

Gold recovery from electronic scrap waste by low-temperature chloridizing roasting

E. E. Zholdasbay, Associated Professor, Head of Department of Mining, Metallurgy and Natural Sciences¹

A. A. Argyn, Associated Professor, Department of Mining, Metallurgy and Natural Sciences¹

N. K. Dosmukhamedov*, Professor, Department of Metallurgy and Mineral Processing², e-mail: nurdos@bk.ru

V. A. Kaplan, Academic Consultant, Department of Material and Interfaces³, e-mail: valery.kaplan@weizmann.ac.il

¹ Zhezkazgan University named after O. A. Baikonurov, Zhezkazgan, Kazakhstan.

² Satbayev University, Almaty, Kazakhstan.

³ Weizmann Institute of Science, Rehovot, Israel.

In the work the scientific and technical analysis of modern methods of E-waste processing is carried out. It is shown that on the territory of Kazakhstan there are no E-waste recycling technologies. The relevance and importance of collection and processing of E-waste increases with the fact of lack of application of rational technology of their processing. Many valuable, technologically recoverable metals are lost irretrievably.

The results of the chemical composition of the crushed product — computer boards of computers, which were used as an object of research for gold extraction from them, are presented. The results of studies of qualitative assessment of initial E-waste showed a wide range of changes in metal compositions. Precious metals in the studied E-waste are represented by Au, Ag and Pd, the average content of which is 225, 425 and 15 ppm, respectively.

The paper presents the scheme of the laboratory installation and the methodology of low-temperature chloridizing roasting of E-waste with gaseous chlorine. Comprehensive studies of the chemical and phase composition of the solid residue obtained after the experiment using the SEM instrument (Leo Supra Carl Zeiss AG, Germany) and Agilent 7700 Series ICP-MS (Agilent Technologies, USA), Rigaku, Ultima III (Rigaku Corporation, USA) showed the presence of metal chlorides and amorphous phase representing unburned parts of plastic and other organic compounds in them. The quantitative ratio of solid and amorphous phase in the obtained solid residue is 31.5% and 69.5%, respectively. The phase composition of the solid residue was determined: 5.4% CuCl₂; 7.8% FeClO and 17.2% Cu₂Cl(OH)₃. As a result of the experiments, the optimal process parameters were established: temperature — 250 °C, duration — 30 min, chlorine consumption — 150 ml/min. It is established that at optimum firing parameters high up to ~98% of gold extraction from E-waste in the form of gaseous sublimate of gold chlorides is achieved.

Key words: E-waste, gold, chlorine gas, temperature, chlorine consumption, gold sublimate, solid residue, roasting, metal chlorides.

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Introduction

Involvement of secondary raw materials in processing is an important and promising direction from the point of view of resource saving of primary raw materials and reduction of costs for obtaining valuable metals. This practice is widespread in European countries, where there is a significant shortage of raw materials. These approaches seem quite understandable. The deteriorating environmental situation in the global world has led to a revision of non-ferrous and precious metals production technologies in developed countries and a transition not only to new technologies that ensure a high level of their ecologization, but also to the processing of secondary raw materials.

The recycling of electronic and electrical equipment waste, referred to in the scientific community as electronic waste (E-waste), is gaining great interest and development. The growth in the generation and accumulation

of large volumes of E-waste and their processing have become attractive, first of all, from the technological point of view, concerning the extraction of precious metals from them [1–4].

The widespread practice of E-waste disposal — direct open burning of the plastic component with subsequent recovery of valuable metals — poses a great risk to the environment. Primitive “private” disposal, like burning cable to extract copper, exposes people to hazardous substances. At high temperatures, dangerous toxic substances such as phenols, benzenes, copper, cadmium, lead and arsenic are released into the atmosphere. The ash generated from the combustion of end-of-life equipment is equally toxic [5–8].

One of the promising directions for E-waste processing is chlorinating technologies, which provide selective extraction of precious metals into commercial products and a high degree of ecologization of the technology [9]. Only fragmentary knowledge is known in the scientific literature with respect to high-temperature chlorination of metals and their compounds from various types of raw

*Correspondence author.

materials [10–13]. At the same time, the issues of metal distribution between the products obtained under low-temperature chlorination conditions are practically not studied and remain open. There are practically no data on application of chlorinating technologies for E-waste processing, although they, in combination with already available results, could form a fundamental basis for new chlorinating technologies for complex extraction of valuable metals from E-waste.

The purpose of this work is to study the extraction of gold from different type and composition of E-waste (computer boards) by their low-temperature chlorination with gaseous chlorine. The use of this method will allow selective extraction of gold in the form of auric chloride sublimate in the initial stage of technology with further extraction of valuable metals by known technologies, which will significantly increase the complexity of the use and processing of E-waste.

Materials and methods

The methodology of low-temperature roasting of E-waste is based on thermodynamic evaluation of gold and non-ferrous metals reactions with gaseous chlorine, in which gold chlorides are obtained as one of the roasting products in the gaseous phase.

For thermodynamic calculations as a standard state of substances are taken: gold — in crystalline ($\text{Au}_{(s)}$), molecular chlorine — in gaseous Cl_2 , gold chlorides — in crystalline ($\text{Au}_x\text{Cl}_y(s)$) and gaseous state ($\text{Au}_x\text{Cl}_y(g)$). The standard state of non-ferrous metal chlorides is $\text{MeCl}_{2(s)}$, where Me is Cu, Pb, Zn, ΔG_7° .

The calculations were based on the determination of the Gibbs free energy loss (ΔG_7°) of precious (Au, Ag, Pd, Pt) and other non-ferrous metals chlorination reactions as a function of temperature. Thermodynamic calculations were carried out using HSC Chemistry 8.1.5 software by Outotec Technologies (Licensee: KazNTU).

Computer boards were used as the initial object. Grinded materials of computer boards were prepared using cutting mill SM 300 of Retsch GmbH company.

Roasting was carried out in a temperature-controlled laboratory electric furnace Nabertherm HTC-03/15/B170 at a temperature of 250 °C in an atmosphere of excess chlorine gas. The furnace heating rate was constant and was 12 °C/min. The roasting duration in all experiments was 20 min.

Solid residues and AuCl_3 sublimate obtained after roasting were subjected to electron microscopy using SEM (Leo Supra Carl Zeiss AG, Germany), and X-ray phase analysis on Agilent 7700 Series ICP-MS (Agilent Technologies, USA), Rigaku, Ultima III (Rigaku Corporation, USA) instruments.

Results and discussion

Initial materials

Dynamics of transformation of the general appearance of the source material, in the process of its preparation for the operation of chloridizing roasting with gaseous chlorine, is presented in Fig. 1.

A large assortment of computer boards was used as starting material, which were pulverized to a certain coarseness: -35 mesh using a cutting mill. The results of qualitative assessment of the crushed material for the content of basic metals in them, given in Table, showed a wide range of their variation.

The shredded material of the computer boards was used to conduct experimental studies on chloridizing roasting of E-waste using chlorine gas.

Thermodynamic studies of E-waste components interaction with chlorine gas

Thermodynamic calculations of interaction reactions between metals and gaseous chlorine were carried out in the temperature range of 323–773K, which covers the area of low-temperature chlorination, as applied to the processing of E-waste.

Table
Elemental composition results (by metals)

Metal	Content, wt. %
Cu	7–20
Al	2–10
Pb	2–3
Zn	0.5–2
Ni	0.2–1.0
Fe	2–8
Sn	2–4
As, ppm	0.5–2
Au, ppm	150–300
Ag, ppm	350–500
Pd, ppm	10–20

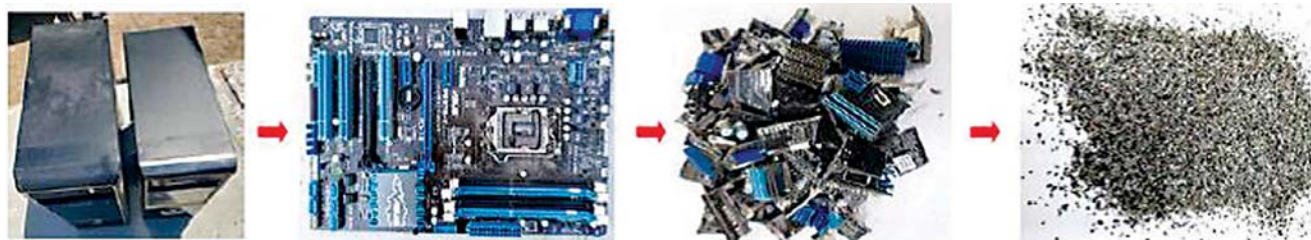
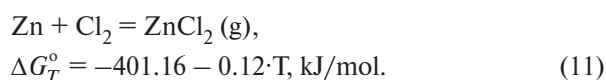
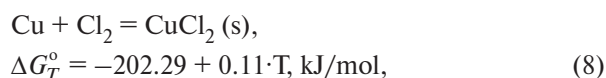
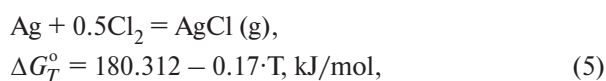
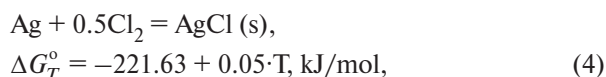
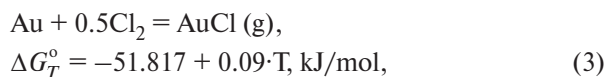
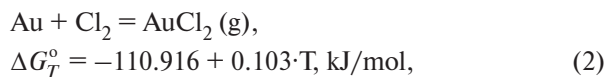
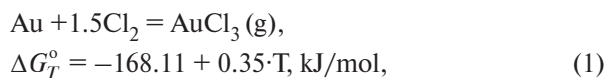


Fig. 1. Preparation of initial material for chloridizing roasting

The mechanism of chlorination of precious (Au, Ag, Pt, Pd) and non-ferrous metals (Cu, Pb, Zn) by chlorine gas can be represented by the following system of reactions:



It was found that the formation of gaseous AuCl_3 at low chlorination temperature is more preferable than gold monochloride ($\text{AuCl}_{(\text{g})}$). This is evidenced by the Gibbs free energy values of reactions (1) and (3), which show negative values at 323K: $\Delta G_{323\text{K}}^\circ = -78.99$ kJ/mol and $\Delta G_{323\text{K}}^\circ = -26.67$ kJ/mol, respectively. The gold chlorides formed as a result of reactions (1) and (3) remain stable up to the temperature of 473K. Further temperature increase reduces their formation, which is associated with their thermal decomposition. The obtained results are in agreement with the data of the works [7, 14].

The thermodynamic possibility of silver chlorination by reaction (4) is rather high. The formation of silver chloride as a gas by reaction (5) is difficult, due to the positive values of Gibbs free energy in the whole range of considered temperatures.

In the lower limits of temperature change (323–473 K) thermodynamic probability of platinum chlorination is high. Chlorination of palladium by reaction (7) is excluded, due to positive values of Gibbs free energy.

The probability of chlorination of non-ferrous metals (Cu, Pb, Zn) with chlorine to form solid chlorides is quite high. The value of the Gibbs free energy of

the reaction of copper chlorination (8) at 373K, equal to $\Delta G_{323\text{K}}^\circ = -169.77$ kJ/mol, is more than 2.5 times (abs.) higher than the value of ΔG_T° of the reaction of gold chlorination ($\Delta G_{323\text{K}}^\circ = -78.99$ kJ/mol). The ΔG_T° values of the chlorination reaction of lead (9) and zinc (11), equal to $\Delta G_{323\text{K}}^\circ = -310.3$ kJ/mol and $\Delta G_{323\text{K}}^\circ = -365.6$ kJ/mol, respectively, are more than 4 times higher than the ΔG_T° values of the chlorination reaction of gold. The thermodynamic probability of gaseous lead chloride formation by reaction (10) is high. The value of Gibbs free energy at temperature 323 K is $\Delta G_{323\text{K}}^\circ = -183.5$ kJ/mol, which is more than 2 times higher than the value of $\Delta G_{323\text{K}}^\circ$ of reaction (1). This indicates that in order to obtain pure gold chloride sublimate and ensure high environmental friendliness of E-waste processing technology, it is necessary to provide conditions for the preliminary removal of lead.

The results of thermodynamic analysis show the principal possibility of gold chlorination at low temperatures. From the practical point of view it means that at low-temperature chlorination of E-waste with gaseous chlorine, favorable conditions are achieved for selective sublimation of gold in the form of AuCl_3 sublimate, which can be further condensed in cold sections and captured in the form of small crystals. To maximize the recovery of gold from the E-waste, it is necessary to provide a constant removal of the gas phase. This will allow to shift the equilibrium of reaction (1) towards the formation of gold trichloride (AuCl_3), and increase the rate of interaction of gold with gaseous chlorine.

Laboratory experiments on gold recovery from E-waste

The general scheme of the laboratory plant for gold recovery is shown in Fig. 2.

The initial suspension was loaded into a boat inlet 4, and placed in a quartz reactor 2, installed in the zone of a uniform temperature field of electric furnace 1. The working zone of the furnace allows to place four boats at the same time, which allows to increase the amount of source material subjected to roasting. In our case, we used one boat with a minimum weight equal to 15 g.

The quartz reactor is plugged from opposite sides with a plug, which have holes for gas inlet and outlet. Roasting was carried out in a current of chlorine gas, which was supplied from the cylinder 8 through a plug with a hole 7 into the quartz reactor 2.

The sublimate (AuCl_3) formed during roasting was discharged from the reactor by pipeline 3 and captured in a specially designed device 6. Waste gases were captured in absorption flasks with milk of lime. At the end of the experiment the furnace was turned off. The solid residue obtained after the experiment was removed from the furnace, weighed and subjected to chemical and phase analysis. The degree of chlorination of gold in different conditions of experiments was determined by the difference, taking into account the amount of the initial suspension and the obtained residue and the content of gold in them.

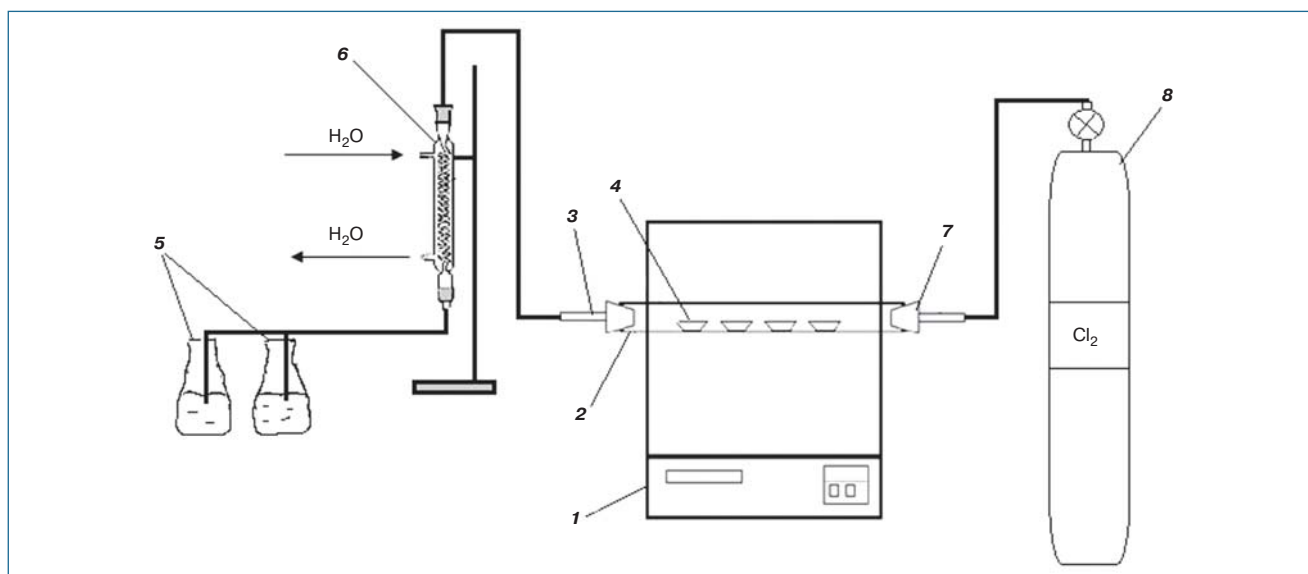


Fig. 2. General scheme of the laboratory installation for gold extraction from E-waste: 1 – electric furnace Nabertherm HTC-03/15/B170; 2 – quartz reactor; 3 – gases containing sublimable AuCl_3 ; 4 – boat inlet for suspensions; 5 – absorbers of exhaust gases; 6 – device for capturing sublimable AuCl_3 ; 7 – plug with a hole for chlorine supply to the reactor; 8 – cylinder with chlorine (gas)

Each experiment was repeated three times in order to make them reproducible and to obtain reliable results.

Figs. 3, 4 show the results of SEM and XRD analysis of the solid residue obtained under the following roasting conditions: T – 250 °C, chlorine flow rate – 150 ml/min, time – 20 minutes.

In the obtained solid residue the presence of amorphous phase representing unburned parts of plastic and organic compounds and metal chlorides was established. The quantitative ratio of phases in the solid residue was: 69.5% – amorphous phase, the rest – chlorides. The phase composition of the latter is represented by chlorides, % wt: 5.4 CuCl_2 ; 7.8 FeClO and 17.2 $\text{Cu}_2\text{Cl}(\text{OH})_3$ (**Fig. 4**).

The obtained results allow us to make a number of important for practice. The high content of amorphous phase present in the residue indicates that thermal degradation and removal of toxic organic substances should not be expected during low-temperature chloridizing roasting. This position is fully confirmed by numerous data of known works, where it is indicated that in E-waste (computer boards, notebooks, etc.) the content of non-

metallic part (plastic, polystyrene, etc.) is ~70% of the total mass of E-waste. Consequently, the main part of the amorphous phase is burned during high-temperature melting. This principle is the basis for the existing technologies for E-waste processing.

The present work does not consider environmentally safe options of preparatory operations for separation of e-waste into non-metallic fraction (plastic, polystyrene, fiberglass, etc.) and metallic fraction. The *in vitro* pre-combustion of the shredded E-waste was necessary to separate the carbon-containing components of the e-waste, which block gold recovery in the chlorination process. Obviously, carrying out such an operation in industrial conditions will lead to environmental pollution. When carrying out verification and extensive testing of the technology proposed in the article, there will certainly be methods of preliminary separation of non-metallic fraction, for example, by air separation of non-metallic fraction from the crushed sample. The separated non-metallic fraction can be used in the production of new electronic boards. Unfortunately, there are no laboratory installations of this type yet,

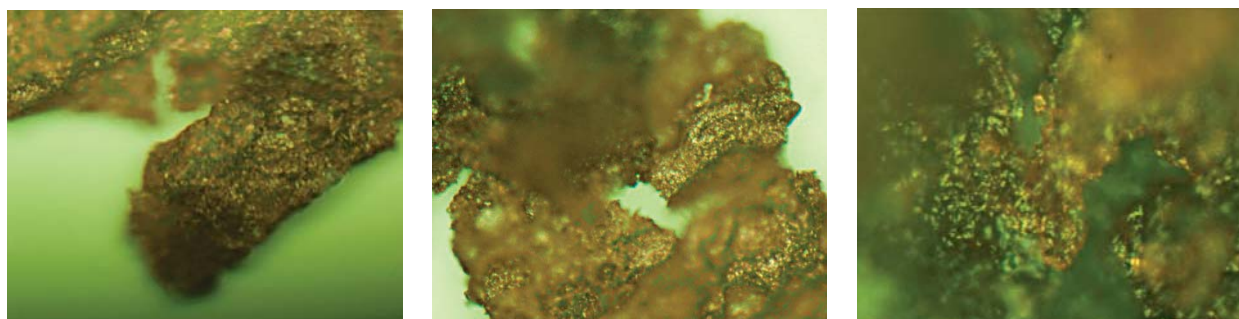


Fig. 3. SEM-analysis fragments of the solid residue obtained after chloridizing roasting ($\times 200$)

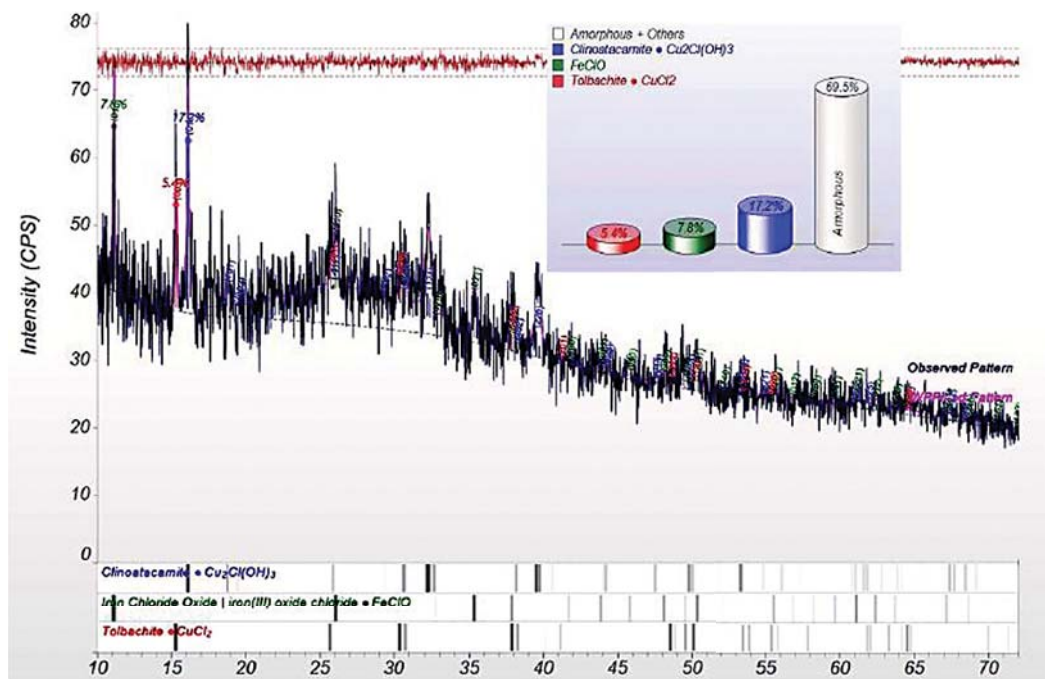


Fig. 4. Results of XRD measurements of solid residue obtained after chloridizing of E-waste at $T = 250\text{ }^{\circ}\text{C}$ and firing duration – 20 min

however, there are stably operating industrial units for air separation of non-metallic fraction from crushed sample.

The possibility of gold chlorination and its capture in the form of AuCl_3 sublimate in the process of chloridizing roasting of E-waste can be indirectly judged by the weight reduction of the initial suspension as a result of roasting. Considering the high vapor elasticity of AuCl_3 , compared to other metal chlorides, on the one hand, and the practical absence of thermal degradation of the plastic on the other hand, it can be argued that the weight difference established in the experiments during low-temperature chlorinating firing identifies the chlorination of gold and its volatilization in the form of AuCl_3 sublimate.

The obtained positive results fully confirm the conclusions made on the basis of thermodynamic analysis about selective chlorination of gold and its capture in the form of AuCl_3 sublimate under low temperature conditions.

The results of the conducted experimental experiments showed good convergence with each other and high positive results. The residual amount of gold, after each chlorination experiment, was not less than 0.3 mg. Increasing the duration of roasting up to 30 minutes, had no significant effect on the chlorination of gold: the residual amount of gold in the solid residue after the experiment remained at the same level (~ 0.33 mg) as at 20 minutes.

The yield of gold in the form of AuCl_3 sublimate captured in the device after three experiments was ~ 44 mg. Further melting of gold sublimate without special costs and efforts will allow to extract gold into pure metal by known methods.

The results obtained indicate a high, up to 98%, degree of gold chlorination at $250\text{ }^{\circ}\text{C}$, and show the possibility of

using the developed laboratory unit and methodology for the extraction of gold from other various E-wastes.

Conclusion

1. The principal possibility of gold extraction from E-waste (computer circuit boards) by chloridizing roasting at low temperatures has been shown. The optimal parameters of roasting were established: temperature – $250\text{ }^{\circ}\text{C}$, duration – 20 min, chlorine consumption – 150 ml/min, providing high up to 98% selective extraction of gold in the form of AuCl_3 sublimate.

2. It is established that at low-temperature chloridizing roasting there is practically no thermal destruction of non-metallic part of E-waste. The phase composition of the solid residue obtained after roasting contains: 5.4% CuCl_2 ; 7.8% FeClO and 17.2% $\text{Cu}_2\text{Cl}(\text{OH})_3$ chlorides and 69.5% amorphous phase.

3. The obtained data were used for further studies aimed at establishing the optimal technological parameters of low-temperature chloridizing roasting of different types and composition of E-waste, in relation to the large-scale laboratory scale of their processing.

Acknowledgement

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References

1. Baldé C. P., Forti V., Gray V., Kuehr R., Stegmann P. The Global E-waste Monitor – 2017, Quantities, Flows, and Resources. United Nations University (UNU), International Telecommunication Union (ITU) & International Solid Waste Association (ISWA), Bonn/Geneva/Vienna, 2017. URL: <https://www.itu.int/en/ITU-D/Climate-Change/Documents/GEM%202017/GEM%202017-R.pdf> (Accessed Date: 20.03.2024).
2. Gadekar J. Extraction of Gold and Other Precious Metals from E-Waste. *International Journal of Pharmacy & Pharmaceutical Research*. 2017. Iss. 1. pp. 24–34.
3. Hagelüken C., Corti C. W. Recycling of Gold from Electronics: Cost-effective Use Through ‘Design for Recycling’. *Gold Bulletin*. 2010. Vol. 43. pp. 209–220.
4. Blake V., Farrelly T., Hannon J. Is Voluntary Product Stewardship for E-Waste Working in New Zealand? A Whangarei Case Study. *Sustainability*. 2019. Vol. 11. 3063.
5. Kaya M. Recovery of Metals from Electronic Waste by Physical and Chemical Recycling Processes. *International Scholarly and Scientific Research & Innovation*. 2016. Vol. 10, Iss. 2. pp. 259–270.
6. Khaliq A., Rhamdhani M., Brooks G., Masood S. Metal Extraction Processes for Electronic Waste and Existing Industrial Routes: A Review and Australian Perspective. *Resources*. 2014. Vol. 3. pp. 152–179.
7. Al Balushi M., Kaithari D. K. Recovery of Gold from E-Waste. *International Journal of Students’ Research In Technology & Management*. 2016. Vol. 4, Iss. 3. pp. 44–48.
8. Cui J., Zhang L. Metallurgical Recovery of Metals from Electronic Waste: a Review. *Journal of Hazardous Materials*. 2008. Vol. 158, Iss. 2-3. pp. 228–256.
9. Brigden K., Labunska I., Santillo D., Johnston P. Chemical Contamination at E-Waste Recycling and Disposal Sites in Accra and Korforidua, Ghana. *Greenpeace Research Laboratories Technical Note*. 2008. Iss. 10. 23 p.
10. Ledesma E. F., Lozano-Lunar A., Ayuso J., Galvín A. P., Fernández J. M., Jiménez J. R. The Role of pH on Leaching of Heavy Metals and Chlorides from Electric Arc Furnace Dust in Cement-Based Mortars. *Construction and Building Materials*. 2018. Vol. 183. pp. 365–375.
11. Dosmukhamedov N., Kaplan V., Zholdasbay E., Argyn A., Kuldeyev E., Koishina G., Tazhiev Ye. Chlorination Treatment for Gold Extraction from Refractory Gold-Copper-Arsenic-Bearing Concentrates. *Sustainability*. 2022. Vol. 14. 11019.
12. Guo X., Zhang B., Wang Q., Li Zh., Tian Q. Recovery of Zinc and Lead from Copper Smelting Slags by Chlorination Roasting. *JOM*. 2021. Vol. 73, Iss. 6. pp. 1861–1870.
13. Dosmukhamedov N., Kaplan V., Zholdasbay E., Daruesh G., Argyn A. Alumina and Silica Produced by Chlorination of Power Plant Fly Ash Treatment. *JOM*. 2020. Vol. 72, Iss. 10. pp. 3348–3357.
14. Zyryanov M. N., Leonov S. B. Chloride Metallurgy of Gold. Moscow: SP “Internet ingeneering”, 1997. 288 p. 