

SELECTIVE RECOVERY OF COPPER FROM HYDROMETALLURGICAL PROCESSING OF E-WASTE

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Abstract

One of the environmental aspects of processing electronic waste using hydrometallurgical methods is the generation of waste solutions. Solutions after leaching and recovery of target metals are destined for disposal and contain valuable non-ferrous metals such as Cu, Sn, Ni, and others. Their disposal leads to wasting their material potential. The aim of this work is to propose a method by which selected non-ferrous metals can be selectively recovered from these solutions prior to disposal. The results of the experimental work show that the combination of pH adjustment with sodium hydroxide followed by cementation with iron is a suitable procedure for copper displacement from the solution. The cemented copper contains impurities. Removal of these impurities is possible by washing in sulfuric acid. pH adjustment can also be achieved using waste material containing copper. The results confirm that copper can be selectively recovered from waste solutions.

Keywords: Hydrometallurgy, Waste from electrical and electronic equipment, Precipitation, Copper, Recycling

1. INTRODUCTION

Waste from electrical and electronic equipment (WEEE), also known as e-waste, belongs to the fastest-growing waste streams worldwide. The expansive growth of the electronic sector, driven by increasing demands for efficient information and telecommunication systems, causes accelerated device obsolescence and thus a significant rise in the volume of waste produced. WEEE includes a wide range of discarded electronic devices, their components, and consumables [1], [2].

In 2019, 53.6 million tons of this waste were generated globally, of which only 9.32 million tons were officially collected and subsequently recycled. This type of waste contains significant amounts of hazardous substances, such as halogen compounds and toxic metals, the presence of which poses serious ecological and health risks [1].

Despite these environmental risks, e-waste is a valuable source of secondary raw materials. It contains important metals such as copper, iron, aluminum, nickel, gold, silver, and platinum group metals, whose recovery through recycling contributes to reducing the need for primary raw material extraction. Efficient management of WEEE supports the principles of the circular economy. Due to the presence of toxic substances and valuable secondary raw materials in e-waste, proper management is essential. They are processed by various methods using pyrometallurgy, hydrometallurgy, or a combination of both. In the case of hydrometallurgical processing, the by-product is wastewater, i.e., waste solutions, which may contain low concentrations of valuable metals. For this reason, before neutralization or disposal, it is advisable to first recover the metals.

Various methods exist for metal recovery from solutions, such as cementation, precipitation, or electrolysis [3].

The subject of this work is the recovery of metals from waste solutions after hydrometallurgical processing of e-waste using precipitation.

2. EXPERIMENTAL

2.1 Hydrometallurgical processing of WEEE

Hydrometallurgical processing of WEEE consists of mechanical pretreatment of the material transfer of metals into solutions, and subsequent selective recovery of metals from solutions. The advantages of hydrometallurgical processing compared to pyrometallurgy include lower energy consumption and operating costs, higher selective yield of metals, and a smaller environmental footprint. However, compared to pyrometallurgical methods, hydrometallurgical procedures are often more time-consuming [4].

2.2 Mechanical pretreatment

Before hydrometallurgical processing, WEEE must first undergo mechanical pretreatment to release metals from the composite structure of e-waste. This may include manual dismantling prior to mechanical-physical processing. Mechanical-physical treatment involves crushing and grinding the material, which is subsequently subjected to separation of individual fractions based on different physical and chemical properties. Examples include density separation, particle size classification, magnetic separation, or eddy current separation [5], [6].

2.3 Leaching

After mechanical pretreatment, the material undergoes leaching processes to transfer target substances into solution. Leaching agents may include organic or inorganic substances such as sodium hydroxide (NaOH), sulfuric acid (H₂SO₄), hydrochloric acid (HCl), nitric acid (HNO₃), aqua regia (3HCl + HNO₃), acetic acid, oxalic acid, citric acid, and others. Thermodynamic studies of leaching are an integral part of research, as they indicate which metals will or will not dissolve in different reagents. The leaching process is also influenced by temperature, mixing speed, and the pH of the leaching medium [4].

2.4 Metal recovery methods

Various methods are used to recover metals from solutions. The choice of method depends mainly on metal concentration. They are classified as physical, chemical, and physico-chemical, including crystallization, ion exchange, precipitation, cementation, electrolysis, solvent extraction, and others. The selection depends on multiple physical and chemical factors; therefore, it is important to choose methods that enable selective recovery of present components [7].

Cementation

Cementation is an electrochemical process for recovering metals from solutions, based on displacing a more noble metal with a less noble one according to the electrochemical series. An example is copper displacement using iron [7]. The principle is illustrated in Equation 1:



Precipitation

Precipitation is a process of recovering metals based on reactions between chemical agents and metals in solution, forming poorly soluble compounds. The reaction rate and efficiency of precipitation can be enhanced by increasing the initial metal concentration, adjusting pH, or raising

the temperature. In practice, heavy metals are most commonly removed as hydroxides, sulfides, or carbonates [8], [9].

2.5 Characterization of waste water solutions

The waste solutions used for experiments were from hydrometallurgical processing of WEEE. While the target metals are mainly platinum group metals, gold, and silver, e-waste also contains other valuable metals such as copper, nickel, zinc, and lead. Different reagents are used to transfer metals into solutions, followed by various methods for selective recovery.

First solution, named IH, contains a solution of spent nitric acid, second one, named LK, contains spent aqua regia, and OV contains spent sulfuric acid. These were analyzed by atomic absorption spectrometry (AAS) using a Varian SpectrAA20+ device with a detection limit of 0.3–6 ppb, wavelengths of 213.9–422 nm, and lamp current of 4–12 mA, manufactured in Belrose, Australia. The results are shown in Table 1.

Table 9. Chemical analysis results

		Cu	Sn	Ni	Pb	Fe	Zn	Al	Ca	Ag	Pt	Pd	Au
LK		74100	3980	3293	1807	1247.2	515	241	188	32.79	4.3	2.5	0
IH	[µg/ml]	124373	41.3	2215.6	476	4154	2009	141	50.8	1.42	2.7	0.73	0
OV		6135	312	57.7	1.67	18.12	101	0	13.7	0	8.3	1.01	0

The analyses revealed the presence of copper, tin, nickel, lead, iron, zinc, aluminum, calcium, and trace amounts of silver, platinum, and palladium. Copper was the most abundant element, with 124.373 g/l in the waste solution IH, 74.1 g/l in waste solution LK, and 6.135 g/l in waste solution OV.

Based on the chemical analysis of the waste solutions, a material balance was calculated to determine which solution has the highest material potential. Considering the differences in metal prices, it is possible that metals with lower concentrations but higher market values may represent economically valuable products. Table 2 presents the material potential of individual metals in the solutions, calculated as the concentration of a metal per unit volume of solution (l or m³) multiplied by the current market price of the metal (expressed in USD per ton).

Table 10. Material potential of solutions

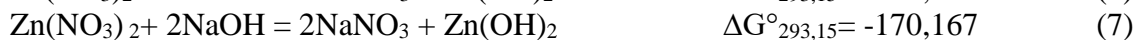
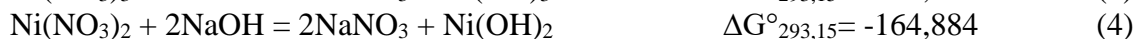
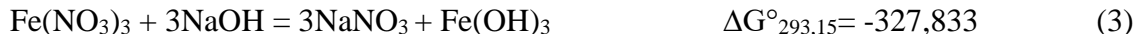
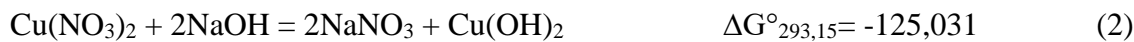
		Cu	Sn	Ni	Pb	Fe	Zn	Al	Ag	Pt	Pd
LK	[\$/m ³]	683.35	117.37	99.92	3.93	-	1.75	0.64	25.58	140.91	135.78
IH	[\$/m ³]	1 146.97	1.22	67.23	1.03	-	6.81	0.37	1.11	88.48	39.65
OV	[\$/m ³]	56.58	9.20	1.75	0.00	-	0.34	-	-	271.99	54.85

From the material balance calculations, it follows that the most valuable element in solution IH is copper, with a potential value of 1,146.97 \$/m³. Solutions LK and OV are also of interest due to their platinum and palladium contents. In LK, platinum reaches a value of 140.91 \$/m³ and palladium 135.78 \$/m³, while in OV, platinum reaches 271.99 \$/m³.

For the experimental study of metal precipitation, the waste solution IH was chosen, as it showed the highest material potential.

2.6 Thermodynamic study

Based on thermodynamic studies, sodium hydroxide (NaOH) was chosen as the precipitating agent for selective copper recovery from solution IH. Precipitation reactions are shown in equations (2)–(7).



Fractional precipitation diagrams constructed with Medusa/Hydra indicate precipitation pH values as follows:

- Cu²⁺: begins at pH 3.5, complete at pH 5
- Sn²⁺: begins at pH 3, complete at pH 4
- Ni²⁺: begins at pH 6, complete at pH 7
- Zn²⁺: begins at pH 7, complete at pH 8.5
- Fe²⁺: begins at pH 7, complete at pH 8.5
- Fe³⁺: begins at pH 1.5, complete at pH 2
- Sn⁴⁺: begins at pH 0, complete at pH 1

2.7 Precipitation of metals from waste water solution IH

In the experimental part, NaOH solution was added in volumes of 0.5–4.5 ml to 20 ml of IH solution. After precipitation, 5 ml samples were taken, and pH was measured. Recorded pH values ranged from 0 to 7.4.

AAS results combined with pH measurements (Figure 1) revealed that iron started precipitating after the first NaOH addition and was completely removed at pH 2.63. Compared to theoretical predictions, copper precipitation occurred earlier—already after the first NaOH addition. Lead, aluminum, and tin also precipitated immediately. Nickel and zinc followed a similar trend.

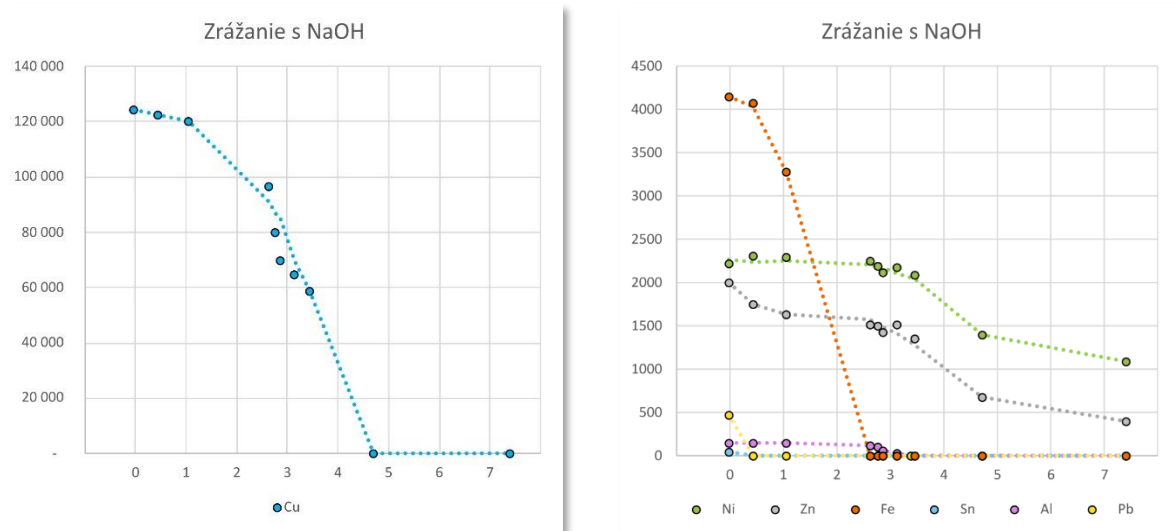


Figure 10. Results of the precipitation of Cu, Fe, Zn, Ni

The results confirm that selective recovery of copper from the solution is not possible by this method due to the presence of impurities in the form of iron, zinc, nickel, tin, lead, and aluminum.

The aim of the second precipitation experiment was first to remove iron from the solution, which is completely precipitated at pH 2.63 using sodium hydroxide, and then to selectively precipitate copper. The results confirmed that during iron precipitation, 22% of copper is lost, as it begins to precipitate together with iron. The remaining 78% of copper present in the solution can be removed by further precipitation; however, it contains impurities in the form of nickel and zinc. Figure 2 shows the filtered copper hydroxide obtained after precipitation with NaOH.



Figure 11. Precipitated copper hydroxide

The resulting blue-green copper powder contains not only copper but also nickel and zinc. Such a product is unsuitable for commercial use. Precipitation is therefore evaluated as an inappropriate selective method. Cementation is proposed as an alternative approach for copper recovery from the solution and will be the subject of further study.

3. CONCLUSION

E-waste is a type of waste whose annual production is continuously increasing. Due to the content of valuable metals in this waste, their recycling is essential. Recycling prevents the depletion of primary raw materials. The most widely used methods for recycling e-waste are pyrometallurgical or hydrometallurgical approaches, each with their own advantages and disadvantages. A drawback of hydrometallurgical recycling is the generation of waste solutions. These waste solutions may contain low concentrations of valuable metals, which should be recovered before disposal. Metals are most often recovered from solutions using precipitation, cementation, or electrolysis.

The experimental part of this work focused on the processing of waste solutions with the aim of recovering selected target metals using precipitation. Analysis of the solutions and calculation of the material balance showed that copper is the most valuable element present in the waste solutions. For this reason, copper was chosen as the target metal for recovery by precipitation.

The experimental results showed that copper can be recovered from solution, but up to pH 2.63 it co-precipitates with iron. During iron removal, 22% of copper is lost, which means material losses. The remaining 78% of copper can be precipitated later, but this product also contains nickel and zinc. Copper contaminated with these metals is not a suitable marketable product.

Thus, precipitation proved to be a non-selective method for copper recovery from waste solutions. The subject of further research will be the use of cementation as a method for recovering copper from waste solutions after hydrometallurgical processing of e-waste.

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REFERENCES

- [1] "Electronic waste (e-waste)". Cit: 26. marec 2024. [Online]. Available at: [https://www.who.int/news-room/fact-sheets/detail/electronic-waste-\(e-waste\)](https://www.who.int/news-room/fact-sheets/detail/electronic-waste-(e-waste))
- [2] Slov-lex, "79/2015 Z.z. - Zákon o odpadoch a o zmene a doplnen...", Slov-lex. Cit: 28. apríl 2024. [Online]. Available at: <https://www.slov-lex.sk/pravne-predpisy/SK/ZZ/2015/79/>

- [3] “Hazardous Substances in e-Waste | ECS Environment”. Cit: 28. april 2024. [Online]. Available at: <https://www.ecsenvironment.com/what-is-e-waste/hazardous-substances-in-e-waste/>
- [4] V. Gunarathne, A. Upamali Rajapaksha, M. Vithanage, D.S. Alessi, R. Selvasembian, M. Naushad, S. You, P. Oleszczuk, Y. Sik Ok, *Crit. Rev. Environ. Sci. Technol.*, 52 (6) (2022) 1022–1062.
- [5] L.M. Martelo, M.M.S.M. Bastos, H.M.V.M. Soares, *Miner. Eng.*, 206 (2024) 108529.
- [6] Z. Wang, Y. Zhang, P. Feng, L. Meng, J. Wang, Z. Guo, Z. Gong, *J. Environ. Chem. Eng.*, 12 (1) (2024) 111801.
- [7] T.T.H. Nguyen, M.S. Lee, *Hydrometallurgy*, 215 (2023) 105969.
- [8] R. Sarup, K. Behl, M. Joshi, a S. Nigam, “Chapter 18 - Heavy metal removal by cyanobacteria”, v *New Trends in Removal of Heavy Metals from Industrial Wastewater*, M. P. Shah, S. Rodriguez Couto, a V. Kumar, Ed., Elsevier, 2021, s. 441–466. doi: 10.1016/B978-0-12-822965-1.00018-0.
- [9] A. Santaolalla, P.N.L. Lens, A. Barona, N. Rojo, A. Ocio, G. Gallastegui, *Minerals*, 11 (9) (2021).