Association of Metallurgical Engineers of Serbia
AMES

Scientific paper
UDC: 628.477.6

HYDROMETALLURGICAL PROCESS FOR EXTRACTION OF METALS FROM ELECTRONIC WASTE-PART II: DEVELOPMENT OF THE PROCESSES FOR THE RECOVERY OF COPPER FROM PRINTED CIRCUIT BOARDS (PCB)

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Received 13.06.2011
Accepted 15.08.2011

Abstract

Rapid technological development induces increase of generation of used electric and electronic equipment waste, causing a serious threat to the environment. Waste printed circuit boards (WPCBs), as the main component of the waste, are significant source of base and precious metals, especially copper and gold. In recent years, most of the activities on the recovery of base and precious metals from waste PCBs are focused on hydrometallurgical techniques as more exact, predictable and easily controlled compared to conventional pyrometallurgical processes. In this research essential aspects of the hydrometallurgical processing of waste of electronic and electrical equipment (WEEE) using sulfuric acid and thiourea leaching are presented. Based on the developed flow-sheet, both economic feasibility and return on investment for obtained processing conditions were analyzed. Furthermore, according to this analysis, SuperPro Designer software was used to develop a preliminary techno-economical assessment of presented hydrometallurgical process, suggested for application in small mobile plant addressed to small and medium sized enterprises (SMEs). Following of this paper, the described process is techno-economically feasible for amount of gold exceeding the limit value of 500ppm. Payback time is expected in time period from up to 7 years, depending on two deferent amounts of input waste material, 50kg and 100kg of WEEE per batch.

Key words: waste printed circuit boards, recycling, hydrometallurgy, copper leaching, gold leaching, techno-economical assessment

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Introduction

As a result of rapid technical and technological development, waste electric and electronic equipment (WEEE) is becoming one of the major environmental risks for its high quantity and toxicity in recent years. In terms of materials and components WEEE is non-homogeneous and very complex, and the major challenge for recycling operations is how to respond to poor recovery of metals by mechanical treatment as well to avoid gas handling problems or hazard gas compounds release using pirometallurgical process. Printed circuit boards (PCBs), as a key component of WEEE, can be considered as a significant secondary raw material due to its complex composition, mainly consisted of plastic, glass, ceramics and metals (copper, aluminum, iron, zinc, nickel, lead and precious metals). In the past two decades much attention has been devoted to development of techniques for recycling WEEE, especially copper and precious metals [1, 2, 3]. The state of the art in recovery of precious metals from electronic waste highlights two major recycling techniques, such as pyrometallurgical and hydrometallurgical, both combined with mechanical pre-treatment. Pyrometallurgical processing including incineration, smelting in a plasma arc furnace or blast furnace, sintering, melting and reactions in a gas phase at high temperatures has been a conventional technology for recovery of metals from WEEE [4, 5, 6]. However, state-of-the-art smelters are highly depended on investments. In the last decade, attention has been moved from pyrometallurgical to hydrometallurgical process for recovery of metals from electronic waste [7, 8].

This paper describes essential aspects of the hydrometallurgical processing of WEEE using sulfuric acid and thiourea leaching. Previous studies, reported by authors [9, 10] were conducted in order to investigate optimal processing conditions concerning hydrometallurgical recovery of base and precious metals from WPCBs. In this paper some results obtained in these studies are also presented. Based on these results, regarding characterization and development of the hydrometallurgical treatment of waste material, both economic feasibility and return on investment for obtained processing conditions were analyzed. Furthermore, this analysis was used in order to develop a preliminary techno-economical assessment of presented hydrometallurgical process adopted for use in small mobile plant taking into account limitation of necessary quantities of waste material as well as investment, addressed to small and medium sized enterprises (SMEs).

Materials

Material used in presented research is comminuted and mechanically pre-treated waste PCBs, as described in previous studies by authors [1, 9, 10]. Chemical composition of two samples was analyzed using atomic absorption spectroscopy, X-ray fluorescence spectroscopy and, inductively coupled plasma atomic emission spectroscopy. Obtained results together with literature data are presented in Table 1. In this paper, fractions (F), 0.071mm< F <1 mm were used for further analysis.

Apparatus and methodology

Previous to leaching tests materials dynamics within leaching reactor was tested as a function of particle size and stirring rate (rpm). Impact of stirring rate on fractions -

2mm and -1mm was examined in the range of 100 to 700 rpm. Solution used for testing was 30 wt. % NaCl, whose density matches the density of H_2SO_4 solution used for leaching.

Table 1. Chemical composition of sample of WPCBs [9]

Materials	Sample 1* %(w/w)	Sample 2** %(w/w)	Literature data [3] %(w/w)
Cu	27.99	25.24	20
Al	0.47	0.69	2
Pb	2.17	2.22	2
Zn	2.01	2.05	1
Ni	1.23	0.93	2
Fe	1.18	0.98	8
Sn	3.26	3.17	4
Au/ppm	440	890	1000
Pt/ppm	57	17	-
Ag/ppm	1490	1907	2000
Pd/ppm	50	47	50
Ceramics	20.41	22.14	max 30%
Plastics	32.07	32.41	max 30%

* WPCBs collected by S.E.Trade d.o.o. Belgrade, fraction –6mm

** WPCBs collected by Institute Mihajlo Pupin, fraction –1+0.071mm

In a first step fraction -2mm was examined. It was shown that the increase of the stirring rate did not produce any effect on the waste material which remained at the bottom of the laboratory glass.

In the next step fraction -1mm was examined when the intensification of material mixing was noticed at 200 rpm. At 300 rpm, all the granulate particles from the container are raised and caught mixing while floating particles slowly transit into the solution. Finally, at 600 rpm all particles of the waste materials are fully affected by mixing.

In the industrial leaching conditions, stirring rate of 600 rpm is relatively high and could cause great trouble for carrying out of the process of leaching. It is assumed that with proper solid:liquid ratio, results obtained at 300 rpm will be satisfactory, and thus this parameter was fixed in the further analysis.

According to experimental set up, reported in a previous study [1, 9,10], leaching tests were performed in a glass vessel with 15.6 cm in diameter, with a condenser, steel impeller, oxygen dispersion tube and hydrogen peroxide dozer. Experimental set up is shown in Figure 1.

Electrowinning (EW) was performed in a rectangular electrolytic cell with dimensions 100×88×300mm with effective volume 2000 mL made of high density polypropylene. The cathode material was copper (Cu 99,99%) and anode was lead antimony alloy (PbSb7).

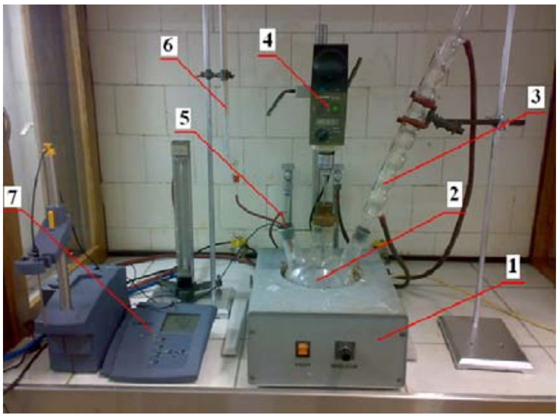

Fig.1. Experimental apparatus for leaching: 1.Electro-resistant heater; 2.Reaction glass vessel; 3.Cooler with condenser; 4.Mixer; 5.Oxygen tube; 6.Peroxide dozer; 7.Digital pH and temperature measurement device

Results and discussion

Optimum processing conditions were obtained by variation of different leaching parameters. Hydrometallurgical extraction of copper from the waste material was performed using sulfuric acid as leaching agent. Solid residue after copper leaching step, was leached by thiourea in the presence of ferric ion ($Fe_2(SO_4)_3$) as an oxidant in sulfuric acid solution, in order to extract gold. In the case of copper leaching, analysis was performed for both, laboratory and pilot scale, while gold leaching was tested only for laboratory scale. According to summarized results, optimum copper and gold leaching parameters are presented in Table 2.

Table 2. Optimal gold and copper leaching conditions

Parameter	Copper leaching		Gold leaching
	Laboratory scale	*Pilot scale*	
Acid conc.			
H_2SO_4 conc.	1.5-2M	1.5-2M	10 g dm^{-3}
thiourea conc.	/	/	20 g dm^{-3}
Oxidants conc.			
H_2O_2	40mL/h	50 kg/t	/
O_2	16L/h	80 L/kg/h	/
Fe^{3+}	/	/	6 g dm^{-3}
Solid-liquid ratio	50-100g/L	150-200g/L	20 % of solid
Temperature	75-80°C	70°C	40°C
Stirring rate	>300rpm	~300rpm	600 rpm
Time	>5h	<10h	≥ 200 min

EW was performed in order to extract metallic copper from leaching solution. Optimal EW conditions are shown in Table 3, while obtained copper deposit is illustrated in Figure 2.

Table 3. Optimal EW conditions

Voltage	2.1V
Current density	120-200A/m^2
Temperature	40ºC
Time	15h
Steering rate	100rpm

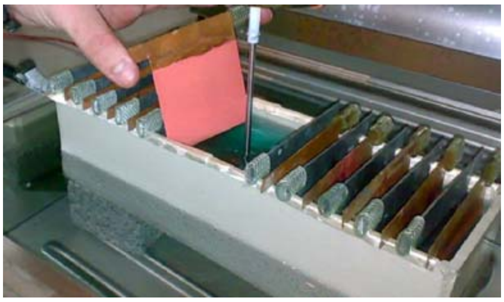

Fig.2. Copper deposited on the cathode

According to presented optimal processing parameters, block diagram for hydrometallurgical recovery of base and precious metals, using selective leaching agents from WPCBs was developed. Block diagram for hydrometallurgical processing of WPCBs using sulfuric acid and thiourea leaching is shown on Figure 3.

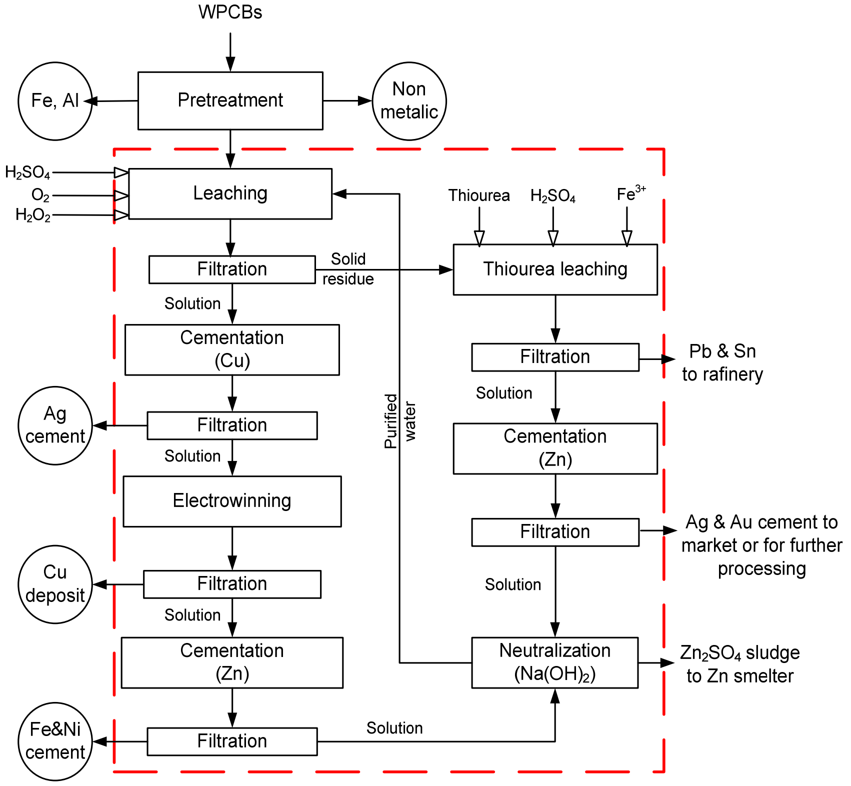

Fig.3. Block diagram for hydrometallurgical recovery of base and precious metals [9]

Although hydrometallurgy is relatively widely used in base and precious metals processing plants, the objective of this work was to discuss the possibility of providing a purely hydrometallurgical alternative to the pyrometalurgical process as more exact, easily controlled, less expensive, and less subjected to losses for recovery of base and precious metals from WEEE. On the other hand, by adopting an entirely hydrometallurgical route for use in small mobile plant, economic benefits for SMEs may be possible, regarding low capital investment and necessary quantities of waste material.

Process option investigated in this paper was based on preliminary results carried out on the pilot scale in the scope of the European project "Innovative Hydrometallurgical Processes to recover Metals from WEEE including lamp and batteries – HydroWEEE" (FP 7 – research activities addressed to SMEs). Core objective of this project was development of suitable multi functional hydrometallurgical process for recovery of base and precious metals from fluorescent powders coming from CRT and spent lamps, printed circuit boards, LCD and lithium spent batteries. The experience and knowledge obtained in the preliminary pilot plant tests gave important technological indications for the development of the small mobile plant HydroWEEE. Furthermore results obtained during the activities of project, particularly related to WPCBs in this paper, have been used for the development of techno-economical assessment for the new mobile hydrometallurgical plant. Schematic outline of HydroWEEE mobile plant is presented in Figure 4.

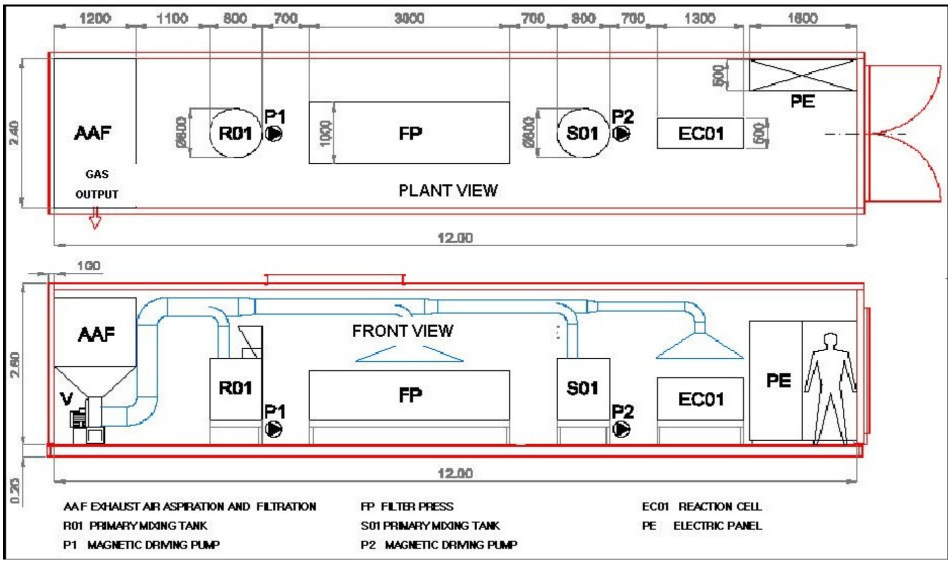

Fig.4. Outline of the mobile pilot plant placed in a transportable container [11]

The techno-economical assessment for hydrometallurgical processing route presented in Figure 3, was applied on the small mobile plant schematically shown in Figure 4. For this purpose the SuperPro Designer software was used. Conceptual outline of hydrometallurgical treatment of WPCBs is shown in Figure 5.

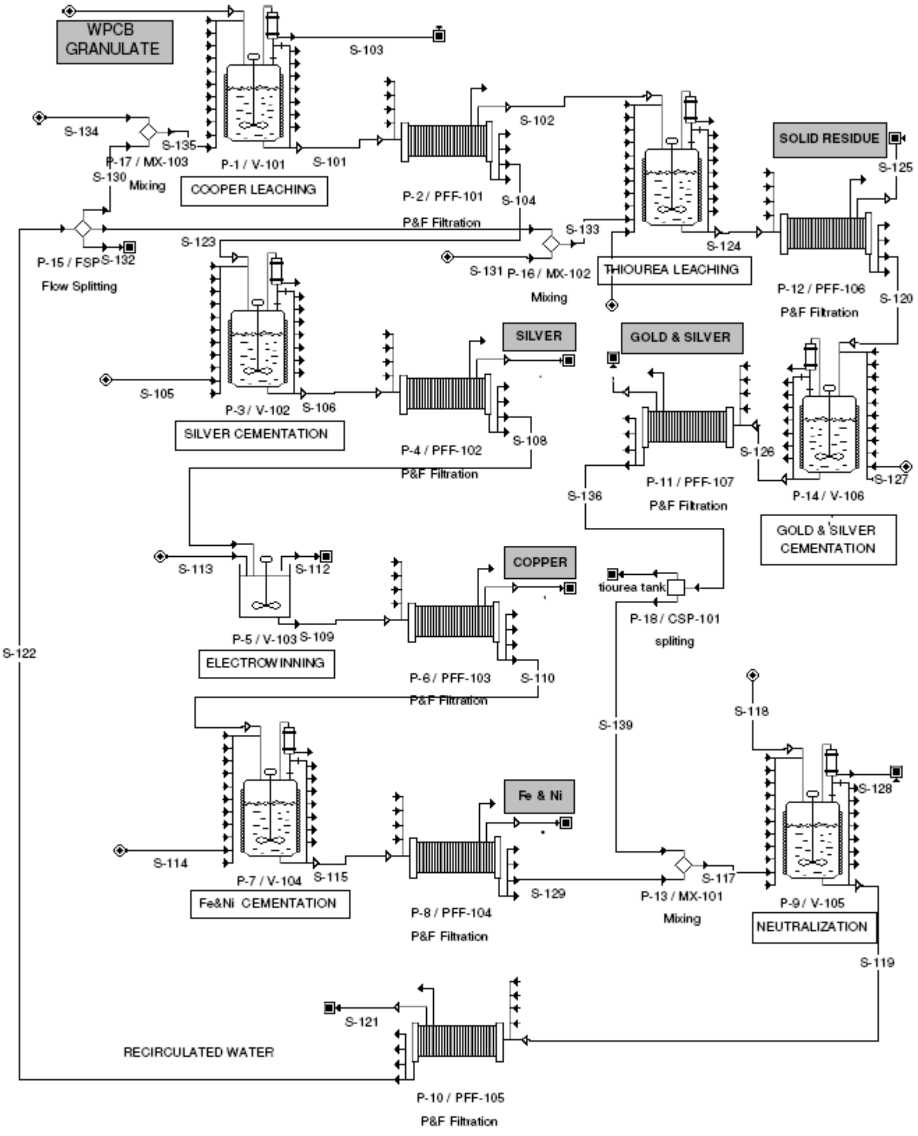

Fig.5. Outline of hydrometallurgical treatment of WPCBs

With the intention to open up the possibility for an economic evaluation of presented hydrometallurgical processing route, the techno-economical assessment is achieved through the development of gold amount variation models, present in waste material, as a crucial economical component of WPCBs. The models, developed by SuperPro Designer software, calculate system efficiencies, total capital costs and production (operating) costs. This methodology was applied to the development of all models and obtained results are directly comparable regarding time needed for return of investment.

Assessment was performed by modeling two different amounts of input waste material, 50kg and 100kg of WEEE per batch, following the presented solid:liquid ratio, whereas for gold this ratio was in the range from 200ppm to 1000ppm. These data were combined to give cost and performance analysis for the integrated system.

Prior to hydrometallurgical treatment, the mechanical pre-treatment of WPCBs was performed. This procedure, in addition to other mechanical operations, includes granulation of input waste material according to previously described results [1]. Therefore, presented models exclude mechanical pre-treatment cost.

Fixed parameters, i.e. total capital cost and operating cost, were calculated according to prices in Serbia, October 2010, involving all economic factors in final executive summary, regarding total plant direct cost, total plant indirect cost, labor, utilities and raw material costs.

Table 4 shows results obtained by performing simulation focused on calculation of payback time related to different amounts of gold. This calculation was used to assess the operational time, needed to achieve economical sustainability of such hydrometallurgical plant. Calculations were focused on the determination of total revenues of presented hydrometallurgical process regarding gold recovery. Total income for each model was calculated according to LME prices, October 2010 [12] for revenues, and it was crucial to determine economic sustainability of the whole process. Finally, based on these results, Diagrams 1 and 2 show the dependence between the operational time needed for return on investment and gold amount present in the waste material, concerning increase of payback time with decreasing gold amount.

Table 4. a) Calculated dependence of gold amount vs. payback time, 50 kg of waste input material per batch

EXECUTIVE SUMMARY – 50 kg			
Total Capital Investment			148,000$
Capital Investment Charged to this Project			148,000$
Operating Cost			97,000$/yr
Gold amount, ppm	*Total revenues, $/yr*	*Return on investment, %*	*Payback time, years*
200	62,000	-15.97	not feasible
300	83,000	-1.96	not feasible
440	92,000	3.14	31.84
500	100,000	8.39	11.92
600	115,000	14.65	6.83
700	132,000	21.29	4.70
800	148,000	27.99	3.57
890	159,000	32.36	3.09
1000	161,000	32.95	3.02

Table 4. b) Calculated dependence of gold amount vs. payback time, 100 kg of waste input material per batch

EXECUTIVE SUMMARY – 100 kg			
Total Capital Investment			149,000$
Capital Investment Charged to this Project			149,000$
Operating Cost			144,000$/yr
Gold amount, ppm	*Total revenues, $/yr*	*Return on investment, %*	*Payback time, years*
200	99,000	-21.68	not feasible
300	129,000	-2.71	not feasible
440	169,000	17.32	5.77
500	188,000	24.88	4.02
600	219,000	37.44	2.67
700	252,000	50.75	1.97
800	281,000	62.30	1.61
890	299,000	69.65	1.44
1000	339,000	85.55	1.17

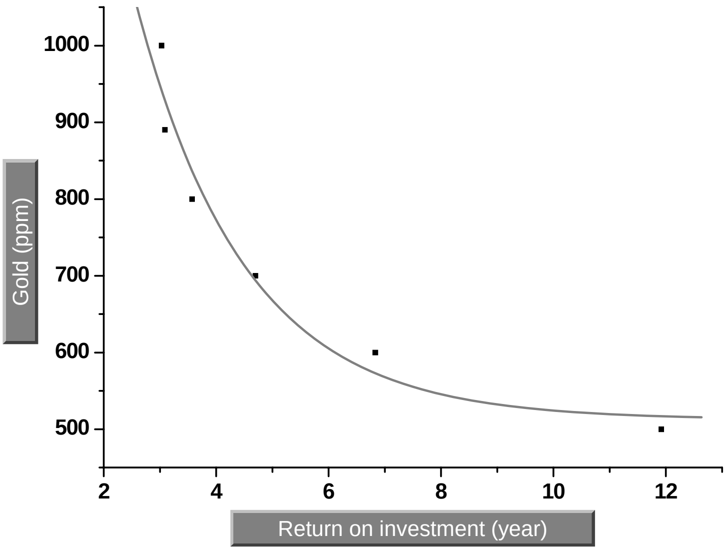

Diagram 1. Dependence of gold amount vs. payback time, 50 kg of waste input material per batch

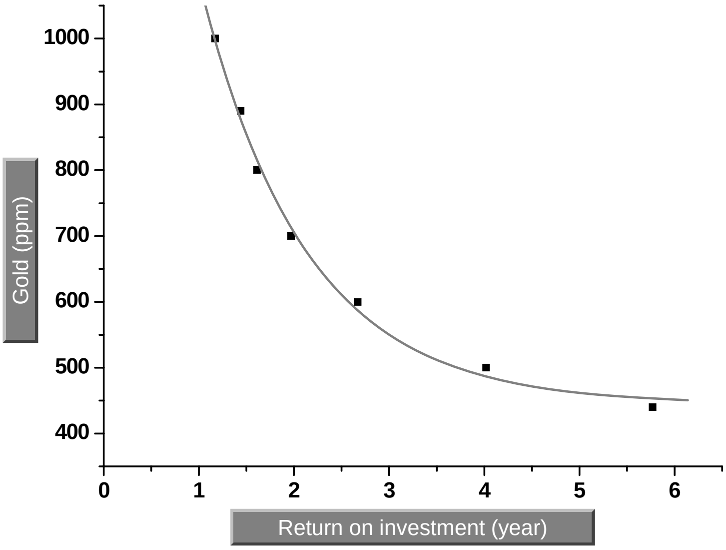

Diagram 2. Dependence of gold amount vs. payback time, 100 kg of waste input material per batch

Conclusion

In the presented work the techno-economical feasibility of the hydrometallurgical treatment of WPCBs has been demonstrated, concerning great environmental and economical potentials that the development of an efficient hydrometallurgical route for recovery of base and precious metals may offer. According to these facts the development of such a technology responding to contemporary strict environmental requirements would be much easier. In addition, presented hydrometallurgical technology will allow the production of material with purity suitable for commercial use.

According to models evaluated in this paper it is clear that the most important economic criteria is related to gold amount present in the waste material. Following these results, process is techno-economically feasible for amount of gold exceeding the limit value of 500ppm. Gold and silver obtained as cement powder could be sold to refinery or internally refined up to commercial purity Au and Ag metal powders in small a rafination equipment.

Relatively insufficient widespread presence of hydrometallurgy in a field of WEEE recycling still signifies domination of the pyrometallurgy. On the contrary to SMEs requirements, it is quite clear that presented technology imply a future alternative to pyrometalurgical process that can be readily applied in small plants, unlike large multisector companies not so dependent on investment as well for market share.

Acknowledgments

This work has been carried out with financial support of the EU within the project “Innovative Hydrometallurgical Processes to recover Metals from WEEE including lamp and batteries – HydroWEEE”, FP 7 – Funding Scheme: research activities addressed to SMEs and Ministry of Science and Technical Development, Republic of Serbia, project “Innovative synergy of by-products, waste minimization and clean technology in metallurgy”, No. 34033.

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