF spectrum are presented in below diagram Fig.7.

Results of anode slime samples Analyzed by XRD method

Anode slime sample was analyzed with the support of XRD method, in order to determine the number of elements in the sample.

X-ray diffractogram illustrating the contents of the sample is given in Fig. 8.

XRF composition analyzes show the significant amount of copper, silver, iridium, gold, and platinum group of metals, etc., which are present in anode slime.

The heterogenity of slime composition varies and it is complex. The composition of slime depends on the characteristics such as composition of the copper anode and the conditions of refining. Anode slime contains significant amounts of copper, antimony, arsenic, bismuth, gold, lead, nickel, platinum metals, selenium, silver, and tellurium. The Cu is present largely as Cu_2O

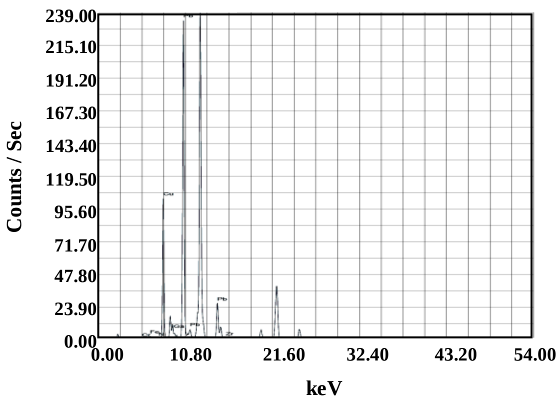

Fig. 7: Analysis through the wavelength dispersive XRF spectrum.

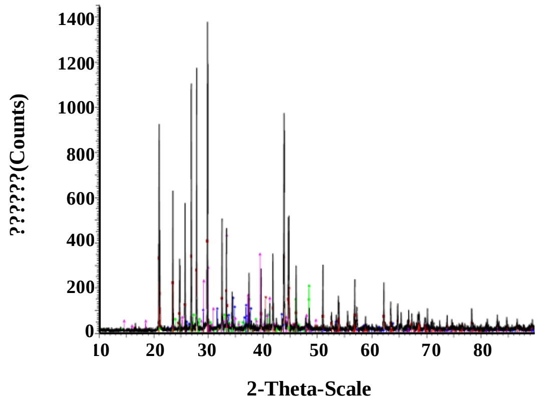

Fig. 8: X-ray diffractogram of the anode slime.

and metallic copper. It is also combined with Ag and Se/Te in various compounds and solid solutions.

CONCLUSIONS

This slime generated during the electrorefining of copper anodes, refining process contains, among other base metals recoverable quantities of gold, silver and the platinum group metals.The electrolytic refining of metals is highly possible for extraction of precious metal and PGM from the anode slime. Anode slime from copper electrolysis, though a byproduct of copper industry, contains many valuable and important metals like nickel, copper, selenium, tellurium, and noble metals, the recovery of which not only makes copper production economical but also gives important metals. For this reason, many laboratories, semi-industrial and industrial tests have been carried out with anode slime of Cu, which have provided enviable results as regards the process of separating precious metals and those that belong to platinum group.

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