



University of Belgrade, Technical Faculty in Bor  
29<sup>th</sup> International Conference Ecological Truth  
& Environmental Research



# EcoTER'22

## Proceedings



*Editor*

*Prof. Dr Snežana Šerbula*

*21-24 June 2022, Hotel Sunce, Sokobanja, Serbia*



University of Belgrade, Technical Faculty in Bor  
29<sup>th</sup> International Conference Ecological Truth  
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**29<sup>th</sup> INTERNATIONAL CONFERENCE**

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## **PREFACE**

*In today's world, the environment has been endangered by the use of outdated technology, fossil fuels and environmental law violations. Therefore, environmental and many other scientists all over the world have been concerned about finding sustainable technology in resolving these issues. That is why environmental research and ecological truth are at the focus of the 29<sup>th</sup> International Conference Ecological Truth & Environmental Research 2022 (EcoTER'22), which will be held in Sokobanja, Serbia, 21–24 June 2022. On behalf of the Organizing Committee, it is a great honor and pleasure to wish all the participants a warm welcome to the Conference.*

*We hope to convey the message of the conference, which is that a transformation of attitudes and behavior would bring the necessary changes. This is also an opportunity for the participants who are experts in this field to exchange their experiences, expertise and ideas, and also to consider the possibilities for their collaborative research.*

*The 29<sup>th</sup> International Conference Ecological Truth & Environmental Research 2022 is organized by the University of Belgrade, Technical Faculty in Bor, and co-organized by the University of Banja Luka, Faculty of Technology, the University of Montenegro, Faculty of Metallurgy and Technology – Podgorica, the University of Zagreb, Faculty of Metallurgy – Sisak, the University of Pristina, Faculty of Technical Sciences – Kosovska Mitrovica and the Association of Young Researchers, Bor.*

*These proceedings include 85 papers from the authors coming from the universities, research institutes and industries in 6 countries: Bulgaria, Italia, Albania, Bosnia and Herzegovina, Montenegro and Serbia.*

*As a part of this year's conference, the 4<sup>th</sup> Student section – EcoTERS'22 is being held. We appreciate the contribution of the students and their mentors who have also participated in the Conference.*

*Financial assistance provided by the Ministry of Education, Science and Technological Development of the Republic of Serbia is gratefully acknowledged by the Organizing Committee of the EcoTER'22 conference.*

*The support of the Platinum donor and their willingness and ability to cooperate have been of great importance for the success of EcoTER'22. The Organizing Committee would like to extend their appreciation and gratitude to the Platinum donor of the Conference for their donation and support.*

*We appreciate the effort of all the authors who have contributed to these Proceedings. We would also like to express our gratitude to the members of the scientific and organizing committees, reviewers, speakers, chairpersons and all the Conference participants for their support to EcoTER'22. Sincere thanks go to all the people who have contributed to the successful organization of EcoTER'22.*

*Prof. Snežana Šerbula,*

*President of the Organizing Committee*



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## RECYCLING GOLD FROM WASTE PRINTED CIRCUIT BOARDS

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### Abstract

*The rapid growth of the world's population and the permanent need of modern consumer society for more energy-efficient products, have led to the accumulation of electronic waste. In order to protect the environment and preserve the concept of sustainability, intensive work has been done in recent years on the development of recycling technologies. Among the numerous components of discarded electronic devices, printed circuit boards stand out for their high content of precious metals. This paper provides an overview of previous research in the field of hydrometallurgical process, such as gold recovery from waste printed circuit boards. Therefore, solutions containing cyanides, thiosulfates, thiourea, halides, and aqua regia are used for gold leaching from waste printed circuit boards. However, due to the high toxicity and possible side effects on the environment and human health, research has focused on the use of non-cyanide solutions in recent years.*

**Keywords:** waste printed circuit boards, recycling, leaching, gold, non-cyanide solutions

### INTRODUCTION

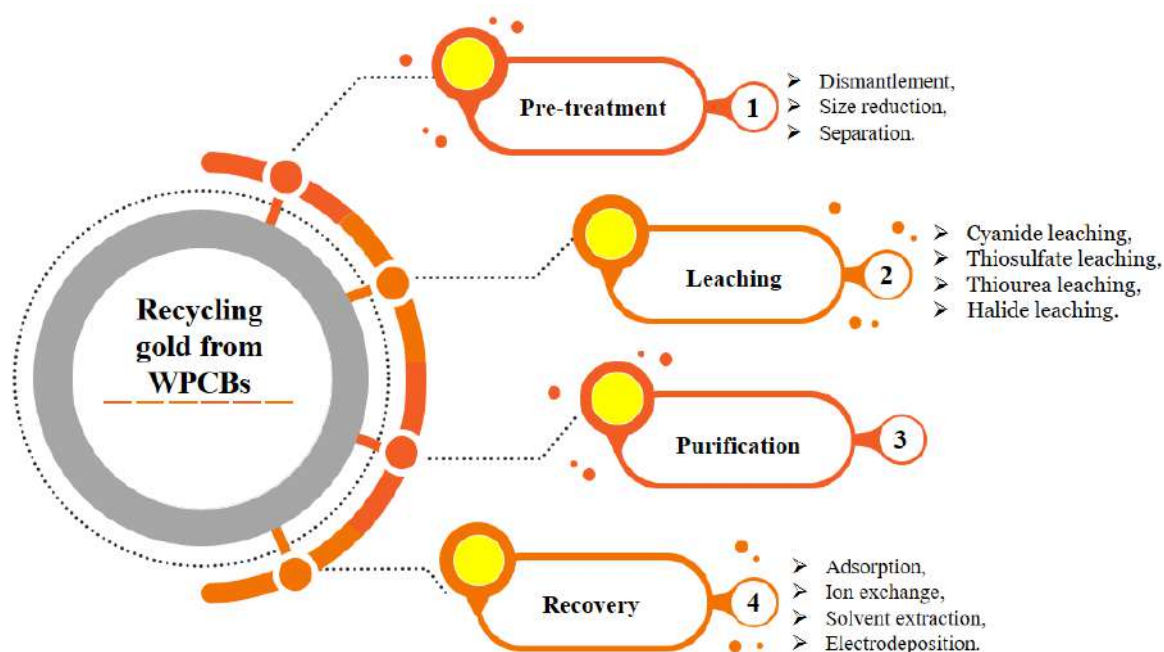
The development of the electronics industry has led to increased demand for precious metals. Since the annual need for gold exceeds the capacity of mining, the lack of gold is compensated by recycling [1]. Cyanide solutions are most often used in primary production (mining) for leaching gold ores. From the obtained leach solutions, gold is recovered by the method of adsorption on activated carbon, followed by stripping steps, before gold metal is deposited by electrowinning or cementation [2]. Primary gold production using cyanide solutions leads to increased emissions of hydrogen cyanide, as well as the production of huge amounts of tailings, given the low concentrations of gold in minerals [3]. The production of gold from secondary sources is accompanied with huge energy savings, which is a consequence of the chemical composition of electronic waste. On average, waste printed circuit boards (PCBs) contain 40% metal, 30% plastic and 30% ceramic [4]. Ventura *et al.* [5] in their study state that 1 t of waste PCBs can contain 250 g of gold, which is a significantly higher share of metal compared to gold ore, where average gold concentrations range from 1–10 g/t ore. The following methods are used in the process of gold recovery from waste PCBs: hydrometallurgy, bio-hydrometallurgy, pyrometallurgy and physical-mechanical methods. Compared to other methods, hydrometallurgy is characterized by a high degree of process efficiency, reduced emissions and easier control of the production process. Hydrometallurgical treatment of waste PCBs can be divided into two phases, leaching and

metal extraction. In the process of leaching, the PCBs dissolve and the solid metal is converted to dissolved form. From the obtained leach solutions, metals are converted from dissolved to solid form using the following methods: adsorption, ion exchange, electrodeposition and solvent extraction [6].

This paper gives an overview of hydrometallurgical procedures for obtaining gold from waste PCBs. The emphasis is placed on the leaching process because it is the most demanding step in the hydrometallurgical process of gold recovery from electronic waste.

## GOLD LEACHING FROM WASTE PCBs

The process of gold recovery from waste PCBs begins with pre-treatment. Pre-treatment of electronic waste involves mechanical and physical operations that can be divided into three phases: disassembly, shredding and separation of materials. The goal of pre-treatment of waste PCBs is the preparation of metallic granules and the concentration of targeted metals, which facilitates the leaching process. The leaching process is followed by purification of metals from leaching solution and recovery of metals as final products. A schematic representation of the hydrometallurgical process of gold valorization from waste PCBs is given in Figure 1.



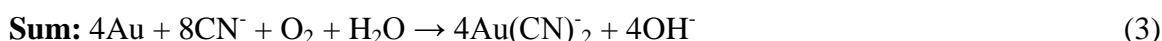
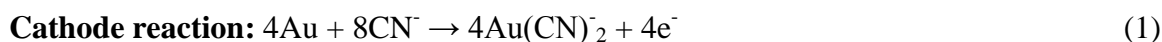
*Figure 1* Process flow of recovery of gold from WPCBs

### Cyanide leaching

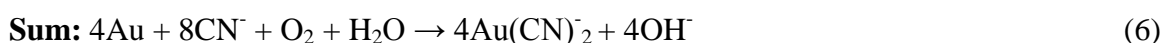
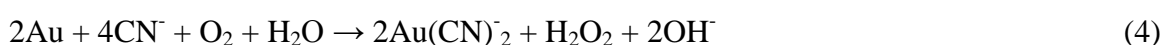
Valorization of gold from primary production using cyanide solution is a process that has been used for more than 100 years. In recent years, intensive work has been done on the development of other non-cyanide methods, due to the high toxicity of the applied procedure. However, the high efficiency of this procedure, as well as its simple implementation, is the

reason why cyanide leaching is also used in the process of gold recovery from electronic waste [7].

Gold cyanidation is an electrochemical process that can be divided into two half-reactions. In the anodic reaction (reaction 1) there is an alkaline dissolution of gold and the formation of a cyanide complex ( $\text{Au}(\text{CN})_2^-$ ). At the same time, the cathodic reaction takes place, i.e. the reduction of oxygen after reaction 2. The cumulative reaction of dissolving gold using cyanide is represented by reaction 3 [8]:

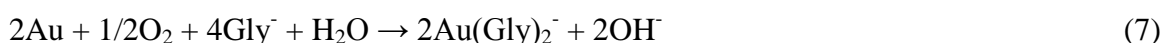


The chemical reaction of gold leaching using cyanide can be represented by the following reactions [8]:



The solubility of gold in cyanide solutions depends on the oxygen concentration, temperature, mixing rate, pH value, surface area of gold ore/concentrate /waste, as well as the presence of other anions or cations. Among the mentioned parameters, the pH value of the alkaline solution is the most important factor in the leaching process of waste PCBs. If the pH value of the cyanide solution is lower than 9, toxic hydrogen cyanide is released, the substance that can seriously damage human health. In order to reduce the amount of cyanide solution used in the process of gold leaching from PCBs, a two-stage leaching was introduced. In the first phase, base metals are leached, while in the second phase of the process, precious metals are leached. Another way to reduce the amount of reagent is to use a new alkaline agent, which in combination with cyanides will form metal complexes [9].

Li *et al.* [10] state in their paper that glycine can complex gold according to reaction 7:

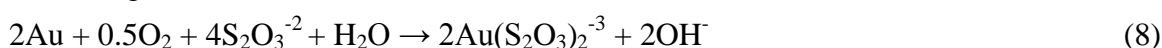


Adding copper ions to the glycine-peroxide solution can further accelerate the dissolution of gold. This indicates that  $\text{Cu}(\text{Gly})_2$  may act as an additional oxidant in the glycine-cyanide system during leaching of waste PCBs [10].

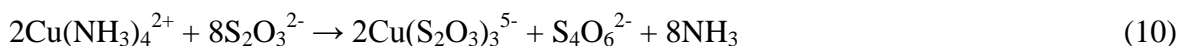
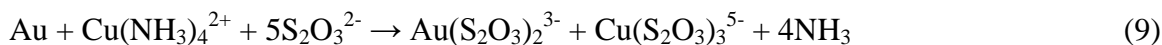
The introduction of new compounds in the cyanide process can reduce, but not completely eliminate the toxic effects of cyanide. For this reason, in recent years, preference has been given to non-cyanide solutions, among which the most common are thiosulfate and thiourea solutions.

### Thiosulfate leaching

Thiosulfates ( $\text{S}_2\text{O}_3^{2-}$ ) are widely used in photography and in the pharmaceutical industry, and are often used as a suitable alternative to cyanide solution in the gold leaching process [11]. Thiosulfate leaching is based on the formation of a stable anionic complex according to the following reaction [12]:



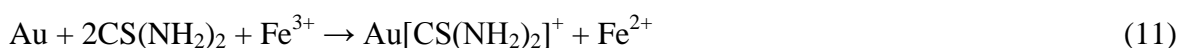
Although the thiosulfate complex is quite stable, an alkaline environment is necessary to maintain its stability [12]. It is known that the presence of ammonia and copper ions facilitates the conversion of gold into thiosulfate solution by forming gold(I) thiosulfate complex (reaction 9). This process was followed by reduction of copper(II) ions by thiosulfate (reaction 10). It is important to note that reaction 10 not only reduces the concentration of copper ions, but also the consumption of thiosulfate ions [13].



The main disadvantage of thiosulfate leaching is the high consumption of reagents with extremely unfavourable process kinetics. In the presence of ammonia, the use of oxygen as an oxidant can accelerate the kinetics of the process, but the high consumption of reagents makes the process uneconomical [12].

### Thiourea leaching

Thiourea leaching is a hydrometallurgical process, where thiourea is used as a leaching agent. Since thiourea is unstable in alkaline environment, leaching reactions should take place in an acidic medium. If ferrous ions are used as an oxidant, the total gold leaching reaction in an acidic medium can be shown as follows [14]:



However, thiourea is easily oxidized in an acidic environment by ferrous ions, forming formamidine disulfide (reaction 12).



Since formamidine disulfide is not stable in acidic media, it decomposes to form sulfur and cyanamide:



One part of the thiourea is also lost by the formation of a stable ferric sulphate complex:



Leaching kinetics as well as low toxicity make thiourea solution more efficient in the process of leaching gold from waste PCBs compared to alkaline thiosulfate leaching [15]. However, the main disadvantage of these procedures is reflected in the high consumption of reagents, its instability and the need for additional mechanical treatment.

### Halide leaching

Halide leaching involves the use of halides (fluorine, chlorine, bromine, iodine and astatine) in the process of leaching gold. Gold can form both  $\text{Au}^+$  and  $\text{Au}^{3+}$  complexes with chloride, bromide and iodide according to the following reactions [7]:



Where L are halide elements,  $\text{L}_2$  is the oxidizing agent, and  $\text{L}^-$  are the complexing agents.

The traditional medium for dissolving gold is an aqueous medium, i.e. a mixture of hydrochloric and nitric acid in a ratio of 3: 1. The mechanism of dissolving gold in aqua regia takes place according to the following reactions [12]:



Chlorination rates are favoured by low pH, high chlorine and chloride concentrations, high temperatures and high surface areas. However, the process of chloride leaching requires special equipment due to the corrosive nature of the agent used and constant monitoring due to the release of toxic chlorine [11].

Table 1 shows the optimal conditions for leaching gold from waste PCBs using different leaching agents. Based on the presented data, it can be concluded that all leaching agents provide high efficiency of the gold valorization process. However, the economic aspect of the hydrometallurgical process, the generation of significant amounts of wastewater, the toxicity and corrosive properties of the leaching agents make it difficult to apply these processes at the industrial level.

*Table 1 The studies of leaching Au from used PCBs*

Raw material	Reaction conditions	Recovery rate of Au, %	References
PCBs from computer	4 × stoichiometric amount of glycine, 250 ppm cyanide; pH = 11; leaching time 96 h; room temperature.	90.1	[10]
PCBs of waste mobile phones	24 g/L thiourea, 0.6% Fe <sup>3+</sup> ; pH = 1; leaching time 2h; room temperature.	90.0	[14]
PCBs of waste mobile phones	0.5 M thiourea in 0.05 M H <sub>2</sub> SO <sub>4</sub> , 0.01 M Fe <sup>3+</sup> ; leaching time 2 h, temperature 45 °C.	90.0	[16]
PCBs of cell phones	0.7 M sodium thiosulfate; ammonia added dropwise until the solution reached a pH = 10.5; leaching time 6 h; room temperature.	81.0	[17]
PCBs of waste mobile phones	Ammonium thiosulfate (20 mM copper, 0.12 M thiosulfate, 0.2 M ammonia); pH = 10-10.5; leaching time 10 h; room temperature.	90.0	[18]
PCBs of waste mobile phones	iodine-iodide system (I <sub>2</sub> 40 mM, KI 200 mM); pH 9, leaching time 2 h; room temperature.	98.5	[19]
PCBs	iodine-iodide system (I <sub>2</sub> 2 g/L, KI 12 g/L); leaching time 12 h; temperature 40°C.	99.0	[20]
PCBs	Aqua regia (HNO <sub>3</sub> /HCl-1/3); leaching time 10 h; room temperature.	97.0	[21]

## CONCLUSION

Hydrometallurgical processes are traditional methods of obtaining gold from primary and secondary sources. The high efficiency of these processes justifies their application. However, a large part of the analysed studies is focused on the selective leaching of individual metals, without the development of an integrated hydrometallurgical process of valorization of all valuable metals from electronic waste. Also, the conducted numerous researches do not provide a detailed techno-economic analysis of the process, in order to justify their application at the industrial level. A review of the available literature indicates that the gold

valorization from waste PCBs is a current topic, and there is plenty of room for further research.

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