

SEPARATION OF COPPER FROM ACIDIC ETCHING SOLUTIONS

Martina UJHÁZY¹ , Vladimír ČABLÍK¹ , Hong N. VU² , Radmila KUČEROVÁ¹ 

¹ VSB – Technical University of Ostrava, Faculty of Mining and Geology, Department of Environmental Engineering, Ostrava, Czech Republic

² University of Chemistry and Technology Prague, Faculty of Chemical Technology, Department of Metals and Corrosion Engineering, Prague, Czech Republic

E-mail: martina.ujhazy@vsb.cz

ABSTRACT

This study deals with the issue of copper separation from acidic etching solutions formed during the process of production of printed circuit boards (PCBs) for the electrical and electronic industries. The article describes the selected methods of copper separation and summarizes the results of an experiment, in which the efficiency of copper recovery from the depleted acid solutions by the cementation and precipitation method was verified. In the process of cementation, iron in the form of metallic swarf was used as a precipitant. To verify the efficiency of the precipitation method, CaCO₃ limestone, Ca(OH)₂ calcium hydroxide and NaOH solution were used. During the measurement, the amount of Cu in the solution was observed for both methods in dependence on time, temperature, and pH.

Keywords: Acid etching; Cementation; Copper; Precipitation; Printed circuit boards (PCB).

1 INTRODUCTION

As a result of the massive advent of digitization and robotization in all areas of human life, there is a worldwide increase in demand for printed circuit boards, which are an essential component in the production of electrical and electronic products [1, 2]. The technology of PCB production consists of several partial mechanical, chemical, galvanic and photo-optical operations that are associated with the circulation of water and chemicals [3, 4]. One of the main production operations is the process of acid etching, which eats away copper from the predetermined points on the PCB and creates the basic design. The waste bath from this process is a solution with a high content of copper, which represents a burden on the environment and a hitherto little-used source of valuable metal [5, 6].

Wastewater and sludges from the PCB production process (depleted electrolytic, pickling or etching baths) contain, in addition to copper, many substances with a negative impact on the environment, as well as other valuable metals [7]. Therefore, in addition to economic reasons, the use of these sludges as secondary raw materials for further production brings also ecological benefits [8–11]. The most efficient way to deal with these wastewaters and the generated sludges is the recovery of metals [9, 12]. In the recovery of metals, the form, in which metals are recovered from waste, is very important, the most advantageous is the pure metal in the solid form [5, 7, and 8].

Given the growing demand for copper worldwide, recycling and reusing copper is the only way for a sustainable future for many industries [13, 14]. This study deals with the issue of copper separation from acidic etching solutions generated during the PCB production process. The subject of the experiment was to verify the efficiency of Cu recovery by the method of cementation and precipitation.

2 METHODS AND MATERIALS USED

2.1 Cementation

The essence of the cementation method is to remove metals from solutions of metals. The process is based on an electrochemical reaction between the cementing metal and the metal ion that is to be removed from the solution [15]. The possibility of cementation is determined by the relationship between the electrode potential values of both metals. The metal, by which we want to displace (the precipitant) must have a more negative electrode potential than the metal to be removed. The process stops after achieving equilibrium values of the electrode potentials [16, 17].

For industrial cementation of copper, ferrous waste is most commonly used as a precipitant due to its easy availability and favourable price [18]. Nickel or zinc are also other suitable precipitants. During the cementation process, metallic copper is removed and then replaced by an equivalent amount of iron, which passes into the solution [15]. The copper cementation process using Fe as a precipitant is shown in Figure 1 [5, 16].

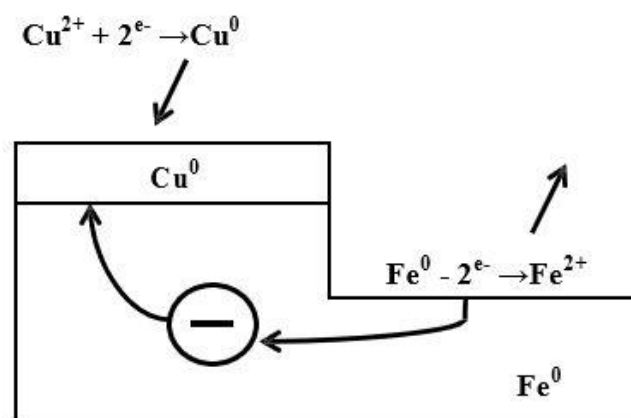


Figure 1. Schematic diagram of the cementation process [19]

The duration of contact necessary for deposition of the copper depends on the following factors:

- the purity of the iron used;
- temperature;
- the pH of the solution;
- mixing rates;
- the area of the contact surface;
- the total concentration of copper in the solution [8].

The raw material recovered by cementation has a very low content of the metal itself, so it must be refined before further use. In the case of copper, this refining is usually done by smelting followed by electrolytic refining [13, 18].

2.2 Precipitation

Precipitation of metals is one of the chemical procedures for obtaining metals from aqueous solutions. The principle of the process is the deposition of metal in the form of a poorly soluble compound. This process may be final or one of the refining steps of hydrometallurgical processes for obtaining metals [16]. In practice, precipitation processes in the form of hydroxides and sulphides are usually used. For deposition of heavy metals in the form of poorly soluble hydroxides, the addition of NaOH or milk of lime is most often used. The solubility of hydroxides of metals is highly dependent on the pH value of the solution and this value is specific to each type of metal [15, 20].

For cations of metals, such as Cu, Ni, Co, Zn, Cr or Cd, it is best to use precipitation procedures in the form of hydroxides [12]. For some heavy metals, however, a solution of sulphides or sulphates to form poorly soluble sulphates is a more suitable precipitant [12]. Sulphide precipitation is used as an alternative method for separating heavy metals in wastewater and solutions. Sulphide precipitation has a large number of advantages, such as high stability and low solubility of metal sulphides, which makes it possible to achieve a high degree of precipitation from the solution in a wide pH interface, including acidic areas. The resulting precipitates are also better filterable [16].

According to the type of precipitating agents used, sulphide precipitation is divided into the classical method of precipitation using hydrogen sulphide gas, the soluble sulphide method and the insoluble sulphide method. Aqueous solutions of Na₂S, NaHS, CaS or (NH₄)₂S are used as a donor for the soluble sulphide method. For the insoluble sulphide method, insoluble or very poorly soluble sulphides, such as zinc sulphide are used as precipitating agents, but in practice, it is applied only exceptionally [18]. This method is also used in the precipitation of mercury cations [16].

2.3 Input material

Acid etching of printed circuit boards is performed in a bath containing chemically pure hydrochloric acid, hydrogen peroxide, cupric chloride, water and additives. Copper etching occurs in several minutes and during the etching process, the bath becomes considerably heated.

Etching with the use of cupric chloride runs within the following chemism:



At the moment when the bath ceases to be functional, it is called a depleted bath. The waste bath from this production process is characterized by a high copper content and a low pH value [21]. The characteristic composition of the depleted etching bath is shown in Table 1.

Table 1. Characteristics of the depleted etching bath

Specified parameter	Unit	Measured sample values
pH		0.1
RI	mg/l	287000
Ni	mg/l	30
Knacker	mg/l	135000
COD _{Cr}	mg/l	3840
BOD ₅	mg/l	146
Ammoniacal nitrogen	mg/l	112
Total nitrogen	mg/l	7140
Chlorides	mg/l	728000
Sulphates	mg/l	cannot be determined
P	mg/l	38.1
Total cyanides	mg/l	0.015
AOX	mg/l	50.5
Cd	mg/l	< 0.5
Cr	mg/l	< 3
Cu	mg/l	131000
Hg	mg/l	0.0051
Ni	mg/l	< 2
Pb	mg/l	< 5
Zn	mg/l	698

3 EXPERIMENTAL PROCEDURE AND APPARATUS

3.1 Sample preparation and measuring devices used

Before the performance of the experiment, the pH values of the solution and the Cu content were verified on the sample. The input sample had a very low pH value of -1.22 and the detected amount of Cu found in the solution was 148.100 mg/l. The exact content of metal elements was determined using atomic absorption spectroscopy using the GBC 932 AA instrument at the Department of Metals and Corrosion Engineering of the University of Chemistry and Technology Prague (VŠCHT), the pH value of the solution was measured using a calibrated glass electrode on two-channel pH meter Thermo Orion 525A+.

Due to the negative pH value, the sample was first neutralized using CaCO_3 (finely ground limestone D7 according to ČSN 72 1220 [22]), which resulted in an increase in pH to the required value of 1.5. The amount of limestone consumed to achieve the required pH value (1,5) was 83.856 g. The sample thus treated was used for subsequent cementation, as well as for the precipitation method.

Throughout the cementation and precipitation, the sample temperature was measured using TC, IKA – WARKE; the redox potential and the pH of the solution were measured using calibrated glass electrodes on a two-channel pH meter Thermo Orion 525 A+. The content of metallic elements was determined by atomic absorption spectroscopy using the GBC 932 AA instrument at the Department of Metals and Corrosion Engineering of the University of Chemistry and Technology Prague.

3.2 Copper recovery by the cementation method

The selection of a suitable precipitant depended on different values of electrode potentials. For experimental cementation, iron in the form of metallic swarf was used. The electrode potential of iron is -0.44 V and that of copper 0.34 V [16]. These different values should lead to the fact that the surface of the lump iron after immersion into a solution containing copper ions is immediately covered with a precipitated layer of copper.

Each neutralized sample was first diluted 2 times (250 ml of distilled water was added to the 250 ml of the sample with the adjusted pH value) and then the pH value of the sample was measured again with a resulting value of 1.9.

For the cementation itself, the necessary amount of added Fe was found, which was always added in excess (within the range of approx. 5 to 1.5 times the calculated amount of Fe (175 g). Cementation of all samples was carried out at 40 °C; the last sample was subjected to cementation at a temperature of 25 °C. The precipitant (iron swarf) was kept moving by force during the experiment so that the cemented copper was abraded by constant mutual friction and the surface could remain electrochemically active for a longer time. After heating the solution to the required temperature, a determined amount of Fe was added under constant stirring ensured by the EUROSTAR digital IKA - WERKE stirrer at a set speed of 360 rpm, and the measurement of the duration of cementation was started.

Immediately after the addition of Fe, the temperature of the sample began to rise sharply. For this reason, all measurements were performed under the suction device. After certain time intervals (0 min, 5 min, 10 min, 15 min, 30 min, 45 min, 60 min) samples of 20 ml were taken, which were filtered through a filter paper – “Filtrá acido hydrochlorico et hydroflourico extracta 388”. One drop of concentrated HCl was added to the filtered samples to prevent the formation of sediment. Subsequently, the amount of Cu and Fe was determined in the samples using atomic absorption spectrophotometry (AAS). After completion of the cementation (after 60 minutes), the remaining solution was allowed to cool; afterwards, the solution was filtered and the filter cake with added iron coated with copper was dried. The dry sample was handed over for further processing by electrolytic refining.

3.3 Removal of copper by the precipitation method

Precipitation was carried out by two procedures. For one measurement, an already neutralized sample with a pH value of 1.5 was used. For the second measurement, an untreated input sample was used. Both samples were first diluted 2 times (250 ml of distilled water was added to 250 ml of the sample) and then the pH value of the solution was measured again.

Precipitation was performed at temperatures of 25 °C and 40 °C, the solution was stirred all the time using the EUROSTAR digital IKA – WERKE stirrer at a set speed of 360 rpm.

Various precipitants were used for precipitation. For the first measurement, limestone (CaCO_3) was used, which was added till the initial formation of the precipitate. Subsequently, precipitation was continued using calcium hydroxide Ca(OH)_2 .

For the second sample, a 50% solution of NaOH was used as a precipitant, which was added till the initial formation of the precipitate. At this moment a 25% solution of NaOH began to be added to subsequently slow down the reaction.

During the measurement, 20 ml samples were taken at different pH values and then filtered. The samples were filtered under reduced pressure using a Buchner funnel through a filter paper – “Filtrá acido hydrochlorico et hydroflourico extracta 388”. In the filtered samples, the pH value and redox potential were measured using glass electrodes on a two-channel pH meter. In the samples taken, the amount of Cu was also measured using atomic absorption spectrophotometry (AAS). Subsequently, 1 drop of concentrated HCl was added to each sample taken to prevent the formation of a precipitate. Precipitation was stopped when the determined pH value was reached, and the remaining sample was filtered according to the same procedure used for the samples taken. The filter cake was then dried and handed over for further analysis.

4 RESULTS AND DISCUSSION

4.1 Evaluation of the cementation method

The cementation method has been verified in 6 measurements. For the first 5 measurements, after dilution of the samples, the input pH value was 1.9. The samples were then heated to an initial temperature of 40 °C. After achieving the desired temperature, cementation was started with the addition of the calculated dose of Fe (700 g, 560 g, 420 g, 280 g, 210 g).

For all measurements performed, the temperature increased during the first 5 minutes to an average of 70.8 °C and then gradually decreased. The amount of copper in the solutions decreased rapidly after the start of cementation, causing a discolouration of the solution, see Figure 2. Almost in all measurements, copper afterwards cemented with 99% efficiency during a time interval of max. 15 minutes (when a larger excess of Fe was added, this efficiency was achieved already in the 5th minute of measurement). The amount of Fe released into the solution was up to 25% of the total amount added.

The final 6th measurement was performed on a sample with the same pH value of 1.9 and an initial temperature of 25 °C. Altogether 280 g of Fe was added to the sample (this amount was chosen based on previous measurements where the highest separation efficiency was achieved at this amount). The temperature increased to a maximum temperature of 58 °C within the first 5 minutes and the highest efficiency was reached after 15 minutes of cementation. The resulting measured and recalculated values are presented in Table 2. The progress of cementation of two samples with different initial temperatures and the same amount of added iron precipitant is graphically shown in Figure 3.



Figure 2. Discoloration of the sample after 15 minutes of cementation

Table 2. Cementation efficiency of all measurements after 15 minutes

Evaluation of cementation efficiency after 15-min measurement					
Measurement number	Initial temperature [°C]	Input pH value	Amount of Fe added [g/l]	The efficiency of Cu recovery [%]	Amount of released Fe [%]
1	40	1.9	700	99.85	5
2	40	1.9	560	99.98	13
3	40	1.9	420	99.91	15
4	40	1.9	280	99.89	25
5	40	1.9	210	97.15	22
6	25	1.9	280	99.98	22

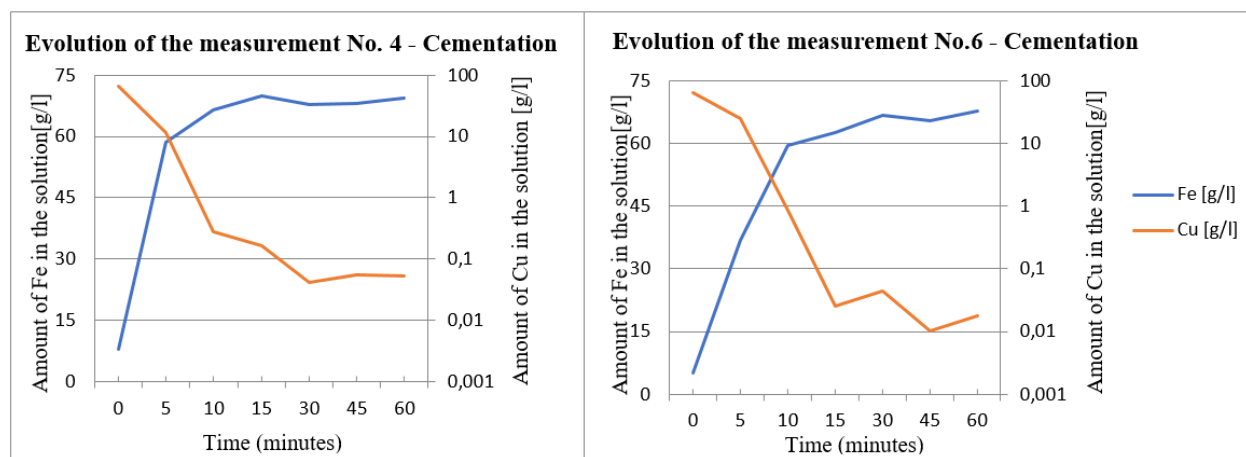


Figure 3. Evolution of the cementation process for the samples with different temperatures (measurements no. 4 and no. 6)

4.2 Evaluation of the precipitation method

The precipitation method has been verified in 2 measurements. For the first measurement, an already neutralized and diluted sample with a pH value of 1.9 and an initial temperature of 25 °C was used. CaCO₃ limestone was used as precipitant, which was added till the initial formation of the precipitate (pH value 2.7) and precipitation subsequently took place with the help of Ca(OH)₂. Precipitation ran under constant stirring using the EUROSTAR digital IKA – WERKE stirrer at a set speed of 360 rpm. The precipitation reaction was stopped when the pH value of 3.5 was achieved.

For the second measurement, a diluted original sample with a pH value of -0.55 was used. The initial temperature was raised to 40 °C and a 50% NaOH solution was used as a precipitant, which was added till the initial formation of the precipitate (pH value 2.7). Further precipitation ran using a 25% solution of NaOH to slow down the evolution of the precipitation reaction. The precipitation reaction was stopped at a pH value of 5.

Filtration of the samples was performed under reduced pressure using a Buchner funnel through a filter paper – “Filtracido hydrochlorico et hydroflourico extracta 388”. The resulting precipitate was very poorly filtrable in both samples, even at the increased temperature. In the filtered samples, the pH value and redox potential were measured using glass electrodes on a two-channel pH meter.

In both measurements, after the addition of precipitants, the solution became gradually brighter and thickened, see Figure 4. The efficiency of Cu removal from the solution was 95% at maximum. With the increasing pH value, activity in both measurements increased too. The redox potential decreased during precipitation reactions in both samples. The resulting measured and recalculated values are given in Tables 3 and 4. The decrease in redox potential and the decrease in Cu content in solution are graphically shown in Figures 5 and 6.



Figure 4. Change of colour and consistency of the solution during the precipitation process

Table 3. Resulting values of the 1st measurement of the precipitation method

Measurement no. 1 – Precipitation (T 25 °C. CaCO ₃ . Ca(OH) ₂)						
Sample no.	pH value	Amount of Cu in solution [g/l]	Amount of recovered Cu [g/l]	The efficiency of Cu recovery [%]	Redox potential [MV]	Temperature [°C]
input	1.9	148.10	0.00	0.00	399.40	25
1 - 1	2.7	37.52	110.58	74.67	334.60	25
1 - 2	3.0	9.22	138.88	93.77	299.20	25
1 - 3	3.5	6.91	141.19	95.33	262.80	25

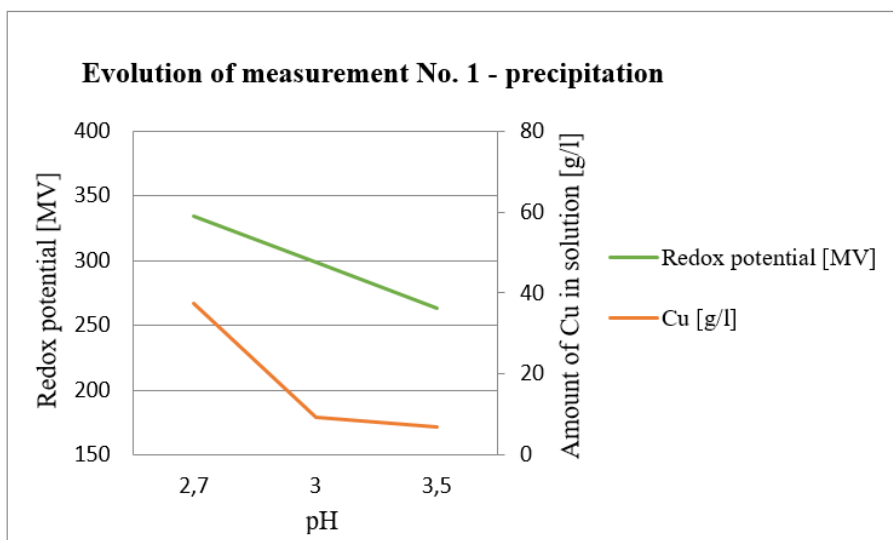


Figure 5. Decrease in redox potential and decrease of Cu content in the solution

Table 4. Resulting values of the 2nd measurement of the precipitation method

Measurement no. 2 – Precipitation (T 40 °C. NaOH)						
Sample no.	pH value	Amount of Cu in solution [g/l]	Amount of recovered Cu [g/l]	The efficiency of Cu recovery [%]	Redox potential [MV]	Temperature [°C]
input	-0.55	148.10	0.00	0.00	407.0	40
2 - 1	2.70	61.40	86.70	58.54	369.9	50
2 - 2	3.00	34.85	113.25	76.47	340.2	40
2 - 3	3.50	20.19	127.91	86.37	279.6	40
2 - 4	4.50	15.85	132.25	89.30	217.8	40
2 - 5	5.00	7.54	140.56	94.91	171.8	40

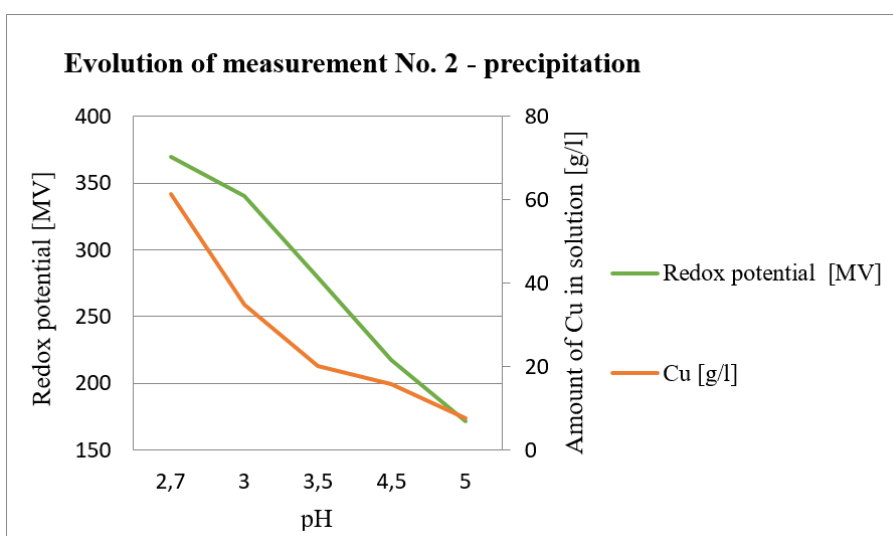


Figure 6. Decrease in redox potential and decrease in Cu in solution

4.3 Discussion

The cementation method was verified in 6 measurements when the pH value of the input samples was adjusted. Cementation was performed at a temperature of 40 °C and in one case also at a room temperature of 25 °C. For individual measurements, different amounts of the iron precipitant (iron swarf) were added to the samples.

From all measurements, it is obvious that the greatest efficiency of the cementation process was achieved within the first 15 minutes when more than 99% Cu was recovered by cementation. The evolution of this intense reaction for all measurements was indicated by an immediate increase in temperature immediately after the addition of Fe. Although the cementation process continued to take place during subsequent time intervals, the increase in the Cu recovered from the solution was already minimal (only in hundredths of %). It is also clear from the measurement results that the amount of Fe added affects the cementation process when a larger amount of Fe accelerates the process but at the cost of higher purchase costs of Fe. The measurement did not confirm the positive effect of the initial higher temperature (preheating of the sample) on the evolution of cementation, since the cementation ran similarly as in the samples preheated to 40 °C and the sample tested at room temperature of 25 °C. It follows from the experiment performed that the most efficient was the evolution of cementation in measurement no. 6 when the initial pH value was 1.9, the temperature was 25 °C and the amount of added Fe was 280 g. Cementation performed under these conditions was the most efficient both in terms of speed of the cementation process itself, as well as from the point of view of the amount of energy supplied and the amount of Fe added.

The efficiency of the precipitation method for Cu recovery from acidic etching solutions was verified using two different precipitants. During the measurement, the influence of the pH value on the amount of recovered Cu was monitored, as well as the decrease in the value of the redox potential. In these measurements, the efficiency of Cu removal increased with increasing pH. For both used precipitants, the maximum efficiency achieved was approximately 95%. The resulting precipitate was poorly filtrable even at the increased temperature. The obtained dried precipitate in the sample from one measurement contained a higher chloride content, which represents a complication for further downstream processes to obtain pure Cu.

5 CONCLUSIONS

This study was conducted to verify the efficiency of copper recovery from waste acid baths generated during the production of printed circuit boards. In the experimental part, the method of cementation and the method of precipitation were practically verified.

The final discussion shows that the efficiency of both tested methods is high. However, the method of cementation using an iron precipitant in the form of a Fe swarf seems to be more efficient. This method achieved almost 100% efficiency of Cu recovery from the solution.

In the case of the precipitation method, the maximum efficiency was 95%. The resulting precipitate was poorly filtrable and after drying it contained a higher concentration of substances (chlorides) complicating further downstream processes for obtaining pure copper.

Copper obtained by the cementation method is also not in a pure state and requires further treatment, such as mechanical separation of Cu from the surface of the iron precipitant, remelting into anodes and final refining electrolysis for obtaining pure copper. The copper thus obtained should be suitable for reuse in production processes based on Cu processing.

According to available information sources, electrolysis is also another suitable method for recovery Cu from acidic etching solutions, the great advantage of which is obtaining copper in a pure state. Verification of the efficiency of recovery Cu by this method in practice would mean another step toward the implementation of waste-free technologies in similar production processes as the production of PCB.

REFERENCES

- [1] FORTI, V., C.P. BALDÉ, R. KUEHR and G. BEL. *The Global E-waste Monitor 2020: Quantities, flows and the circular economy potential* [online]. Bonn, Geneva and Rotterdam: United Nations University/United Nations Institute for Training and Research, International Telecommunication Union, and International Solid Waste Association, 2020. ISBN 9789280891140. Available at: <https://collections.unu.edu/view/UNU:7737>
- [2] AWASTHI, A.K., J. LI, L. KOH and O.A. OGUNSEITAN. Circular economy and electronic waste. *Nature Electronics*. 2019, vol. 2, pp. 86–89. ISSN 2520-1131. DOI: [10.1038/s41928-019-0225-2](https://doi.org/10.1038/s41928-019-0225-2)
- [3] HADI, P., M. XU, C.S.K. LIN, C.-W. HUI and G. MCKAY. Waste printed circuit board recycling techniques and product utilization. *Journal of Hazardous Materials*. 2015, vol. 283, pp. 234–243. ISSN 0304-3894. DOI: [10.1016/j.jhazmat.2014.09.032](https://doi.org/10.1016/j.jhazmat.2014.09.032)
- [4] ATTAH-KYEL, D., G. AKDOGAN, C. DORFLING, J. ZIETSMAN, D. LINDBERG, F. TESFAYE and Q. REYNOLDS. Investigation of waste PCB leach residue as a reducing agent in smelting processes. *Minerals Engineering*. 2020, vol. 156, art no. 106489. ISSN 0892-6875. DOI: [10.1016/j.mineng.2020.106489](https://doi.org/10.1016/j.mineng.2020.106489)
- [5] BIRLOAGA, I., V. COMAN, B. KOPACEK and F. VEGLIÒ. An advanced study on the hydrometallurgical processing of waste computer printed circuit boards to extract their valuable content of metals. *Waste Management*. 2014, vol. 34(12), pp. 2581–2586. ISSN 0956-053X. DOI: [10.1016/j.wasman.2014.08.028](https://doi.org/10.1016/j.wasman.2014.08.028)
- [6] ALI, A.H.M., S. SOBRI, A. SALMIATON and M.Y. FAIZAH. Recovery of Heavy Metals from Spent Etching Waste Solution of Printed Circuit Board (PCB) Manufacturing. *Pertanika Journal of Science & Technology*. 2013, vol. 21(2), pp. 375–386. ISSN 0128-7680. Available at: <http://www.pertanika.upm.edu.my/pjst/browse/regular-issue?article=JST-0258-2011>
- [7] HSU, E., K. BARMAK, A.C. WEST and A.A. PARK. Advancements in the treatment and processing of electronic waste with sustainability: a review of metal extraction and recovery technologies. *Green Chemistry*. 2019, vol. 21(5), pp. 919–936. ISSN 1463-9270. DOI: [10.1039/C8GC03688H](https://doi.org/10.1039/C8GC03688H)
- [8] RUML, V. and M. SOUKUP. *Likvidace toxických odpadů z kovoprůmyslu [Disposal of Toxic Waste from the Metal Industry]*. Praha: SNTL, 1984. Ochrana životního prostředí.
- [9] PTÁČEK, M., J. ERLEBACH, P. LISCHKE and Z. MATĚJKA. *Čištění odpadních vod z galvanotechniky a chemické povrchové úpravy kovů [Wastewater Treatment from Galvanotechnics and Chemical Surface Treatment of Metals]*. Praha: SNTL, 1981.
- [10] KAYA, M. Recovery of metals and nonmetals from electronic waste by physical and chemical recycling processes. *Waste Management*. 2016, vol. 57, pp. 64–90. ISSN 0956-053X. DOI: [10.1016/j.wasman.2016.08.004](https://doi.org/10.1016/j.wasman.2016.08.004)
- [11] CUCCHIELLA, F., I. D'ADAMO, S.C.L. KOH and P. ROSA. Recycling of WEEEs: An economic assessment of present and future e-waste streams. *Renewable and Sustainable Energy Reviews*. 2015, vol. 51, pp. 263–272. ISSN 1364-0321. DOI: [10.1016/j.rser.2015.06.010](https://doi.org/10.1016/j.rser.2015.06.010)
- [12] DOHÁNYOS, M., J. KOLLER and N. STRNADOVÁ. *Čištění odpadních vod [Wastewater Treatment]*. Ed. 2. Prague: Vydavatelství VŠCHT, 1998. ISBN 80-7080-316-9.
- [13] GAUTAM, P., C.K. BEHERA, I. SINHA, G. GICHEVA and K.K. SINGH. High added-value materials recovery using electronic scrap-transforming waste to valuable products. *Journal of Cleaner Production*. 2022, vol. 330, art. no. 129836. ISSN 0959-6526. DOI: [10.1016/j.jclepro.2021.129836](https://doi.org/10.1016/j.jclepro.2021.129836)
- [14] TRINH, H.B., S. KIM and J. LEE. Selective Copper Recovery by Acid Leaching from Printed Circuit Board Waste Sludge. *Metals*. 2020, vol. 10(2). ISSN 2075-4701. DOI: [10.3390/met10020293](https://doi.org/10.3390/met10020293)
- [15] KAYA, M. *Electronic Waste and Printed Circuit Board Recycling Technologies*. Springer Nature Switzerland, 2019. The Minerals, Metals & Materials Series. ISBN 978-3-030-26593-9. DOI: [10.1007/978-3-030-26593-9](https://doi.org/10.1007/978-3-030-26593-9)
- [16] JANDOVÁ, J., N.H. VU and P. DVORÁK. *Metody výroby neželezných kovů a zpracování odpadů [Methods of Production of Non-Ferrous Metals and Waste Treatment]*. Prague: VŠCHT, 2018. ISBN 978-80-7592-026-3.
- [17] LUNDSTRÖM, M., J. LIIPO, P. TASKINEN and J. AROMAA. Copper precipitation during leaching of various copper sulfide concentrates with cupric chloride in acidic solutions. *Hydrometallurgy*. 2016, vol. 166, pp. 136–142. ISSN 0304-386X. DOI: [10.1016/j.hydromet.2016.10.017](https://doi.org/10.1016/j.hydromet.2016.10.017)
- [18] PLAKSIN, I.N. and D.M. JUCHTANOV. *Hydrometalurgie [Hydrometallurgy]*. Prague: Státní nakladatelství technické literatury, 1953.
- [19] KMEŤOVÁ, D. *Teória pyro, hydro a elektrometalurgia [Theory of Pyro, Hydro and Electrometallurgy]*. Košice: Vysoká škola technická, 1981.
- [20] SLEZÁK, M. and J. PALARČÍK. Odstranění iontů kovů z důlních vod biologickou metodou [Removal of Metal Ions from Mine Waters by a Biological Method]. *Ekomonitor* [online]. 2018 [cit. 2021-10-07]. Available at: http://www.ekomonitor.cz/sites/default/files/filepath/prezentace/13_slezak_tabor_2018.pdf

- [21] CAKIR, O. Copper etching with cupric chloride and regeneration of waste etchant. *Journal of Materials Processing Technology*. 2006, vol. 175(1–3), pp. 63–68. ISSN 0924-0136. DOI: [10.1016/j.jmatprotec.2005.04.024](https://doi.org/10.1016/j.jmatprotec.2005.04.024)
- [22] ČSN 72 1220. *Mleté vápence a dolomity [Ground Limestones and Dolomites]*. Prague: The Office for Standards and Measurements, 1984.