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Simulation and economic analysis of a hydrometallurgical approach developed for the treatment of waste printed circuit boards (WPCB)

Birloaga I.* and Veglió F.
Department of Industrial and Information Engineering and Economics, University of L'Aquila, Via Giovanni Gronchi 18, 67100 L'Aquila, Italy
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*to whom all correspondence should be addressed: e-mail: ionelapoenita.birloaga@graduate.univaq.it
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Abstract

This paper presents the main achievements of a hydrometallurgical process to recover base and precious metals from waste printed circuit boards (WPCB). The technology comprises a first leaching process performed in a two-step counter current way with sulfuric acid and hydrogen peroxide for base metals solubilization and a consecutive cross leaching process with thiourea, ferric sulfate and sulfuric acid to extract precious metals. Furthermore, the reach solutions are subjected to cementation procedure with zinc powder to recover the elements of interests as metal powders. The spent solution achieved after cementation of precious metals is partially recycled within the process and the other part is treated by Fenton process and then neutralized with lime. Considering the achieved results at the laboratory level, the entire procedure was simulated using SuperPro Designer software to determine the process economy for an industrial plant. Besides this, the use of this software allows achieving the material balance of a process and the design of the plant. As a result, the process implementation at a larger scale is simulated and the main issues that can result in such a case can be determined and solved.

Keywords: Waste printed circuit board, hydrometallurgical process, process analysis, Super Pro designer.

1. Introduction

The waste electrical and electronic equipment (WEEE) represent about 5% from the total of solid waste generated each year (STEP, 2010). According to Balde *et al.* (Balde *et al.*, 2014), in 2014 about 6.5 Mt of WEEEs have been formally treaded by national take-back systems at worldwide level, which means about 15.5% of the total quantity of these kind of waste generated (41.8 Mt) within the same year. This waste is considered as being both hazardous material due to its content of dangerous substances but also a valuable secondary resource of base, precious and rare element and not limited. According to literature data, over 57 elements are present in the WEEEs structure (Behrendt *et al.*, 2007) (Figure 1). These waste have been mostly incinerated (the most used technologies till a few years ago) (Khetriwal *et al.*, 2009).or sent to landfill. Therefore, in order to avoid the environmental contamination by performing such operations, there have been implemented various regulations that had as main core firstly to collect and minimize and, thereafter, product reuse and materials recovery.

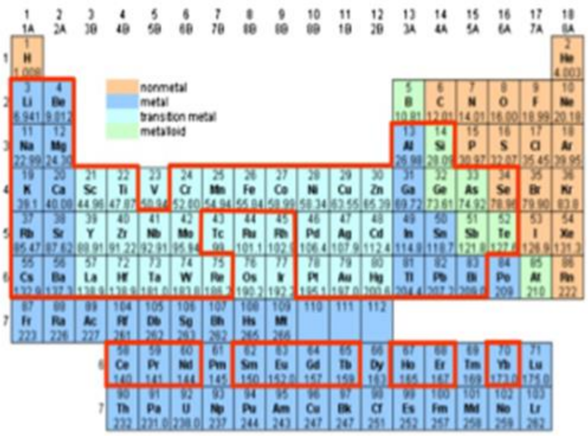

Figure 1. Elements present in the structure of WEEE structure (Behrendt *et al.*, 2007)

Most of all the electrical and electronic equipment present in their structure at least a printed circuit boards. This component has attracted the largest interest of processing due to its relatively high content of base and precious metals compared with their content within the primary ores. However, as the composition of waste printed circuit boards is very heterogeneous, their processing is very difficult. The literature data presents various technologies for the treatment of these wastes. Generally, they consist in a first step of physical-mechanical treatment flowed by a chemical process (Faramarzi *et al.*, 2004; Flandinet *et al.*, 2012; Hagelüken, 2006; Hadi *et al.*, 2015; Havlik *et al.*, 2011; Karwowska *et al.*, 2014; SIlvas *et al.*, 2015). The chemical processes applied for WPCBs treatment are based either on thermal or aqueous methodologies or even a combination of thereof. As is specified in the literature data, the most easily applicable and environmental friendly procedure for the treatment of WPCBS is represented by the aqueous methods, more particularly, the hydrometallurgical procedures. These procedures have the advantages of being more easily of control, do not requires high cost aparatus and have lower energy consumption vs. the pyrometallurgical processes. Comparing with the biometallurgical process, they have a faster kinetic of reaction. The main drawback of hydrometallurgical process is represented by the large amount of generated solid and liquid wastes.

Within this paper the main achievements of the research undertaken for WPCBs treatment by a hydrometallurgical technology are shown. In addition, the process simulation and economic analysis considering a certain capacity of an industrial plant are also exposed here. The use of SuperPro Design software has as main core do simulate the entirely process that was developed at the lab scale and to provide the data that can be further used for implementation of the process at industrial scale.

2. Developed technology, process simulation and economy

2.1. WPCB hydrometallurgical process development

The waste printed circuit boards represent an important secondary resource of precious metals (Au, Ag, Pd) but also of base metals (Cu, Zn, Ni, Sn, Pb, Fe, Al). As was expressed in the paper of Wand and Gaustad (Wang and Gaustad, 2012) the main economic drivers in the recycling of such waste, considering their concentrations and market price, are in the following order: Au, Pd, Cu, Ag, Pt, Sn, Ni.

We have performed various experimental procedures for recovery of main economic drivers (Au, Cu and Ag) from waste printed circuit boards of exhausted personal computers. In a first study we have published the achieved results for the physical and chemical characterization of five different samples (Birloaga *et al.*, 2012). The procedure consisted of characterization consisted of comminution experiments which have shown that the precious metals cannot be separated in a single fraction, these being present in all the chemically analysed fractions. Therefore, this physical process cannot be considered as suitable for WPCBs treatment.

Then, the research activity was continued with a study on various factors influence during the leaching using a first leaching system for Cu composed of hydrogen peroxide as oxidant and sulfuric acid as reagent followed by a second leaching system for Au and Ag with thiourea as reagent and ferric sulfate as oxidant using an acid solution of diluted sulfuric acid as medium (Birloaga *et al.*, 2013). Has been shown that the process temperature, hydrogen peroxide concentration, agitation rate and time had an important influence on copper extraction. Decrease of particle size correlated with increase of oxidant concentration had a favorable effect on the degree of Cu dissolution. Was shown that copper complete dissolution cannot be achieved within a single step of leaching as this is entrapped between the layers of the printed circuit boards. In addition, within the same paper, was shown that copper presence has a detrimental effect on Au and Ag leaching with thiourea and triferric ion. At 75% of Cu recovery, only 45% f Au recovery have been achieved. Therefore, the two step cross leaching using fresh leaching solution each time for the same solid has increased the recovery degree of Cu to over 90%. The subsequent leaching system has revealed an increment of Au recovery of over 69%.

Into another paper, in order to achieve the total extraction of all three elements and also for a better procedure sustainability, the cross current method for both leaching systems has been applied (Birloaga *et al.*, 2014). The cross current leaching with sulfuric acid and hydrogen peroxide with fresh solution each time for the same solid resulted in complete dissolution of Cu. For the second leaching system the cross current method consisted of solution reuse for three different solids already treated with the cross current H_2SO_4 and H_2O_2 leaching process. This technology has provided both Au and Ag almost complete recovery and also the achievement of a rich final solution of Au and Ag.

The experimental work continued to reduce also the high chemicals consumption during the Cu leaching process (Birloaga and Vegliò, 2016). For this, the counter current procedure has been performed, and according to the achieved results, this allowed to recover more than 95% of Cu using a two-step method. The cross leaching process for Au and Ag had as result over 90% of Au recovery and 75% for Ag. In addition, the elements recovery from solution has been also tested and successfully achieved using the cementation procedure with zinc metal powder. The copper precipitate had a purity of about 88%, with Zn, Sn, Ni and Fe as impurities. The gold and silver solid product had over 20% of purity, with Zn and S as impurities.

In order to achieve better purity level for Cu product, the work was continued with various tests which have involved various flocculation/precipitation agents for Sn recovery from solution prior to cementation process with Zn. Over 90% of Sn recovery has been achieved using polyamine C-15 as coagulation agent. Then, by the cementation process, the achieved Cu purity was higher than 93%. In addition, the final solution, with high $ZnSO_4$ content, can be subjected to crystallization process. In addition, tests for waste water treatment of the residual solution achieved after Au and Ag cementation, have been performed using Fenton process for degradation of its organic complex and then a precipitation of the impurities with calcium hydroxide. At the end of both procedures, over 98% of COD and impurities removal has been achieved. In addition, the treated water has been recirculated within the procedure and this had as result the same recovery degrees of elements as in case of fresh water use.

The application of the above described procedures for recovery of Cu, Sn, Au and Ag from waste printed circuit boards can be considered as a suitable technology. This is due to: the use of chemicals that allows a selective recovery of base metals from the precious one; minimization of reagents consumption; reduction of wastewater production by recirculation within the process. Considering all these data, the described hydrometllurgical route has been integrated within the SuperPro Designer software.

2.2. Super Pro designer software brief description

The Super Pro Design software (version 9.0 was used for the simulation presented within this article), by Intelligen Inc. USA, is a computer simulator tool package that tracks the behaviour of chemicals in individual and combinations of unit operations. Within this software database, various chemical are provided, and also it has the allowance to insert new ones. As it has a variety of procedure operations with different kind of equipment, can be easily used for the design and simulation of a working plant in either batch or continuous operation mode. Based on the all the chemical reactions involved within a process, this software allows the mass and energy balance estimation for all streams of the process, estimates purchase costs, and reports stream and equipment data, as well as capital and manufacturing costs. A compressive description of the software and also its way of operating for various processes are fond in the user's guide of each version of this tool (Intelligen, 2017).

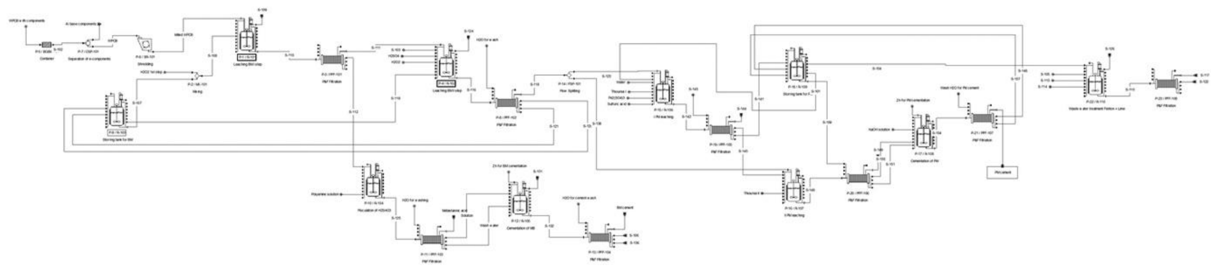

Figure 2. WPCB process flowsheet – simulation by SuperPro Design software

2.3. Results and discussions on process economic simulation

In Figure 2 the developed procedure flow diagram using Super Pro Design process is shown. It is worth to mention that all chemical procedures are taking place at room temperature and ambient pressure. The flowsheet of the process consists in a first section where the aluminium and steel based components are firstly removed from the WPCBs surface (about 25% of the weight) and then the depopulated WPCBs are milled to a particle size of less than 2 mm. Furthermore, two chemical reactors are used for the base metals leaching within a counter current manner. The main chemical reactions involved within this procedure that last 1.1/2 h for each step are as follows:

$$Cu + H_2SO_4 + H_2O_2 = CuSO_4 + 2H_2O \quad (1)$$

$$Zn + H_2SO_4 + H_2O_2 = ZnSO_4 + 2H_2O \quad (2)$$

$$Sn + H_2SO_4 + H_2O_2 = SnSO_4 + 2H_2O \quad (3)$$

According to the laboratory scale results, the recovery degrees for the three elements have been of 99% for Cu and Zn and 45% for Sn. Therefore, these values have been also introduced with the simulation software. The solution separation by solid has been achieved using filter presses. Then, the resulted solution was subjected to coagulation process with polyamine solution and over 95% of Sn recovery from solution was achieved at this stage. After tin precipitate (metastannic acid) recovery from solution by filtration, the resulted solution has been subjected to cementation process with a zinc metal powder. This process takes places according to the reaction:

$$Zn + CuSO_4 = Cu + ZnSO_4 \quad (4)$$

A recovery degree of Cu from solution of 100% has been achieved. The rich solution of $ZnSO_4$ can be further treated to achieve fertilizing agents for agriculture industry.

The solid residue of the counter current leaching process is further subjected to leaching with thiourea, ferric sulfate and sulfuric acid for Au and Ag recovery. The main reactions of this process are as follows:

$$2Au + Fe_2(SO_4)_3 + 4SC(NH_2)_2 + SO_4^{2-} = (Au(SC(NH_2)_2)_2)_2SO_4 + 2FeSO_4 \quad (5)$$

$$2Ag + Fe_2(SO_4)_3 + 6SC(NH_2)_2 + SO_4^{2-} = (Ag\ (CS(NH_2)_2)_3)_2SO_4 + 2FeSO_4 \quad (6)$$

The achieved recovery degree for Au and Ag within this step were of over 99%. Afterwards, the recovered solution after filtration is make-up with a smaller quantity of thiourea than in previous step and then another solid resulted after counter current leaching is used for Au and Ag recovery. Then, the enriched solution with Au and Ag is neutralized with sodium hydroxide and then Zn powder is also added within solution to achieve the recovery of these two precious elements. The efficiency of this process is 100% for both elements. According to lab scale tests, the spent solution cannot be entirely reused. This is due to increment of base metals concentration within solution which further leads to precipitation of precious metals when another leaching step is performed. Therefore, a part of it is treated as residual water and the rest is reused within the process for preparation of a new solution with a suitable water and chemicals make-up. As the wastewater contain dangerous organic complexes and also inorganic ones, the Fenton process followed by neutralization with calcium hydroxide is performed. The physical-chemical characterization of the treated water has shown a good efficiency of these procedures (over 98% of substances removal). The current proposed procedure has the advantage of using simple and relatively fats operations. However, the main drawback is represented by the fact that the final products require a further refining step. The plant within the SuperPro Designer software was designed at a capacity of 1 MT per batch and to run 7200 h per year in a batch mode. With the aid of Super Pro Design, the mass and energy balance calculation as well as the economic analysis were performed.

Table 1. Profitability analysis of the WPCBs hydrometallurgical process

Direct Fixed Capital	4,435,000 €
Working Capital	213,000 €
Startup Cost	222,000 €
Total Investment	4,869,000 €
Investment Charged to This Project	4,869,000 €
Revenues	
Metastannic acid (Revenue)	630,434 €/yr
Base Metals cement (Revenue)	882,373 €/yr
Precious Metals cement (Main Revenue)	3,957,767 €/yr
Zinc sulfate (Revenue)	216,805 €/yr
Total Revenues	5,687,379 €/yr
Annual Operating Cost (AOC)	
Actual AOC	2,125,000 €/yr
J. Unit Production Cost /Revenue	
Unit Production Cost	295.12 €/kg MP
Net Unit Production Cost	295.12 €/kg MP
Unit Production Revenue	789.85 €/kg MP
Gross Profit	3,562,000 €/yr
Taxes (40%)(	1,425,000 €/yr
M. Net Profit	2,559,000 €/yr
Gross Margin	62.64%
Return On Investment	52.55%
Payback Time	1.90 years

Considering the optimal conditions of the developed procedure for waste printed circuit board with gold content of 140 mg/kg, as is shown in Table 1, for an industrial plant, where the investment cost were considered to be of about 3 million of euro and a payback period of one year, at a plant capacity of 990 t/year, the total revenues were over 5 million of euro in one year. To calculate the net value of the profit, the other cost of plant maintenance, reagents, electricity, etc. has been considered and, according, over € 2 million/year can be achieved using the developed process at a depreciation established time of about 2 years. However, these numbers are considered for a Au content of 140 mg/kg in the treated material and also for the plant capacity. A decrease/increase of both afore mentioned factors, will obviously diminish/improve the process economy. As was said above, the gold content in waste printed circuit boards is the main driver within their recycling. Therefore, considering the same process conditions, but at a gold content of 200 mg/Kg in PCB, the process economy is improved with over 25%. In addition, if the treated amount of PCB/year is also increased (1400 t/year), a rose of process economy of about 20% is also achieved.

3. Conclusions

The current paper present the main data of a developed hydrometallurgical process for recovery of Au, Ag, Cu and Sn from waste printed circuit boards. As was described within this article and within our previous papers, the process has been investigated and continuously optimized and, in order to achieve its economic sustainability, the SuperPro Designer software has been used. The simulation of the process with this software showed a good profitability of the proposed procedure. However, this fact is strongly depended on the treated amount of WPCBs and their gold content.

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