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MEETING POINT OF THE SCIENCE AND PRACTICE IN THE FIELDS OF CORROSION, MATERIALS AND ENVIRONMENTAL PROTECTION

STECIŠTE NAUKE I PRAKSE U OBLASTIMA KOROZIJE, ZAŠTITE MATERIJALA I ŽIVOTNE SREDINE

PROCEEDINGS

KNJIGA RADOVA

Under the auspicies of the MINISTRY OF EDUCATION, SCIENCE AND TECHNOLOGICAL DEVELOPMENT OF THE REPUBLIC OF SERBIA

Pod pokroviteljstvom MINISTARSTVO PROSVETE, NAUKE I TEHNOLOŠKOG RAZVOJA REPUBLIKE SRBIJE

May 16-19, 2022 : : Divčibare, Serbia

CIP - Каталогизација у публикацији
Народна библиотека Србије, Београд

620.193/.197(082)(0.034.2)
621.793/.795(082)(0.034.2)
667.6(082)(0.034.2)
502/504(082)(0.034.2)
66.017/.018(082)(0.034.2)

INTERNATIONAL Conference YUCORR (23 ; 2022 ; Divčibare)
Meeting point of the science and practice in the fields of corrosion, materials and environmental protection [Elektronski izvor] : proceedings = Stecište nauke i prakse u oblastima korozije, zaštite materijala i životne sredine : knjiga radova / XXIII YuCorr International Conference = XXIII YuCorr [Jugoslovenska korozija] Međunarodna konferencija, May 16-19, 2022, Divčibare, Serbia = [organized by] Serbian Society of Corrosion and Materials Protection ... [et al.]] ; [organizatori Udruženje inženjera Srbije za koroziju i zaštitu materijala ... [et al.] ; [editors, urednici Miroslav Pavlović, Marijana Pantović Pavlović, Miomir Pavlović]. - Beograd : Serbian Society of Corrosion and Materials Protection UISKOZAM : Udruženje inženjera Srbije za koroziju i zaštitu materijala UISKOZAM, 2022 (Beograd : Serbian Society of Corrosion and Materials Protection UISKOZAM : Udruženje inženjera Srbije za koroziju i zaštitu materijala UISKOZAM). - 1 elektronski optički disk (CD-ROM) ; 12 cm
Sistemski zahtevi: Nisu navedeni. - Nasl. sa naslovne strane dokumenta. - Radovi na engl. i srp. jeziku. - Tiraž 200. - Bibliografija uz većinu radova. - Abstracts.
ISBN 978-86-82343-29-5
а) Премази, антикорозиони -- Зборници б) Превлаке, антикорозионе -- Зборници в) Антикорозиона заштита -- Зборници г) Животна средина -- Заштита -- Зборници д) Наука о материјалима -- Зборници
COBISS.SR-ID 68624905

XXIII YUCORR – International Conference | *Međunarodna konferencija*

PUBLISHED AND CD BURNED BY | *IZDAVAČ I NAREZIVANJE CD*
SERBIAN SOCIETY OF CORROSION AND MATERIALS PROTECTION (UISKOZAM)
UDRUŽENJE INŽENJERA SRBIJE ZA KORZIJU I ZAŠTITU MATERIJALA (UISKOZAM),
Kneza Miloša 7a/II, 11000 Beograd, Srbija, tel/fax: +381 11 3230 028, office@sitzam.org.rs; www.sitzam.org.rs

FOR PUBLISHER | *ZA IZDAVAČA* *Prof. dr MIOMIR PAVLOVIĆ, predsednik UISKOZAM*

EDITORS | *UREDNICI:* *Dr Miroslav Pavlović, Dr Marijana Pantović Pavlović, Prof. dr Miomir Pavlović*

SCIENTIFIC AREA | *OBLAST:* CORROSION AND MATERIALS PROTECTION **|** *KOROZIJA I ZAŠTITA MATERIJALA*

PAGE LAYOUT | *KOMPJUTERSKA OBRADA I SLOG:* *Dr Marijana Pantović Pavlović*

CIRCULATION | *TIRAŽ:* 200 copies **|** *primeraka*
PUBLICATION YEAR | *GODINA IZDANJA:* 2022
ISBN 978-86-82343-29-5

Synthesis : : Materials : : Corrosion : : Environment : : Energy

XXIII YuCorr

Analyse : : Discover : : Coat : : Green : : Protect : : Save : : Sustain

May 16-19, 2022, Divčibare, Serbia

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INSTITUTE OF CHEMISTRY, TECHNOLOGY AND METALLURGY, UNIVERSITY OF BELGRADE

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The effect ultrasound sonification on nitric acid leaching of pyrolyzed printed circuit board powder

Uticaj ultrazvuka na luženje sprašenih i pirolizovanih štampanih ploča azotnom kiselinom

Gvozden Jovanović[1,*], Mladen Bugarčić[1], Nela Petronijević[1], Srećko Stopić[2], Branislav Marković[1], Srđan Stanković[3], Bernd Friedrich[2], Miroslav Sokić[1]

[1] *Institute for Technology of Nuclear and other Mineral Raw Materials, 86 Franchet d'Esperey Street, 11000 Belgrade, Serbia*

[2] *IME Process Metallurgy and Metal Recycling, RWTH Aachen University, Intzestrasse 3, 52056 Aachen, Germany*

[3] *Federal Institute for Geosciences and Natural Resources, Stilleweg 2, 30655 Hannover, Germany*

[*] *Corresponding author: g.jovanovic@itnms.ac.rs*

Abstract

Numerous electronic devices are put out of use every day, and most of them have printed circuit boards (PCBs) that are lased and imbued with various precious and valuable metals in abundant amounts. This makes PCB an unexploited resource of the future from whom many metals such as Cu, Zn, Sn, Al, Li, Co, Nd, Pd, Pt, and Ba can be extracted. Since leaching plastic polymers can lead to the vaporization of toxic fumes, to avoid this the PCB are pyrolyzed. The PCB is crushed and the pyrolyzed product is a powder that can easily be separated into metallic and nonmetalic fractions. The aim of this work is to investigate the influence of ultrasound sonification on the nitric acid leaching of pyrolyzed printed circuit board (PPCB) powder. The impact of ultrasound sonification had a positive effect on the leaching degree for all investigated metals except for Cobalt. The biggest difference in leaching degree was for Lithium while the smallest was for platinum. Because of the complexity of the PPCB powder system overall, the measurement of oxidation-reduction potential (ORP) didn't yield any insight into the leaching mechanism since the measured values mainly followed the expected trend due to nitric acid degradation.
Keywords: *electronic waste; leaching;* ultrasound*; precious metals; pyrolysis*

Izvod

Svakodnevno se brojni električni uređaji izbacuju iz upotrebe, od kojih većina poseduje štampane ploče (PCB) koje sadrže u znatnoj količini raznovrsne dragocene metale. Stoga štampane ploče (PCB) postaju neiskorišćeni resurs budućnosti za eksplotaciju metala kao što su Cu, Zn, Sn, Al, Li, Co, Nd, Pd, Pt, i Ba. Luženje štampanih ploča bez prethodne eliminacije delova od plastičnih polimera dovelo bi do isparivanja toksičnih gasova, da bi se to izbeglo štampane ploče se pirolizuju. Zdrobljene štampane ploče nakon pirolize pretvaraju se u prah koji se lako razdvaja u metalične i nemetalične frakcije. Cilj ovog rada je da se ispita uticaj ultrazvuka na luženje metalične frakcije pirolizovanog praha štampanih ploča azotnom kiselinom. Ultrazvuk je imao pozitivan efekat na stepen luženja svih metala osim na stepen luženja kobalta. Najveću razliku ultrazvuk je imao na izluženje litijuma, dok je najmanji uticaj bio na platini. Usled kompleksnosti unutar sistema pirolizovanog praha štampanih ploča, merenje oksidaciono-redukcionog potencijala (ORP) nije dalo uvida u mehanizme luženja, jer su izmerene vrednosti pretežno pratile očekivani trend degradacije azotne kiseline.
Ključne reči: *električni otpad; luženje; ultrazvuk; dragoceni metali; piroliza*

Introduction

Due to the rapid technological development, everyday life in modern society gave birth to various forms of electronic devices. Currently, the market supply of those numerous devices we commonly use today includes smartphones, tablets, laptops, personal computers, etc. All of those devices are made out of plenty of metals needed for the construction of printed circuit boards (PCBs) which are the essential functional part of every electronic device. These metals and their metalloids present in PCB are a valuable resource since the amount of gold, platinum, palladium, silver and other expensive metals are much higher than in the richest ores [1]. However, in order to reach a high recovery rate of the targeted metal present in e-waste, it is needed to liberate the surface of the metal to the leaching medium but also to modify those materials that hinder the reaction with leaching substances [2]. In their research, Barnwal & Dhawan and Tan et al. applied nitric acid for optimal extraction of the valuable materials from PCB waste [3,4].

In order to efficiently reach the desired leaching degree, leaching agents are chosen that from soluble salts with the metals that should be leached. Thus an important step towards reaching high metal recovery rates is the mass transfer of the leachate with the solid raw material. Depending on whether the raw material has a porous surface, that can allow the leachate to come in contact with the metallic phases, effective leaching can occur. Sonicating employs mechanical waves in frequencies over 20kHz that stimulate the raw material during leaching. This stimulation causes erosion of the unleachable phases away from the metallic surfaces and allows the bleaching agent to penetrate the raw material. Many researchers widely use ultrasound sonicating to assist various leaching chemical reactions [5,6,7].

Utilizing a pyrolyzed sample of waste PCB (PPCB) as a raw material for leaching is beneficial since it is expected that PPCB possesses a larger portion of liberated leachable metals than grounded PCB. Furthermore leaching the solid residue of PPCB is much less toxic than leaching grounded PCB residue [8].

Materials and methods

Printed circuit boards from smartphones were pyrolyzed in a nitrogen atmosphere for 90 min at a heating rate of 300 °C/h at 570 °C. The starting mass of the PCB was 5535g and after pyrolysis and grinding it was 4.088g. This mass of PPCB can be separated into fractions above 500µm (1612g) and below 500µm (2476g). The larger fraction mainly consisted of carbon, glass, and metals, while the smaller fraction can further be magnetically separated into non-metallic (909g) and metallic (1451g) fractions. The fine magnetic fraction (1451g) is labeled pure PPCB powder and its chemical composition is given in Table 1.

Table 1. Chemical composition of pure PPCB powder.

Element	Ag	Au	Al	Be	C	Ca	Ce	Co	Cu	Fe	Li
Concentration (mg/g)	0,180	0,180	48,1	8,30	177	62,4	0,350	0,042	115	11,3	0,023
Element	Nd	Ni	Mn	Pb	Pd	Pt	Si	Sn	Y	Zn	
Concentration (mg/g)	0,218	1,9	0,623	14,3	0,203	0,044	100	26,0	130	9,00	

Leaching conditions

The experiments were carried out in a glass reactor simultaneously set up in a fume cabinet, using a flow meter, type Rota Yokogawa (Yokogawa Deutschland GmbH, Ratingen, Germany) For the leaching agent, nitric acid was chosen with the concentration of 2 mol/L (the nitric acid used was Nitric acid, MERCK, Darmstadt, Germany). The solid-liquid ratio used was 0,1, and the airflow injected into the reactor was between 2 and 2,5 L/min. The stirring speed was between 239 and 245 rpm. The stirrer unit consisted of a motor unit with a drill chuck, type "IKA Eurostar digital" (IKA®-Werke GmbH &Co.KG, Staufen, Germany) IKA®-Werke GmbH & Co. KGIKA®-Werke GmbH & Co. KGIKA and a Polytetrafluorethylen (PTFE) coated impeller including a PTFE stirrer seal. The ultrasonic bath Bandelin Sonorex RK 52H (BANDELIN electronic GMBH&Co, KG, Berlin) was heated to 60°C. The leaching time of the experiments was 8 hours, where every 2 hours samples were taken and the ORP was measured. The device used for ORP measurements is pH-meter 7310 (InoLAb, WTW, Weilheim, Germany. The reactor vessel was three-necked round-bottom flasks with a capacity of 500 mL, the necks with standard ground joints 29/32 served as couplings for a stirrer seal, two gas hose couplers, and as access points for sampling, respectively, as shown in Fig. 1.

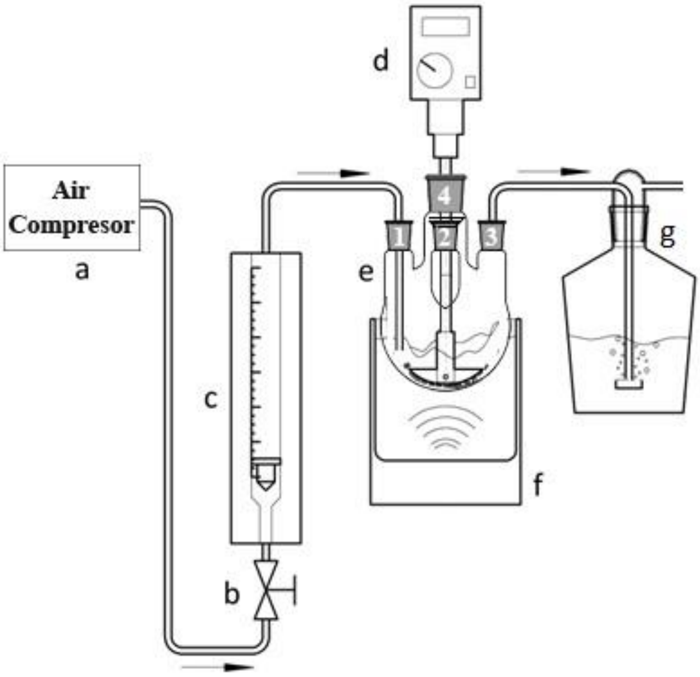

Figure 1. *Experimental reactor setup: a- compressor, b- valve, c- rotameter, d- mechanical stirrer e- reactor, f- ultrasound bath,g- gas washing bottle.*

For the purpose of temperature value measurement, a "Testo720" digital thermometer (Testo SE & Co. KGaA, Lenzkirch, Germany) with a "PT100" thermocouple (Temperatur Messelemente TMH, Hettstedt GmbH, Maintal, Germany) was used.

Throughout the experiments, metal content in the solution was investigated. First, five milliliters of the solution were pumped from the glass reactor using a plastic syringe and PTFE tube and transferred into a small beaker. 1 mL of solution was taken with a pipette and added to a 50 mL round glass flask which was then filled with deionized water up to the 50 mL mark, resulting in a 1 in 50 dilution. This sample solution was transferred again into a 50 mL sample vial and analyzed by the chemistry department at the IME, RWTH Aachen University (Aachen, Germany) by inductively coupled plasma–optical emission spectrometry (ICP-OES) (SPECTRO ARCOS, SPECTRO Analytical Instruments GmbH, Kleve, Germany). The solid sample was analyzed by X-ray fluorescence (Axios FAST, Malvern Panalytical GmbH, Germany).

Results and discussion

The starting mass of PPCB powder for both tests, with and without ultrasound was 15,000g and 15,004g, respectively. However, after leaching the mass of the PPCB powder leached with the aid of ultrasound was 8,187g while the mass of the one without the aid of ultrasound was 11,439g.

Table 2. Chemical composition of PPCB powder after leaching with and without ultrasound

Element		Ag	Al	Au	Ba	Ca	Co	Cu
Concentration (mg/g)	With US*	0.520	45.300	0.187	7.650	50.300	0.011	2.900
	Without US*	1.100	36.400	0.643	6.100	38.100	<0.005	5.100
Element		**Li**	**Nd**	**Pb**	**Pd**	**Pt**	**Sn**	**Zn**
Concentration (mg/g)	With US*	0.016	0.107	16.850	0.165	0.025	39.550	2.800
	Without US*	0.011	0.092	5.200	0.113	<0.005	43.700	4.100

*US-ultrasound

Leaching Degree

The leaching degree is calculated based on the elemental content in the PPCB powder given in Table 2. The calculation is shown in eq (1) and the results are presented in Fig. 2.

$$\text{Leaching degree (\%)} = 1 - \frac{C_x \cdot m_x}{C_0 \cdot m_0} \qquad (1)$$

Where C_0 and C_x are the concentration of elements before (Table 1) and after leaching (Table 2), while m_0 and m_x are the mass of the PPCB powder before and after leaching, respectively. Some of the elements like Ag, Au, and Sn are excluded since they give inconclusive results according to eq (1).

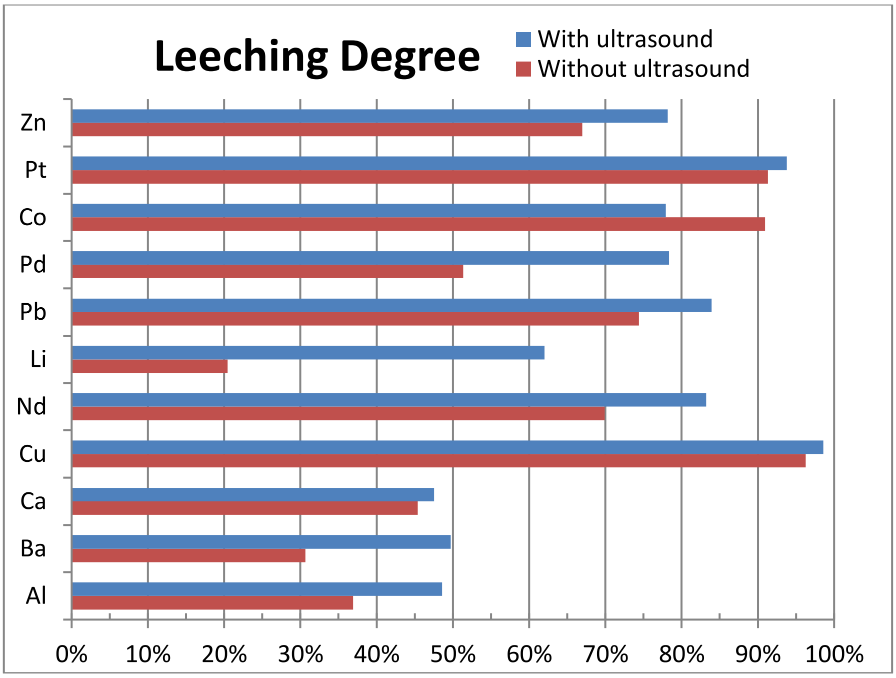

***Figure 2.** Leaching degree with nitric acid for different elements calculated by eq (1).*

As it can be seen in Fig. 2 for the most concentrated metal Cu and the least concentrated precious metal Pt the impact of ultrasound sonification is the smallest. This is due to the decomposition of nitric acid, given by equations (2) and (3) which starts at 40°C and is enhanced by the presence of oxidative metal species whose concentration rises as leaching continues. The presence of oxidative metal species assists the leaching of these two metals regardless of acid concentration or sonicating assistance which is why ultrasound sonification has little effect on their leaching degree.

$$4HNO_{3(aq)} \xrightarrow{T} 4NO_{(g)} + 2H_2O_{(l)} + 3O_{2(g)} \qquad (2)$$

$$4HNO_{3(aq)} \xrightarrow{T} 4NO_{2(g)} + 2H_2O_{(l)} + O_{2(g)} \qquad (3)$$

Leaching mechanism and Oxidation-Reduction Potential (ORP)

As it may be seen in Figure 2 leaching degree of Li in the presence of ultrasound is more than doubled than without. This is due to the form of how lithium is present in raw materials. The presence of lithium in PCB is linked to lithium-ion cells that are mainly produced as $LiCoO_2$, where lithium ions are intercalated between CoO_2^- octahedrons. The mechanical waves that emanate from the ultrasound source push nitrate anions deeper into the intercalation layer and leach lithium in the form of lithium nitrate ($LiNO_3$), the positive charge in imbalance is balanced with oxonium cations (H_3O^+). However, this mechanism is unfavorable to the leaching of cobalt, since the octahedrons consist of an octahedral cage whose edges are O^{2-} ions and in their center lay Co^{3+} ions. This cation of cobalt is a strong oxidative agent and thus hardly reacts with nitrate anions (where nitrogen atoms are in a redox state of +5) when there are no media that may be oxidated. When ultrasound is not present, the acid is not rashly pushed through the intercalation layer, and this enables slow leaching of Co^{3+} as the octahedrons collapse and the liberated ions oxidize the present raw materials.

The barium present in the PCB is in the form of barium sulfate which is used as a fire retardant, expected to be present in solder masks [9]. The leaching of barium sulfate salt is hindered due to its low solubility in water. However, the equilibrium present between barium sulfate and barium nitrate, equation (4) is disrupted with a reaction of the formation of a highly oxidative agent, nitronium cation (NO_2^+). The chemism of the formation of this oxidative agent is given by equation (5). As can be concluded from reaction (5) the portion of sulfuric acid, formed during the ion exchange reaction between barium sulfate and nitric acid, is traped as a hydrogensulfate anion that enables the leaching of barium.

$$BaSO_{4(s)} + 2HNO_{3(aq)} \leftrightarrows Ba(NO_3)_{2(aq)} + H_2SO_{4(aq)} \tag{4}$$

$$H_2SO_4 + HNO_3 \leftrightarrows HSO_4^- + NO_2^+ + H_2O \tag{5}$$

The discussion of aluminum leaching is interesting since the trend line of aluminum concentration grows fast until it reaches approximately 1.8 g/L (Figure 3b). As it is well-established aluminum nitrate acts as a strong oxidative agent, but also Al^{3+} cation is a Lewis acid, therefore it is quite possible that this salt participates as an electron acceptor or as an oxidant. However, the leaching of aluminum is disrupted either with or without ultrasound assistance, since aluminum is present in its elemental form it forms a passive oxide film (Al_2O_3 xH_2O) that hinders the electron transfer and thus stops the leaching process completely. Reactions of aluminum with nitric acid and its consecutive formation of the passive oxide film are given by equations (6) and (7), respectively.

$$2Al_{(s)} + 6HNO_{3(aq)} \leftrightarrows 2Al(NO_3)_{3(aq)} + 3H_{2(g)} \tag{6}$$

$$2Al(NO_3)_{3(aq)} + (x+3)H_2O_{(l)} \longrightarrow Al_2O_3 \cdot xH_2O_{(s)} + 6HNO_{3(aq)} \tag{7}$$

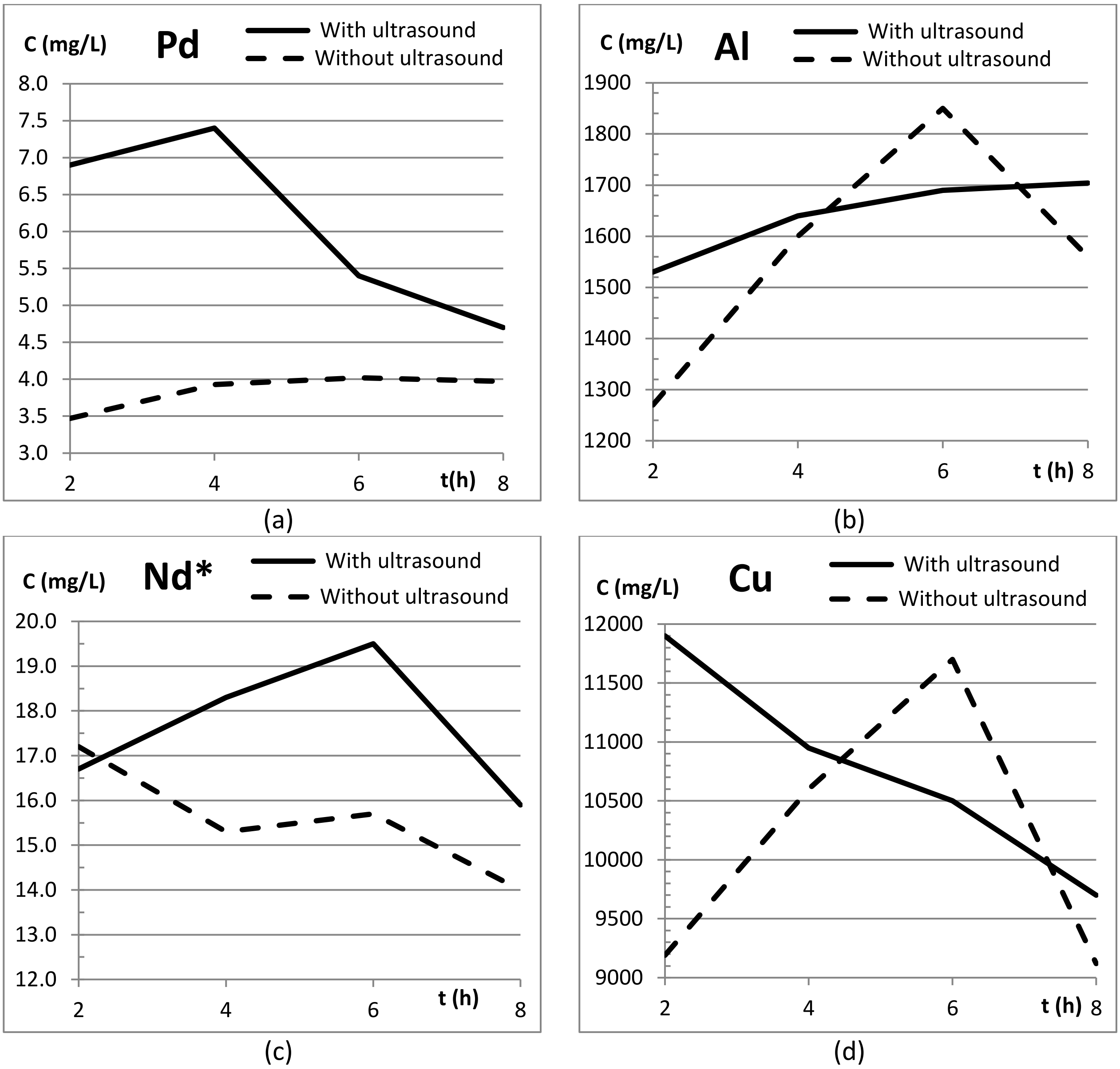

Figure 3. *Change in concentrations of Pb, Nd, Al, and Cu during leaching with nitric acid in the presence and in absence of ultrasound.*

The changes in copper extraction during leaching are unexpected since it is assumed the leaching degree continually grows as time flows, nevertheless it can be easily explained. The concentration trendline of copper extraction with and without ultrasound sonification can be observed in Figure 3d. Since sampling is done every two hours, it can be concluded that for the leaching under ultrasound sonification copper concentration in the solution reached its peak before the second hour. Literature suggests that hydrolysis at 80 °C, initiating the formation of basic copper (II) nitrate [10], However, the leaching temperature in both experiments is 60°C, but it is speculated that the complexity of the PPCB powder system and the influence of the airflow that escorts gasses from the reactor enables hydrolysis at lower temperatures. Furthermore, it is possible that cavities in the material together with the presence of intense mechanical waves elevate local temperature, moving the peak of copper concentration earlier and enabling the precipitation of basic copper (II) nitrate. Equation (8) gives the chemism of copper (II) nitrate formation, while its precipitation reaction is shown with equation (9). For the copper extraction without sonification, the peak is clearly visible and it can be assumed that the copper concentration reaches its maximum between the sixth and eighth hour of leaching.

Moreover, it should be stressed that the precipitation of copper is possible either in a form of basic copper (II) nitrate or some other non-stoichiometric coordination compound

$$3Cu_{(s)} + 8HNO_{3(aq)} \longrightarrow 3Cu(NO_3)_{2(aq)} + 2NO_{(g)} + 4H_2O_{(l)} \quad (8)$$

$$8Cu(NO_3)_{2(aq)} + 6H_2O_{(l)} \longrightarrow 4Cu_2(NO_3)(OH)_{3(s)} + 12NO_{2(g)} + 3O_{2(g)} \quad (9)$$

Calcium fluoride is well known for its insulating or semiconducting electrical properties so its presence explains the origin of calcium in PPCB [11]. Furthermore, calcium fluoride is poorly soluble in water with a solubility product of 4.0 x 10^{-11}, while calcium nitrate is highly soluble in water R($Ca(NO_3)_2$, 20 ^{o}C)=129.3 g [12]. The ion exchange reaction (10) is in equilibrium and since calcium fluoride is less soluble than calcium nitrate backward reaction is dominant.

$$CaF_{2(s)} + 2HNO_{3(aq)} \leftrightarrows Ca(NO_3)_{2(aq)} + 2HF_{(aq)} \quad (10)$$

However, chemical equilibrium from reaction (10) is disrupted with reaction (11) where the hydrofluoric acid reacts with silica, which is found in the form of small glass fibers. This makes reaction (10) forward direction dominant, allowing calcium to be leached as calcium nitrate. In addition, despite the presence of reaction (11) leaching of calcium nitrate is very slow since the reaction (10) gives only a small amount of hydrofluoric acid that may further react with PPCB components.

$$SiO_{2(s)} + 6HF_{(aq)} \longrightarrow H_2SiF_{6(aq)} + 2H_2O_{(l)} \quad (11)$$

Permanent magnets in the form of an alloy $Nd_2Fe_{14}B$ are the main source of neodymium in PPCB [13]. Neodymium transfer from this alloy to an aqueous solution is followed by oxidation of elemental neodymium to Nd^{3+} but also iron to Fe^{3+} chemism of this reaction is given by equation (12).

$$Nd_2Fe_{14}B_{(s)} + 48HNO_{3(aq)} \longrightarrow 2Nd(NO_3)_{3(aq)} + 14Fe(NO_3)_{3(aq)} + 24H_{2(g)} + B_{(s)} \quad (12)$$

The two-component alloy of lead and tin is used as an effective solder material Sn63/Pb37. Although the usage of lead is minimized since its high toxicity as a heavy metal, the solder with this composition is still present in PCB. The chemical reaction between lead and nitric acid occurs together with the evolution of nitrogen oxide gases. When the concentration of nitric acid is not high, most of those gases are nitrogen (II) oxide. The chemical reaction of lead with nitric acid is given by equation (13).

$$3Pb_{(s)} + 8HNO_{3(aq)} \longrightarrow 3Pb(NO_3)_{2(aq)} + 2NO_{(g)} + 4H_2O_{(l)} \quad (13)$$

Palladium, although present in low amounts in PPCB is very valuable, and can readily react with aqua regia, nitric (as shown at Figure 3a) or hydrochloric acid if in powder form. Platinum, however, reacts only with aqua regia and not with nitric or hydrochloric acid by them selfs. Thanks to this property palladium may be extracted as palladium nitrate but in very small amounts since reaction (14) reaches equilibrium really fast thanks to its slightly negative standard Gibbs free energy change [12].

$$3Pd_{(s)} + 8HNO_{3(aq)} \longrightarrow 3Pd(NO_3)_{2(aq)} + 2NO_{(g)} + 4H_2O_{(l)} \quad (14)$$

Oxidation-reduction potential (ORP) trendlines showed similar behavior in the first 6 hours of leaching and it is comparable with the standard potential of 2M nitric acid (753 mV vs. Ag/AgCl (3.5 M KCl)) [12]. During leaching, two types of reactions occur, one type of chemical reaction like reactions (2), (3), (5), (11) – (14) which continuously lower ORP and the other type are reactions that raise ORP potential. Since nitric acid degrades in both cases (with and without ultrasound sonication), during reactions (2) and (3), it can be concluded that the differences in leaching degrees cause such differences in ORP trends (Fig. 4) till the end of hydrometallurgical treatment. Moreover, such complex systems with so many redox pairs and species, together with precipitating reactions that form complex compounds are so numerous that discussing their overall impact wouldn't contribute to any clarity in the discussion section. Such studies could be the subject of some future research work.

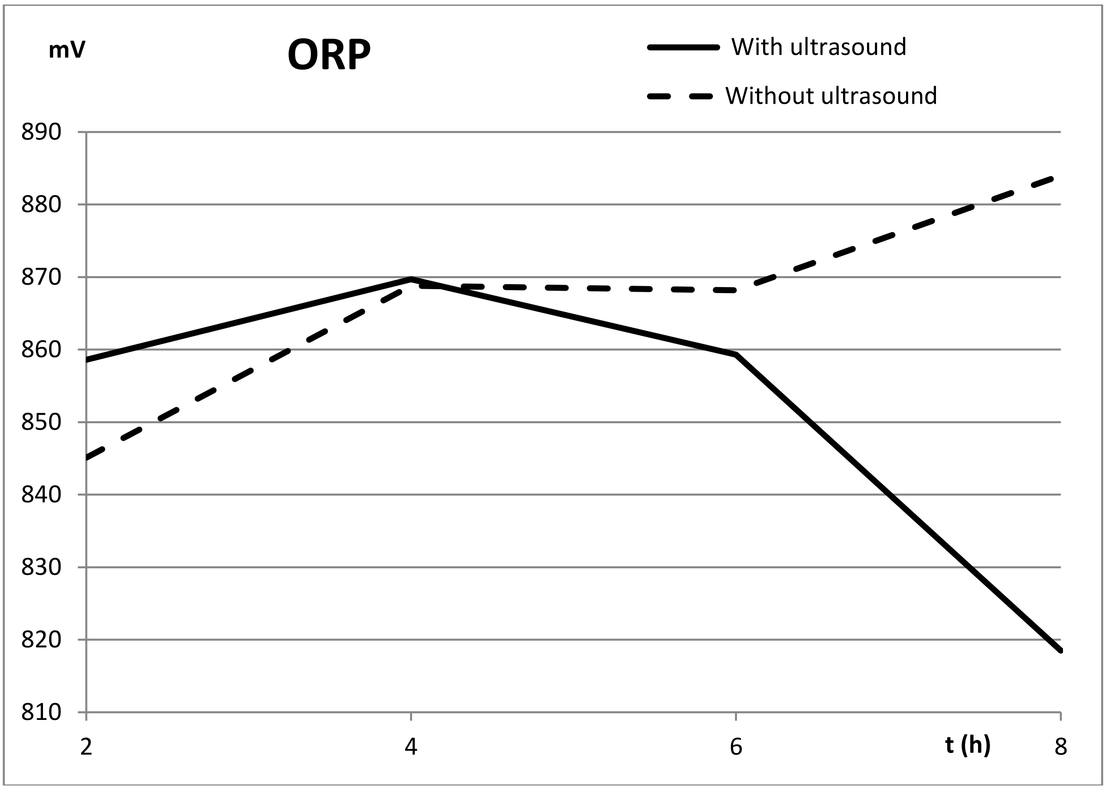

Figure 4. *Change in Oxidation-Reduction Potential (ORP) during leaching with nitric acid in the presence and in absence of ultrasound.*

Conclusion

According to our study the overall impact of ultrasound sonification on the leaching of pyrolyzed printed circuit board powder is as follows:

- Ultrasound sonification has a positive impact on all the species that can be leached with nitric acid
- Ultrasound sonication has the smallest impact on the leaching degree of Cu, and Pd which can be explained by the decomposition of the nitric acid at temperatures above 40°C
- The only metal that ultrasound sonification has a detrimental effect on is Co since its leeching degree is disproportionate to the leaching of Li that the ultrasound enhances.
- Ultrasound sonication has little effect on the leaching of calcium since it is present in the form of calcium fluoride whose leaching is limited by its production of hydrofluoric acid that reacts with fine glass fibers present in PPCB powder.
- Regardless of ultrasound sonification Oxidation-reduction potential changes depending on the degradation of nitric acid and its involvement in the leaching process of various metals

Acknowledgement

This work was supported by the Ministry of Education, Science and Technological Development of the Republic of Serbia (Grant No. 451-03-68/2022-14/200023). The authors would like to thank the Ministry of Education, Science and Technological Development of the Republic of Serbia and DAAD, Germany, for funding of the Project No.: 57513134.

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