

Short communication

Recovery of Ag, Cu, Ni and Fe from the nitrate leach liquor of waste ICs

 Rekha Panda^{a,b}, Manis Kumar Jha^{a,*}, Devendra Deo Pathak^b, Rajesh Gupta^c
^a Metal Extraction and Recycling Division, CSIR-National Metallurgical Laboratory, Jamshedpur 831007, India

^b Department of Applied Chemistry, Indian Institute of Technology (Indian School of Mines), Dhanbad 826004, India

^c M/s Evergreen RecycleKaro (India) Pvt. Ltd., Mumbai 826004, India


ARTICLE INFO

Keywords:

 E-waste
 ICs
 Leach liquor
 Silver
 Precipitation

ABSTRACT

Novel and simple flow-sheet has been reported to process integrated circuits (ICs) for effective recovery of metals. The depopulated ICs from waste PCBs were pulverised, beneficiated and leached in nitric acid. From the nitrate leach liquor, Fe was removed at pH 3.5, temperature 60 °C and air sparging. Subsequently, 99.99% Ag was precipitated as AgCl using 5% NaCl in mixing time 10 min. Further, 99.99% Cu was extracted from the filtrate using 20% LIX 984 N along with 2% isodecanol (ID) diluted in kerosene at pH 2.97, organic to aqueous phase ratio 1 in 10 min, leaving Ni in the raffinate. From the obtained pure solutions, salts of Cu and Ni could be produced using evaporation technique. The developed hydrometallurgical process flow-sheet to recover valuables from the nitrate leach liquor of waste ICs has the potential to be commercialised after pilot/ scale-up trial validations.

1. Introduction

Recent advancement in modern technology is constantly replacing older electronic gadgets with newer, cheaper and more advanced ones. Increase in the consumption of electronic machines and their reduced lifespan has led to the generation of tons of e-waste worldwide. E-waste is a complex mixture of plastics, ceramics, glass and metals (Osibanjo and Nnorom, 2008). Metals of interest (non-ferrous, rare, precious, etc.) present in e-wastes are mainly found in the printed circuit boards (PCBs) (Park and Fray, 2009; Ilyas et al. 2010; Fernando et al. 2019). E-waste is a promising alternative resource and its recycling is gaining more attraction due the presence of precious metals, which is almost 10 times higher in content than their ores (Jeon et al., 2019).

Among all the precious metals, due to unique properties and cheaper price, Ag is widely used in both industrial as well as technological applications such as jewellery, metallurgical, radiography, catalysis, batteries, silverware, electronics, photography, photonics, disinfectants in waste water purification, pharma and food/ beverages processes, etc. (Galarpe and Leopoldo, 2017; Vats and Singh, 2015; Cayumil et al., 2015, Erku et al., 2019; Syed, 2016). Less availability of silver and its improper recycling from various wastes compelled the researchers to develop feasible processes for its recovery.

Several studies were reported to recover Ag from various resources using hydrometallurgical route (Gurung et al., 2013). Leaching of Ag using different lixivants i.e. cyanide, thiourea, thiosulfate, halide,

bacteria, etc. have been reported by many researchers (Andrews et al., 2000; Chmielewski et al., 1997; Quinet et al., 2005; Sheng and Etsell, 2007; Jingwei et al., 2009). Subsequently, to recover Ag from the leach liquor various techniques such as electrodeposition, cementation, chemical reduction have been studied by various researchers (Sadegh Safarzadeh et al., 2007; Alonso et al., 2008; Sulka and Jaskuła, 2006; Syed, 2012).

From the literature survey it has been observed that no viable processes are reported to recover Ag from small components of PCBs surface i.e. ICs, microprocessors, MLCCs, etc. (Ajiboye et al., 2019). Recycling of such small components having complex materials to recover valuables is a challenge for researchers. Lack of feasible processes, unscientific and illegal recycling practices have resulted in the heavy loss of precious metals. Keeping in view of urgent need, present paper reports a novel process flow-sheet to selectively recover Ag, Fe, Cu and Ni as value added marketable product. The systematic studies and scientific validation also support the sustainability of the technological Know-How.

2. Materials and methods

2.1. Raw materials

The integrated chips (ICs) of size ~10 mm which are mounted on the PCBs of scrap computers were depopulated by thermal treatment.

* Corresponding author.

E-mail address: mkjha@nmlindia.org (M.K. Jha).

<https://doi.org/10.1016/j.mineng.2020.106584>

Received 14 January 2020; Received in revised form 2 August 2020; Accepted 5 August 2020

Available online 24 August 2020

0892-6875/ © 2020 Elsevier Ltd. All rights reserved.

Further, the ICs were pulverised to 0.5 mm followed by physical beneficiation to gather the metallic concentrate, which contained about 0.6–0.8% Ag, 12–14% Cu, 1–2% Fe and 1–3% Ni. Leaching of the metallic concentrate was carried out using 4.5 M HNO_3 at 80 °C in 30 min (Panda et al., 2020). The leach liquor generated in nitrate medium was analysed (using AAS and ICP-OES) and found to contain 0.802 g/L Ag, 13.99 g/L Cu, 1.95 g/L Ni and 1.035 g/L Fe. Synthetic solution with similar composition to that of the leach liquor was prepared by dissolving the respective nitrate salts of each metal in distilled water. All chemical reagents (nitric acid, sulfuric acid, hydrochloric acid, potassium chloride, sodium chloride, sodium hydroxide) used were of laboratory grade (Grade: GR) supplied by Merck, India. Chelating reagent LIX 984 N (mixture of LIX 84 and LIX 860 N in the ratio 1:1) procured from M/s Cognis Corporation, Ireland was used as the extractant in solvent extraction. Commercial grade kerosene was used as a diluent and isodecanol as the phase modifier.

2.2. Methodology

Fe precipitation from the leach liquor was carried out using NaOH followed by precipitation of Ag using NaCl. The Eh and pH were measured for each set of experiments. The leach liquor depleted with Fe and Ag was processed to solvent extraction to recover Cu. Equal volume (50 mL) of aqueous and extractant each were mixed for fixed time using magnetic stirrer. The loaded organic phase was subsequently stripped to obtain pure Cu solution using 10% (v/v) H_2SO_4 . The raffinate contained Ni which was recovered as salt by evaporation. Samples were analyzed using atomic absorption spectrometer (AAS) (Perkin Elmer model, Analyst 200; Make-USA) and induced coupled plasma-optical emission spectrophotometer (ICP-OES) (VISTA-PMX, CCD Simultaneous; Make-Australia).

3. Results and discussion

In order to recover the precious metal (Ag) and other metals (Cu, Ni, Fe) from the leach liquor various experimental parameters were studied to optimise precipitation and solvent extraction process, which are discussed below:

3.1. Precipitation of iron (Fe)

Presence of Fe affects the recovery and purity of precious and non-ferrous metals present in the in solution. Therefore, precipitation studies for Fe with scientific validations were carried out and presented in Fig. 1(a & b). Precipitation of Fe is pH dependant, thus dilute NaOH was

used to obtain the desired pH for removal of Fe. The pH of the solution was varied from 0.5 to 4 in a contact time 10 min and temperature 60 °C with air sparging. It was noticed that on increasing pH from 0.5 to 4, precipitation of Fe was found to increase from 3.44 to 99.97% (Fig. 1a). Based on the result pH of 3.5 was considered optimized to precipitate Fe as ferric hydroxide $[\text{Fe}(\text{OH})_3]$ for manufacturing of red oxide. By controlling the Eh and pH of the solution Fe was selectively removed. Standard Eh-pH diagram or Pourbaix diagram was drawn to validate Fe-precipitation and presented in Fig. 1b.

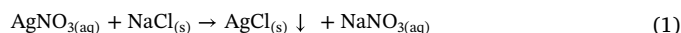
3.2. Ag precipitation

3.2.1. Selection of precipitant

Three different reagents i.e. HCl, KCl and NaCl were initially studied to check precipitation behaviour of Ag. Each precipitant (HCl, KCl and NaCl) of 20% concentration was prepared in distilled water. 1 mL of each precipitant was added to 50 mL of the solution containing Ag with continuous agitation. More than 99% Ag was precipitated with all three precipitant under similar experimental condition. In view of, cost and environmental concerns NaCl was selected as the feasible precipitant. According to the concept of solubility, nitrate complexes are soluble. Furthermore, with the addition of NaCl to the solution containing AgNO_3 , the ionic bond breaks and leads to the release of Ag^+ and NO_3^- due to ion–dipole interaction of H_2O molecules whereas NaCl also ionizes into Na^+ and Cl^- . All ions of Ag^+ , NO_3^- , Na^+ , Cl^- and H_2O molecules are free to move and interact with each other. However, the bonding between Ag^+ and Cl^- is so strong that it cannot be broken up by the ion–dipole force of H_2O molecules. This restrains the interaction of other ions and facilitates the formation of white AgCl precipitate to take place.

3.2.2. Effect of precipitant concentration

Different concentration of NaCl varying from 1 to 5% (w/v) was added to 50 mL of the solution and mixed for 10 min at room temperature. With the increase in concentration of NaCl the precipitation of Ag was found to be increased. About 44.24% Ag was precipitated using 1% NaCl which further increased to 99.99% using 5% NaCl at mixing time 10 min (Fig. 2). Precipitation chemical reaction is as follows:



3.3. Solvent extraction of copper (Cu)

Solvent extraction studies were carried out for the separation of Cu/Ni and optimise the process parameters using LIX 984 N, which are

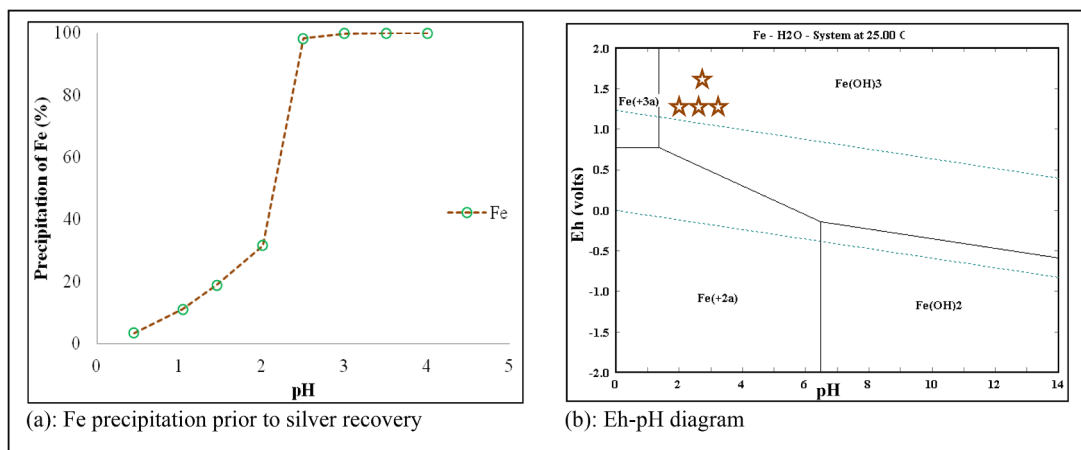


Fig. 1. (a & b): Fe precipitation studies with scientific validations.

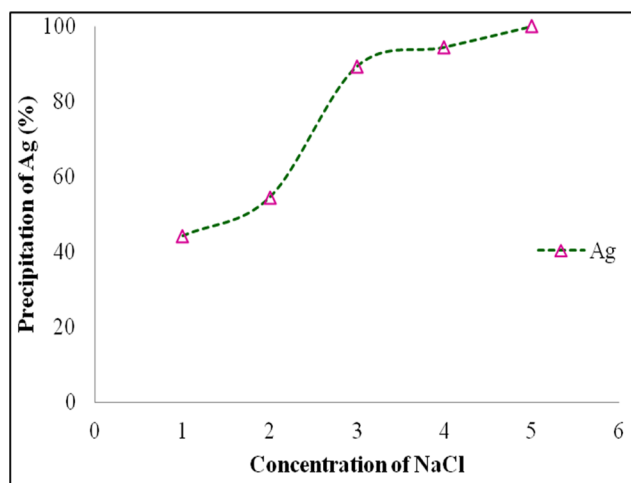
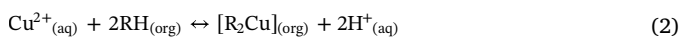


Fig. 2. Effect of precipitant concentration for Ag recovery.

discussed below:

Cu extraction was found to increase from 77.59% to 99.99% with increase in pH from 1.5 to 3.02. About 99.99% Cu was found to be extracted from leach liquor using 20% LIX 984 N in 10 min at an equilibrium pH 2.97, leaving all Ni in the raffinate. The distribution of Cu in organic/ aqueous phases, complex formation and stage requirements were scientifically validated and presented as Fig. 3 (a & b). The plot of log D versus pH for Cu extraction was drawn (Fig. 3a), indicating slope value 2.2 and formation of organo-metallic $[R_2Cu]_{(org)}$ complex. Therefore, the extraction equilibrium of Cu with LIX 984 N (RH) can be expressed as given below:



$$K = \frac{[R_2Cu]_{(org)} [H^+]_{(aq)}^2}{[Cu^{2+}]_{(aq)} [RH]_{(org)}^2} \quad (3)$$

K denotes the equilibrium constant

$$K = \frac{[D][H^+]_{(aq)}^2}{[RH]_{(org)}^2} \quad (4)$$

where

$$D = \frac{[R_2Cu]_{(org)}}{[Cu^{2+}]_{(aq)}} \quad (5)$$

Taking logarithm of Eq. (4) and rearranging

$$\log D = \log K_{ex} + 2\log [RH] + 2pH \quad (6)$$

The slope value is close to the theoretical slope value i.e. 2 indicates the requirement of two moles of extractant for the formation of $[R_2Cu]_{(org)}$ complex (Choubey et al., 2015).

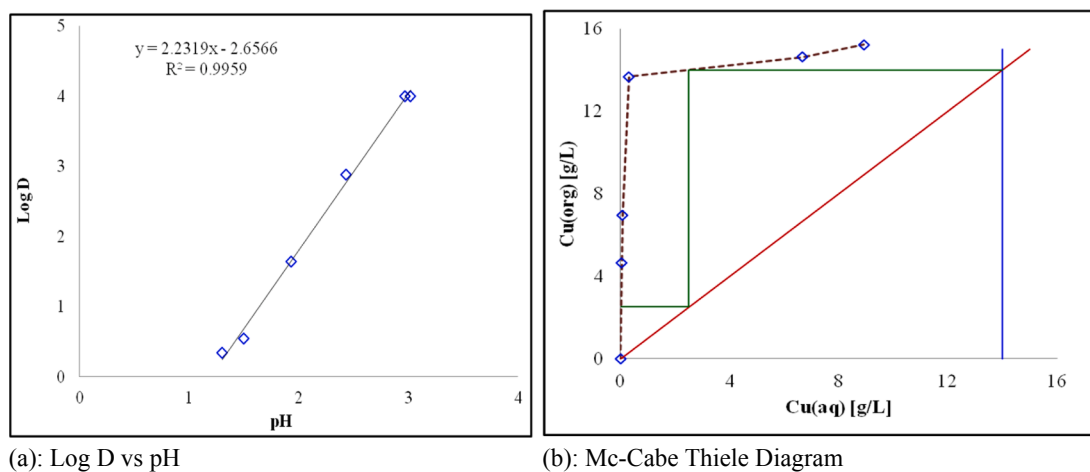
Extraction of Cu increased from 38.28% to 99.65% with the increase in organic/ aqueous (O/A) ratio from 1/3 to 3/1 at equilibrium pH 2.97 in mixing time 10 min. Mc-Cabe Thiele plot was drawn to determine the number of stages required for maximum recovery of Cu from leach liquor using 20% LIX 984 N (Fig. 3b). Two stages of counter current solvent extraction were adequate for complete extraction of Cu at O/A ratio 1/1. In optimised condition, the loading capacity of extractant was checked by repetitive contact of fresh solution and found that 19.43 g of Cu for per litre of extractant.

4. Validation and conclusion

The optimized condition obtained for the recovery of Ag, Fe, Cu and Ni from model leach solution was validated with the actual leach liquor of pulverized ICs. About 99.81% Fe was precipitated as $Fe(OH)_3$ at pH of 3.5 in 10 min. Almost 99% Ag was precipitated as $AgCl$ with high purity from the solution left after Fe removal. And finally from the liquor ~99.9% Cu was extracted at eq. pH 2.97 using 20% LIX 984 N at O/A ratio of 1/1 in mixing time 10 min, leaving Ni in the raffinate. Complete process flow-sheet is presented in Fig. 4. The developed hydrometallurgical flow-sheet for the recycling of small components of e-waste to recover valuable and precious metals is very timely in the current global scenario. The huge quantities of e-waste being generated every year and lack of proper processes to recover precious metals from small components of e-waste, simply results in the loss of metals during the recycling of waste PCBs/ e-waste. The process reported to recover precious metal (Ag) from ICs is simple, economical and feasible. This will be helpful in not only proper management of e-waste but also lead to the production of high value products.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.



(a): Log D vs pH

(b): Mc-Cabe Thiele Diagram

Fig. 3. (a & b): Scientific validation for solvent extraction of Cu.

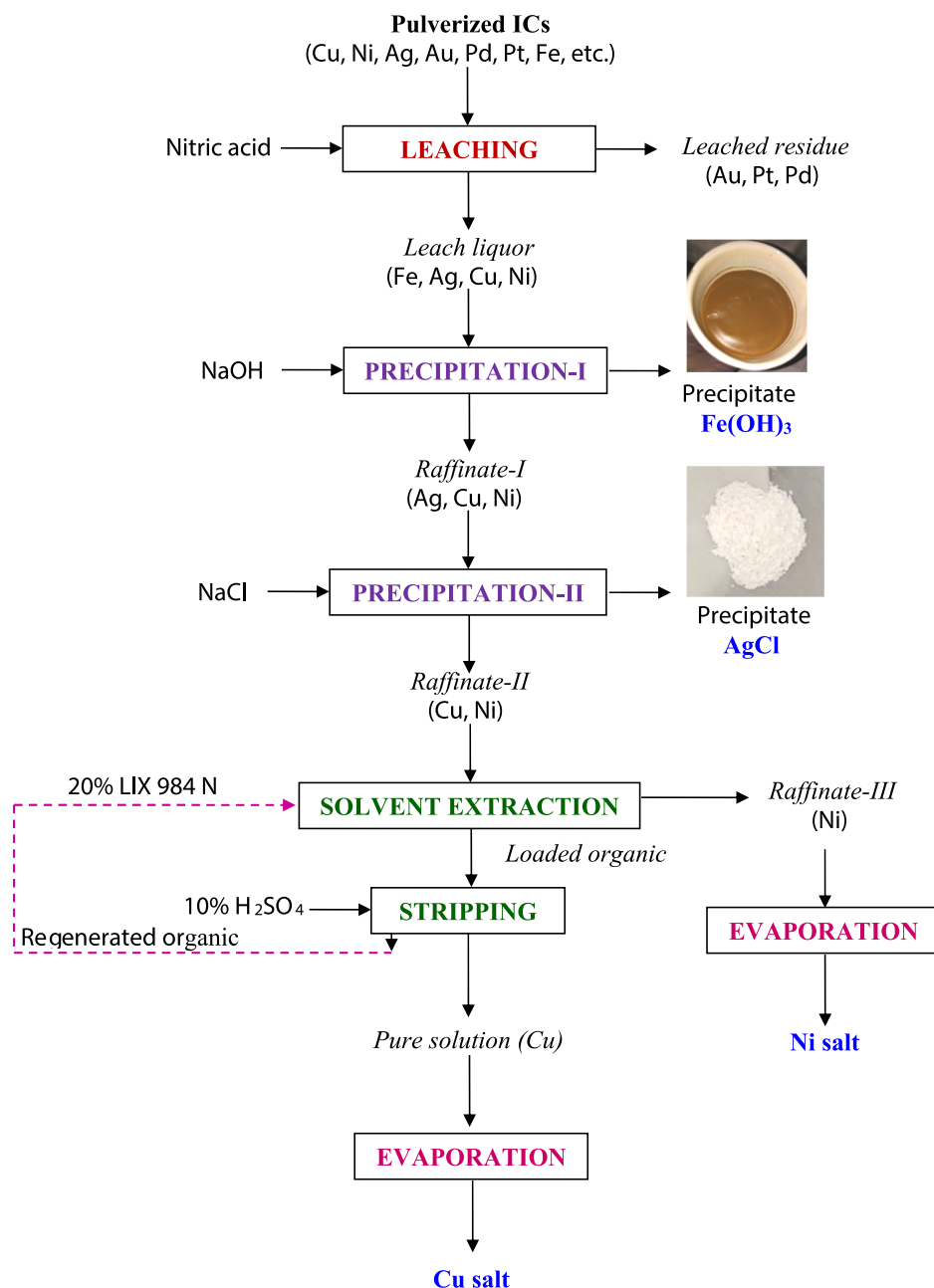


Fig. 4. Complete process flow-sheet for the recovery of Fe, Ag, Cu and Ni from the leach liquor of pulverized ICs of e-waste.

Acknowledgement

Authors are thankful to Director, CSIR-NML and Council of Scientific and Industrial Research, New Delhi for permission to publish this research and financial grant Senior Research Fellowship (Grant: 31/10(64)/2017-EMR-I) respectively.

Appendix A. Supplementary material

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.mineng.2020.106584>.

References

Ajiboye, E.A., Panda, P.K., Adebayo, A.O., Ajayia, O.O., Tripathy, B.C., Ghosh, M.K., Basu, S., 2019. Leaching kinetics of Cu, Ni and Zn from waste silica rich integrated circuits

- using mild nitric acid. *Hydrometallurgy* 188, 161–168.
- Alonso, A.R., Lapidus, G.T., Gonzalez, I., 2008. Selective silver electro separation from ammoniacal thiosulphate leaching solutions using a rotating cylinder electrode reactor (RCE). *Hydrometallurgy* 92, 115–123.
- Andrews, D., Raychaudhuri, A., Frias, C., 2000. Environmentally sound technologies for recycling secondary lead. *J. Power Sources* 88, 124–129.
- Cayumil, R., Khanna, R., Rajarao, R., Mukherjee, P.S., Sahajwalla, V., 2015. Concentration of precious metals during their recovery from electronic waste. *Waste Manage.* 57, 121–130.
- Chmielewski, A.G., Urbanski, T.S., Migdal, W., 1997. Separation technologies for metals recovery from industrial wastes. *Hydrometallurgy* 45 (3), 333–344.
- Choubey, P.K., Panda, R., Jha, M.K., Lee, J.C., Pathak, D.D., 2015. Recovery of copper and recycling of acid from the leach liquor of discarded Printed Circuit Boards (PCBs). *Sep. Purif. Technol.* 156 (2), 269–275.
- Erku, M.D., Yimam, A., Jabasingh, A., 2019. Process optimization for the recovery of silver from waste X-ray photographic films. *Indian J. Chem. Technol.* 26, 404–410.
- Fernando, W.A.M., Ilankoon, I.M.S.K., Krishnan, S.G., Chokshi, V., 2019. The effects of packing shape and structure on liquid distribution of heap T leaching systems: Addition of PCBs as non-ore particles. *Hydrometallurgy* 187, 149–157.
- Galarpe, V.R.K.R., Leopoldo, G.D., 2017. Potential recovery of silver (Ag) from x-ray fixer

- waste by alkaline treatment. *Eng., Technol. Appl. Sci. Res.* 7 (5), 2094–2097.
- Gurung, M., Adhikari, B.B., Kawakita, H., Ohto, K., Inoue, K., Alam, S., 2013. Recovery of gold and silver from spent mobile phones by means of acidothiurea leaching followed by adsorption using biosorbent prepared from persimmon tannin. *Hydrometallurgy* 133, 84–93.
- Ilyas, S., Ruan, C., Bhatti, H.N., Ghauri, M.A., Anwar, M.A., 2010. Column bioleaching of metals from electronic scrap. *Hydrometallurgy* 101, 135–140.
- Jeon, S., Ito, M., Tabelin, C.B., Pongsumrankul, R., Tanaka, S., Kitajima, N., Saito, A., Park, I., Hiroyoshi, N., 2019. A physical separation scheme to improve ammonium thiosulfate leaching of gold by separation of base metals in crushed mobile phones. *Miner. Eng.* 138, 168–177.
- Jingwei, W., Jianfeng, B., Jinqiu, X., Bo, L., 2009. Bioleaching of metals from printed wire boards by *Acidithiobacillus ferrooxidans* and *Acidithiobacillus thiooxidans* and their mixture. *J. Hazard. Mater.* 172, 1100–1105.
- Osibanjo, O., Nnorom, I.C., 2008. Material flows of mobile phones and accessories in Nigeria: environmental implications and sound end-of-Life management options. *Environ. Impact Assess. Rev.* 28, 198–213.
- Panda, R., Jha, M.K., Dinkar, O.S., Pathak, D.D., 2020. Reclamation of precious metals from small electronic components of computer hard disks. In: *Rare Metal Technology* 2020, The Minerals. Metals & Materials Society, pp. 243–250.
- Park, Y.J., Fray, D.J., 2009. Recovery of high purity precious metals from printed circuit boards. *J. Hazard. Mater.* 164, 1152–1158.
- Quinet, P., Proost, J., Van, A.L., 2005. Recovery of precious metals from electronic scrap by hydrometallurgical processing routes. *Miner. Metall. Process.* 22 (1), 17–22.
- Sadegh Safarzadeh, M., Bafghi, M.S., Moradkhani, D., 2007. A review on hydro-metallurgical extraction and recovery of cadmium from various resources. *Miner. Eng.* 20 (3), 211–220.
- Sheng, P.P., Etsell, T.H., 2007. Recovery of gold from computer circuit board scrap using aqua regia. *Waste Manage. Res.* 25 (4), 380–383.
- Sulka, G.D., Jaskuła, M., 2006. Effect of sulfuric acid and copper sulfate concentrations on the morphology of silver deposit in the cementation process. *Electrochim. Acta* 51, 6111–6119.
- Syed, S., 2012. Recovery of gold from secondary sources—a review. *Hydrometallurgy* 115–116, 30–51.
- Syed, S., 2016. Silver recovery aqueous techniques from diverse sources: Hydrometallurgy in recycling. *Waste Manage.* 50, 234–256.
- Vats, M.C., Singh, S.K., 2015. Assessment of gold and silver in assorted mobile phone printed circuit boards (PCBs): original article. *Waste Manage.* 45, 280–288.