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HYDROMETALLURGICAL PROCESS FOR EXTRACTION OF METALS FROM ELECTRONIC WASTE-PART I: MATERIAL CHARACTERIZATION AND PROCESS OPTION SELECTION

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Abstract

Used electronic equipment became one of the fastest growing waste streams in the world. In the past two decades recycling of printed circuit boards (PCBs) has been based on pyrometallurgy, higly polluting recycling technology whic causes a variety of environmental problems. The most of the contemporary research activities on recovery of base and precious metals from waste PCBs are focused on hydrometallurgical techniques as more exact, predictable and easily controlled. In this paper mechanically pretrated PCBs are leached with nitric acid. Pouring density, percentage of magnetic fraction, particle size distribution, metal content and leachability are determined using optical microscopy, atomic absorption spectrometry (AAS), X-ray fluorescent spectrometry (XRF) and volumetric analysis. Three hydrometallurgical process options for recycling of copper and precious metals from waste PCBs are proposed and optimized: the use of selective leachants for recovery of high purity metals (fluoroboric acid, ammonia-ammonium salt solution), conventional leachants (sulphuric acid, chloride, cyanide) and eco-friendly leachants (formic acid, potassium persulphate). Results presented in this paper showed that size reduction process should include cutting instead of hammer shredding for obtaining suitable shape & granulation and that for further testing usage of particle size -3 +0.1mm is recommended. Also, Fe magnetic phase content could be reduced before hydro treatment.

Key words: electronic waste, printed circuit boards, recycling, hydrometallurgy, copper, precious metals

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Introduction

Fast electronic industry development brought the great benefits in everyday life, but its consequences are usually ignored or even unknown. Used electronic equipment became one of the fastest growing waste streams in the world. From 20 to 50 million tonnes of waste electical and electronic equipment (WEEE, e-waste) are generated each year, bringing significant risks to human health and the environment [1]. EU legislative restricts the use of hazardous substances in electrical and electronic equipment (EEE) (Directive 2002/95/EC) such as: lead, mercury, cadmium, chromium and flame retardants: polybrominated biphenyls (PBB) or polybrominated diphenyl ethers (PBDE) and also promotes the collection and recycling of such equipment (Directive 2002/96/EC). They have been in implementation since February 2003. Despite rules on collection and recycling only one third of electrical and electronic waste in the European Union is reported as appropriately treated and the other two thirds are sent to landfills and potentially to sub-standard treatment sites in or outside the European Union. In December 2008 the European Commission proposed to revise the directives on EEE in order to tackle the fast increasing waste stream of these products [2].

Recycling of printed circuit boards (PCBs), as a key component in the WEEE, in past two decades have been based on recovery via material smelting. This is highly polluting, primitive recycling technology that can cause a variety of environmental problems. It is mostly processed, sometimes illegally, in developing countries, for instance China, India, Pakistan and some African countries [3,4]. Goosey and Kellner in their detailed study [5] have defined the existing and potential technologies that might be used for the recycling of PCBs. They pointed out that metals could be recycled by mechanical processing, pyrometallurgy, hydrometallurgy, biohydrometallurgy or a combination of these techniques.

Pyrometallurgy, as traditional method to recover precious and non-ferrous metals from e-waste, includes different treatments on high temperatures: incineration, melting etc. Pyrometallurgical processes could not be considered as best available recycling techniques anymore because some of the PCB componenets, especially plastics and flame retardants, produce toxic and carcinogenic compounds. The most of the research activities on recovery of base and precious metals from waste PCBs are focused on hydrometallurgical techniques for they are more exact, predictable and easily controlled [6,7].

In recent years the great number of investigations have been conducted in order to solve the problem of WEEE and develop appropriate recycling techniques. According to Cui and Zhang [7] recycling of e-waste can be broadly divided into three major steps: a) disassembly-mechanical pretreatment: selectively removing hazardous and valuble components for special treatment and it is necessary step for further operations, b) concentrating: increasing the concentration of desirable materials using mechanical and/or metallurgical processing and c) refining: metallurgical treatment and purification of desirable materials.

Hydrometallurgu, i.e. leaching and cementation process in Serbian mine Bor was first mentioned in 1907 when 200 tons of copper were produced. Since those days till today copper hydrometallurgy has not mount at Serbia and nearby region [8].

Hydrometallurgical processing consist of: leaching – transfering desirable components into solution using acides or halides as leaching agents, purification of the leach solution to remove impurities by solvent extraction, adsorption or ion-exchange, then recovery of base and precious metals from the solution by electrorefining process, chemical reduction, or crystallization. The most efficient leaching agents are acids, due to their ability to leach both base and precious metals. Generally, base metals are leached in nitric acid [9, 10]. The most efficient agent used for solder leach is fluoroboric acid [11]. Copper is leached by sulphuric acid or aqua regia [12]. Aqua regia is also used for gold and silver [11], but these metals are usually leached by thiourea or cyanide [13]. Palladium is leached by hydrochloric acid and sodium chlorate [7].

Biohydrometallurgy is a new, cleaner and one of the most promising eco-friendly technologies. Biosorption is a process employing a suitable biomass to sorb heavy metals from aqueous solutions [14]. This is physico-chemical mechanism based on ion-exchange [15], metal ion surface complexation adsorption or both [16].

Oishi et al. [17] conducted research on recovery of copper from PCBs by hydrometallurgical techniques. Proposed process consists of leaching, solvent extraction and electrowinning. In the first stage of research conducted by Veit et al. [12] mechanical processing was used as comminution followed by size, magnetic and electrostatic separation. After pretreatment, the fraction with concentrated Cu, Pb and Sn was dissolved with acids and treated in an electrochemical process in order to recover the metals separately, especially copper, with two different solutions: aqua regia and sulphuric acid. Frey and Park [11] performed research for recovery of high purity precious metals from PCBs using aqua regia as a leachant. The most significant achievement of this research was synthesis of pure gold nanoparticles.

Sheng and Etsell [9] investigated leaching of gold from computer chips. The first stage was leaching of base metals with nitric acid and the second, leaching of gold with aqua regia due to its flexibility, ease and low capital requirement. Non-metallic materials are also recovered this way, mainly plastic and ceramics. Quinet et al. [18] carried out bench-scale extraction study on the applicability of economically feasible hydrometallurgical processing routes to recover silver, gold and palladium from waste mobile phones. Selective extraction of dissolved metals from solution is very difficult and demanding process [19].

Experimental

Electronic waste is defined as a mixture of various metals, particularly copper, aluminum and steel, attached to different types of plastics and ceramics.

The samples for experimental research presented in this paper were milled PCBs with obtained by mechanical pretreatment of waste computers.

The mechanical pretreatment of end-of-life computers was performed at SETrade, Belgrade. The first stage was manual disassembling of computers, liberation of PCBs and removal of the batteries and capacitors. Liberated PCBs were milled in QZ-decomposer, separating magnetic materials from non magnetic fractions, while aluminum was manually removed from conveyor belt. Material was then milled in shredder Meccano Plastica, after which material was not exposed to another magnetic separation.

Characterization of granulated waste PCBs included determination of following parameters: pouring density, percentage of magnetic fraction, particle size distribution, rate of metal components leachability using optical microscopy, atomic absorption spectrometry (AAS), X-ray fluorescent spectrometry (XRF) and volumetric analysis. Also, appropriate hydrometallurgical system for evaluation of metal components and optimization of process parameters: temperature, time, solid:liquid ratio and mixing velocity are selected.

Sieve analysis was performed using Taylor type sieves and mass of fractions obtained after 30 minutes sieving was measured. Percentage of each fraction was calculateded.

The pouring density of total sample and of each fraction was measured using Hall flowmeter funnel (ASTM B13). Pouring density of total sample was 889 kg/m^3.

The sample was subjected to the magnetic separation process using two permanent magnets each weighing 100g. Percentage of magnetic material content was 5.39%.

Content of metallic and non-metallic components of entire sample as well as for each fraction was determined by leaching with 50 vol.% HNO_3 near to boiling temperature with agitation followed by filtration after cooling. Metallic fraction is transferred to liquid. Solid non-metallic residue mass is measured after filtration. Experimental results are shown in Table 1.

Table 1. Characteristics of PCBs granulated samples

mm	Fraction, wt.%	ρ, kg/m^3	Metallic part, wt.%
5.000	7.07	800	43.84
2.500	37.24	880	50.44
2.000	6.99	830.15	55.47
1.800	8.50	986.33	38.86
1.250	11.68	1235.63	31.57
1.000	5.61	1474.61	48.48
0.800	5.42	1136.59	61.25
0.630	4.81	1022.48	43.95
0.500	1.64	958.63	50.20
0.400	2.75	908.81	44.26
0.315	2.47	794.15	41.31
0.250	1.16	656.74	37.87
0.100	2.82	632.61	35.86
-0.100	1.83	622.05	38.50

Results of the sieve analysis showed that the greatest percent of sample was in fraction +2.5mm. Metallic part was mostly contained in fraction +0.8 mm.

Figures 1a-f are presenting some of the PCB fractions before and after dissolving in nitric acid and removal of metallic components.

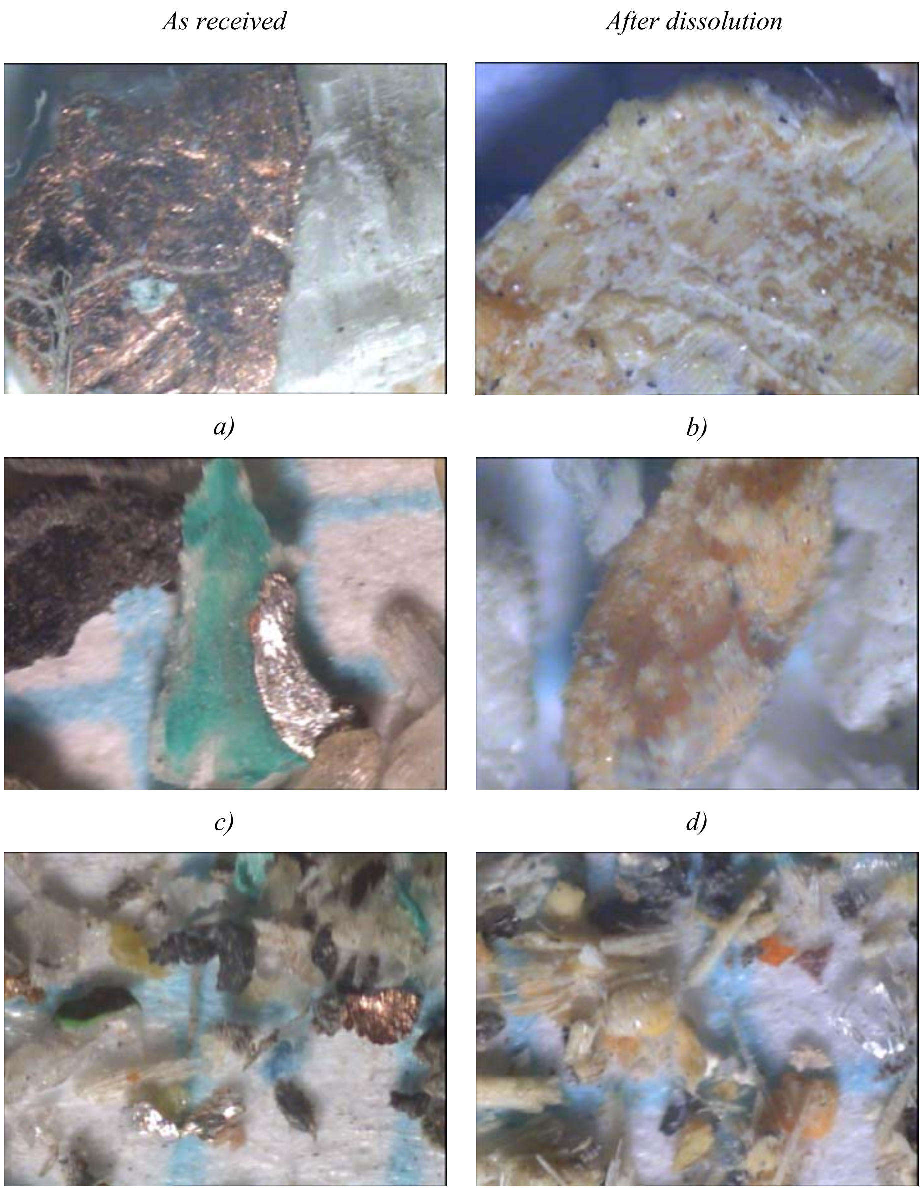

Figure1. PCB fractions before and after dissolving in HNO_3 a&b) 1.8mm; c&d) 1.0mm; e&f) 0.1mm

Analysis of chemical composition of granulated PCBs was performed using volumetric analysis, AAS and XRF spectrometry. Materials used for presented analysis were both granulated samples and samples after sieve analysis dissolved in 50 vol.% HNO_3.

Volumetric analysis was performed using standard sodium tiosulphate solution for treatment of samples dissolved in 50 vol.% HNO_3. Results showed that copper content in granulated PCBs was 21.61 wt%. Also, distribution of copper in fractions was determined by volumetric analysis as presented in Table 2.

Table 2. Distribution of copper in fractions

fraction, mm	Cu, wt.%
5.000	21.96
2.500	18.37
2.000	21.81
1.800	13.90
1.250	17.82
1.000	22.75
0.800	26.34
0.630	17.53
0.500	24.26
0.400	20.22
0.315	15.08
0.250	11.16
0.100	11.45
-0.100	11.47

Presented results show that copper is mostly concentrated in fraction +0.8 mm.

AAS was used for analyzing solutions of each fraction, obtained by dissolving in 50 vol.% HNO_3, in order to determine content of Cu, Zn, Fe, Ni, Pb. It was performed by Perkin Elmer 4000 spectometer calibrated with standard solutions for each measured metal. Results of experimental analysis are shown in Table 3.

Table 3. Chemical composition of WPCBs each fraction in wt.%

mm	Cu	Zn	Ni	Fe	Pb
5.000	11.06	1.89	1.79	5.99	0.89
2.500	30.50	2.25	1.93	0.18	0.71
2.000	30.24	2.28	1.21	2.28	1.53
1.800	24.14	2.04	0.29	0.13	0.78
1.250	35.31	1.73	1.07	1.20	3.85
1.000	33.38	2.23	0.36	1.22	7.15
0.800	27.62	2.21	0.61	0.51	5.91
0.630	28.99	1.68	0.59	0.88	3.56
0.500	40.42	1.81	0.61	1.45	3.44
0.400	40.16	1.24	0.97	1.30	3.50
0.315	23.17	1.27	0.61	1.68	3.76
0.250	14.44	1.18	0.31	1.77	2.09
0.100	7.87	1.31	0.20	2.36	1.50
-0.100	6.32	2.89	0.58	5.22	2.12

Fraction +5mm contained ~6% of Fe, which means that magnetic separation was not efficient enough for this size of particles.

XRF spectrometry was used for direct analysis of granulated PCBs samples. Characteristic parts like contacts, solders and composites were analysed. XRF analysis was performed on Skyray EDX 3000. Measurement spots labeled lom-1 to 4 are presented at Figure 2 and results in Table 4.

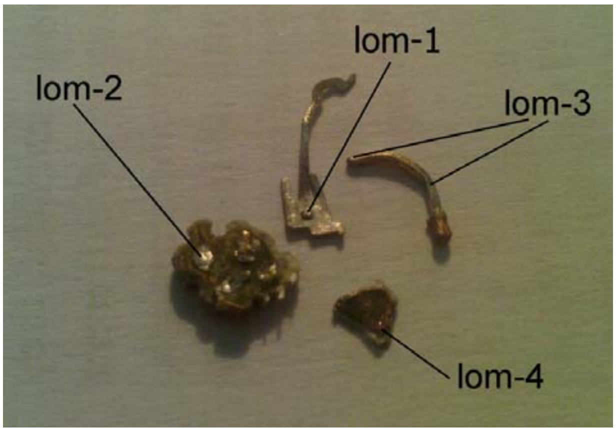

Figure 2. Measurement spots for XRF analysis

Table 4. Results of XRF analysis

	Cu	Ag	Rh	Pd	Pt	Au
Lom 1	96.254	3.746				
Lom 2	95.072	4.928				
Lom 3	73.121	6.45	2.521			17.943
Lom 3	30.749	14.762	8.806		2.353	43.33
Lom 4	95.03			4.97		

XRF analysis showed that metal content varies from sample to sample and it highly depends on measuring spot.

Based on detailed literature review and presented experimental results, several process option were selected as an appropriate hydrometallurgical process for extraction of metals from electronic waste was.

Process option 1-The use of selective leachants and recovery of high purity metals from PCBs

This process option involves four main stages:

1. mechanical pre treatment that includes shredding, magnetic separation, eddy current separation and classification [11],
2. solder leach with fluoroboric acid and Ti(IV) ion as oxidizing agent [20],
3. recovery of copper that includes leaching with ammonia-ammonium salt solution, purification by solvent extraction with organic LIX 26 and electrowinning [17]
4. recovery of high purity precious metals (Au, Ag ang Pd) using aqua regia [11].

Schematic preview of process option 1 is presented in Figure 3.

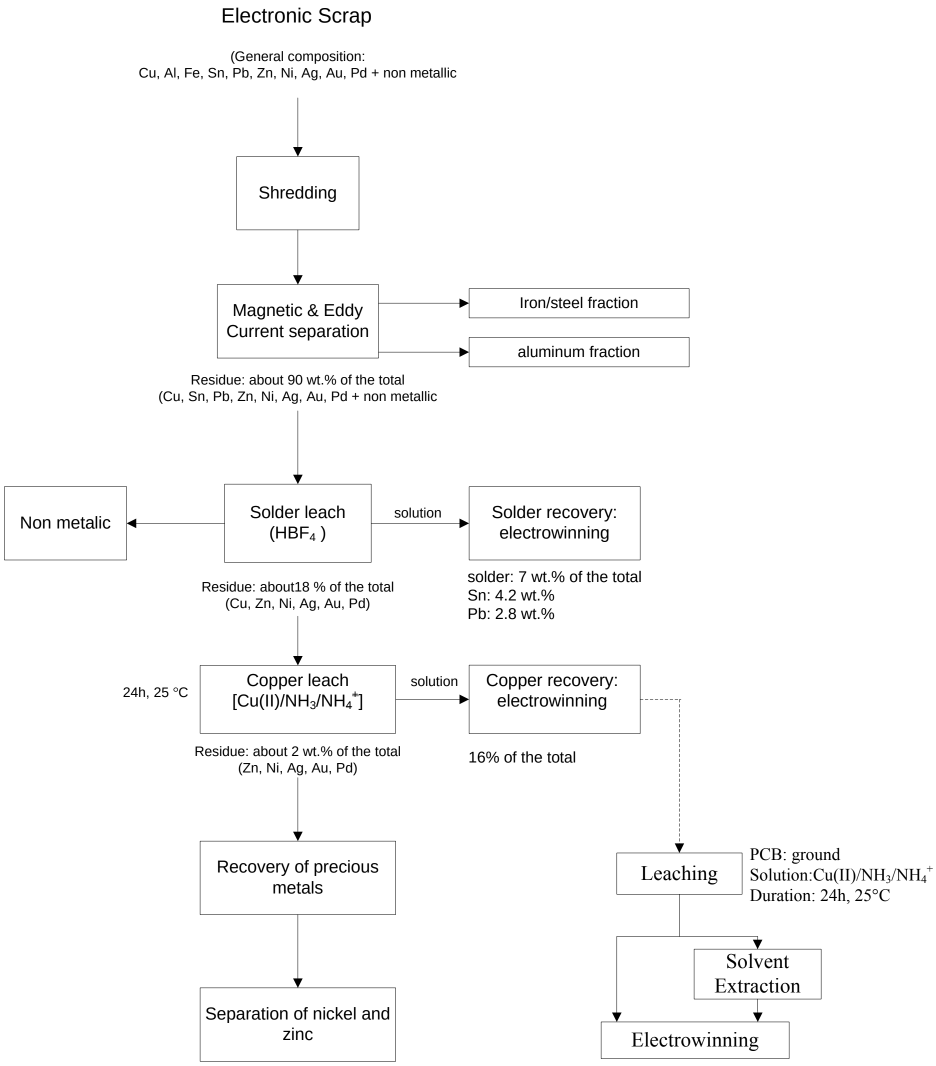

Figure 3. The recycling process of metals contained in PCB waste

Process option 2- The use of conventional leachants for recovery of metals from waste PCBs

This process option represents bench-scale method for extraction and recovery of copper and precious metals from waste PCBs. After comminution, material was subjected to serial of hydrometallurgical processing routes: sulphuric acid leaching and precipitation for Cu recovery; chloride leaching followed by cementation for Pd, Ag, Au and Cu recovery and cyanidation and activated carbon adsorption for recovery of Au and Ag. The proposed flowsheet is presented in Figure 4.

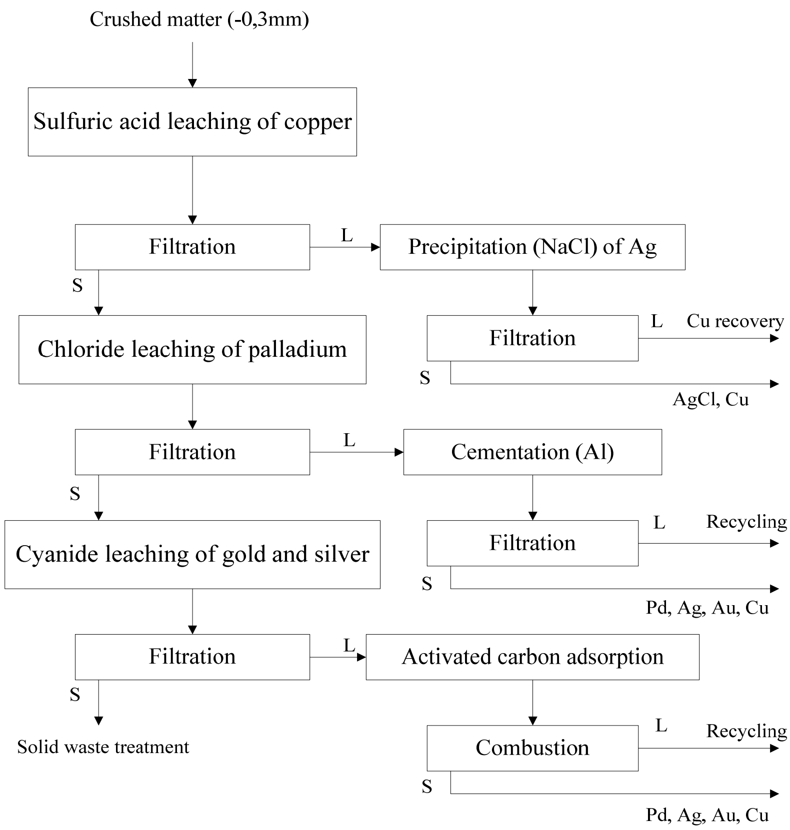

Figure 4. Proposed flowsheet for the recovery of precious metals from WPCBs [18]

Process option 3- The use of green leachants for recovery of metals from waste PCBs

This process option is particulary based on recovery of gold from electronic waste using an "eco-friendly" or "green" reagents. After communition, non-toxic reagents formic acid and potassium persulphate are used for Au leaching at boiling temperature. Base metals, obtained as by-products, in a further steps could be recoverd by electrowining. Gold is recoverd by melting. This process option is presented in Figure 5.

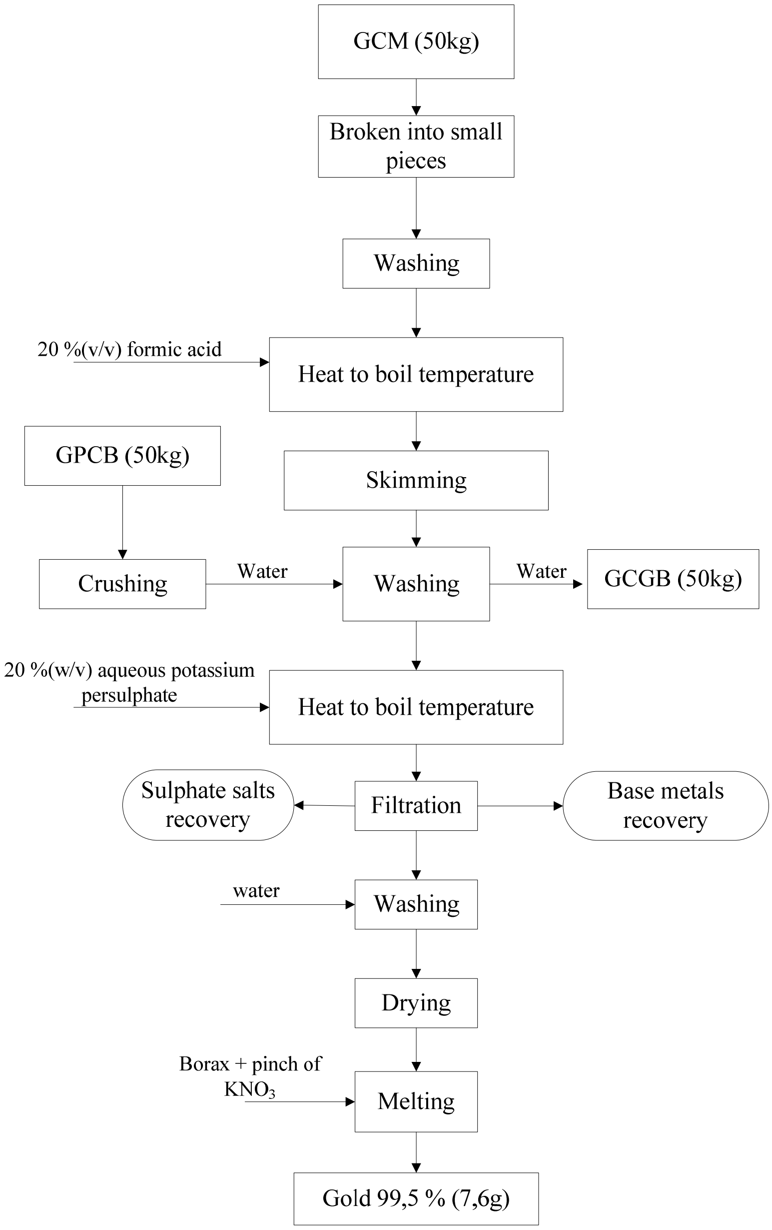

Fig. 5. Flow sheet of gold recovery from gold-plated PCBs (GPCB), gold-coated glass bangles (GCGB) and gold-coated mirrors (GCM)

Conclusion

On the basis of experimental results it can be concluded that properties of investigated material is in accordance with literature and it could be a representative for selection of proper hydrometallurgical recycling technique. AAS chemical analysis has shown that fraction above 5 mm contained high amount of Fe and should be avoided by more efficient magnetic separation. Also, -0.1 mm fracton can cause various difficulties in process, great loses due to large content of metals in this fraction and decreased leachability.

Final selection of the process which could be applied for further analysis depends on input materials characteristics. There is no completely green option. Selection of suitable hydrometallurgical process highly depend on leaching tests and techno-economical analysis and possible solution for electronic waste lies in combination of proposed process options.

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