LIFE12 ENV/GR/000427 LIFE reclaim "Landfill mining pilot application for recovery of invaluable metals, materials, land and energy

TECHNICAL REPORT - ACTION B6
FOR THE POLYGYROS LANDFILL, IN THE MUNICIPALITY OF POLYGYROS, CHALKIDIKI

SUBJECT:

RESULTS FROM BENEFICIATION TESTS OF CONCENTRATES

ENVECO S.A. ENVIRONMENTAL PROTECTION MANAGEMENT & ECONOMICS

HELECTOR

Municipality of Polygyros

NTUA School of Mining & Metallurgical Engineering

With the contribution of the LIFE financial instrument of the European Union

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Contents

Abbreviations

AAS: Atomic Absorption Spectroscopy

ICP: Inductively Coupled Plasma Spectrometry

ICP – MS: Inductively Coupled Plasma Mass Spectrometry

LFM: Landfill Mining

NTUA: National Technical University of Athens

PCBs: Printed Circuit Boards

PDU: Pilot Demonstration Unit

PL: Polygyros Landfill

Chapter 1. Description of Size-Reduction and Beneficiation Works

The size reduction and the beneficiation of the e-waste materials is an important step towards assessing the potential of these materials to be actively recovered, enriched and marketed in order to enhance the overall financial bottom line of the overall landfill mining endeavor. In the next sections the whole process is presented and the results obtained from the beneficiation stage are given in detail and assessed in terms of their efficiency to recover the valuable materials especially found in the printed circuit boards (PCBs).

1.1. Collection of E-Waste

The project expectations were to find electronic and electrical devices. However, the recycling of electronic and electrical devices started along with the operation of the Polygyros Landfill. As a result, during the sample landfill mining process in May 2014 no electrical or electronic waste was found. In order to achieve the target of the project, a sample of e-waste (13.4 kg of electrical and electronic boards) was taken from dismantled old electrical and electronic waste, which were found in the disposal of electrical and electronic devises facility of the landfill. After acquiring the sample of electronic boards, they were given to OIKOKYKLIOS S.A. for size reduction and sorting.

1.2. Size-reduction

The e-waste had to undergo specific treatment in order to acquire the desirable size. To perform this process, OIKOKYKLIOS S.A. was chosen, because of the company's specialization in the recycling of electronic devices, as well as their possession of appropriate equipment and knowhow.

Firstly, the collected electronic boards went through manual separation, in order to be cleansed of impurities and avoid further milling. Also, big parts constructed of the same material (e.g. aluminum) were dismantled and separated manually. Afterwards, the materials were separated by kind through a process including two types of shredders. First, the boards were placed in the crushing machine (pre-shredder) to start the size-reduction process; this downsized the granulometry of the incoming electronic boards to a range of 2 to 10mm. At a second stage, the outcome of the previous process was forwarded to a second shredder, which was a turbo-mill; this downsized the granulometry of the incoming material even further, to a range of 1 to 3mm. This latter fraction of produced materials was driven through closed pipe system to a vibratory sieve, where solid inert residues and dust were removed by an air-separator. The remaining product underwent further separation through a smaller-hole sieve and a magnetic separator.

The results of this procedure were several fractions of materials such as: Ferrous metals, Aluminum, Mixed metals and Plastics. More specifically, the incoming electronic printed circuit boards of a weight of 13.4 kg, were transformed into:

- 1.6 kg of mixed metals

- 0.86 kg of ferrous detritus

- 0.32 kg of cooper parts

- 0.3 kg of aluminum parts

- 0.44 kg of ferrous parts and

- 9.34 of plastic

All of the above separated small metallic and plastic particles were given to NTUA for treatment and retrieval of valuable metals.

1.3. Beneficiation Stage: Sink Float tests

1.3.1. Intoduction

The printed circuit boards (PCBs) found in the e-waste stream are rich in Cu content and fairly rich in precious metals (Pd, Au and Ag). Processing of these wastes for extracting and recovering a significant proportion of the metal values contained in PCBs and removing the non-metallic constituents (plastics, etc.) seems to be a challenge.

Froth flotation methodology was observed to be a promising technique for rejecting plastics from the PCBs comminution product. It has been shown that, nearly reagent-free flotation of relatively coarse size fraction (-1 mm) pulverized e-waste, is feasible with a reasonably good product at an acceptable yield and good recovery.

In this work, froth flotation processing of the fine PCBs pulverized material was investigated, through reverse flotation beneficiation in a scheme described as a natural hydrophobic response. Without reagents, the system uses the pH alteration, the particle size of the treated material, the kinetic parameters of the aeration rate and impeller (rotor) speed of the flotation machine to recover as "sink" product the metal values, contained in the fragmented and classified by sieving fraction of the PCBs material.

A sample of e-waste fine material (100% ≅ -1.5 mm) weighing about 10 kg was received from the initial raw material. Afterwards, with the help of a "Jones" mechanical splitter (sampling device), the feed

was divided in smaller samples of about 200 g each, which will be used for the chemical analysis work and for the flotation tests.

Samples were stored and preserved for laboratory determinations by implementing ISO 18512/2007. Each sample was prepared for chemical analysis according to EUROPEAN STANDARD FINAL DRAFT prEN13657, "Characterization of waste – Digestion for subsequent determination of aqua regia soluble portion of elements".

Further analysis of each element was conducted according to DIN EN ISO 11885 and DIN EN ISO 17294, by utilizing Inductively Coupled Plasma Spectrometry (ICP – AES - Prodigy – Teledyne, Leeman Labs), Inductively Coupled Plasma Mass Spectrometry (ICP – MS) and Atomic Absorption Spectroscopy (AAS – Hitachi Z2000). Each measurement was replicated twice, for different samples and the difference between the two samples was less than 5%. Following the aforementioned procedures, the elements Arsenic (As), Cadmium (Cd), Copper (Cu), Manganese (Mn), Lead (Pb), Iron (Fe), Nickel (Ni), Zinc (Zn), Chromium (Cr), Palladium (Pd), Silver (Ag), Platinum (Pt) and Gold (Au) were measured in each sample.

The chemical analysis of the original sample is given in the Table 1.3-1, which is shown also in Figures 1.3-1 and 1.3-2 for the common metals and the precious metals, respectively.

Table 1.3-1 Chemical Analyses of the original Sample

Element	**Content %**
Cu	3.19
Mn	1.00
Pb	0.67
Fe	4.40
Ni	0.11
Cr	0.01
Zn	0.85
Precious metal content (mg/kg)	
Pd	3.73
Ag	250.59
Pt	<0.05
Au	19.27

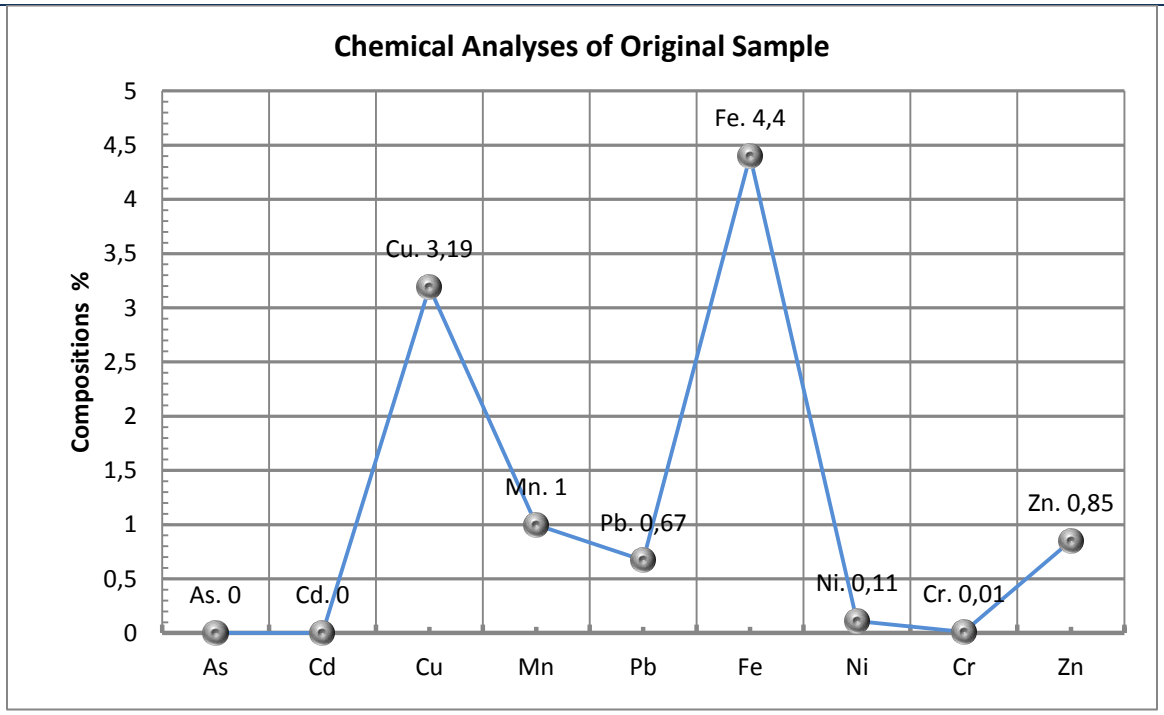

Figure 1.3-1: Metal content % in the original sample

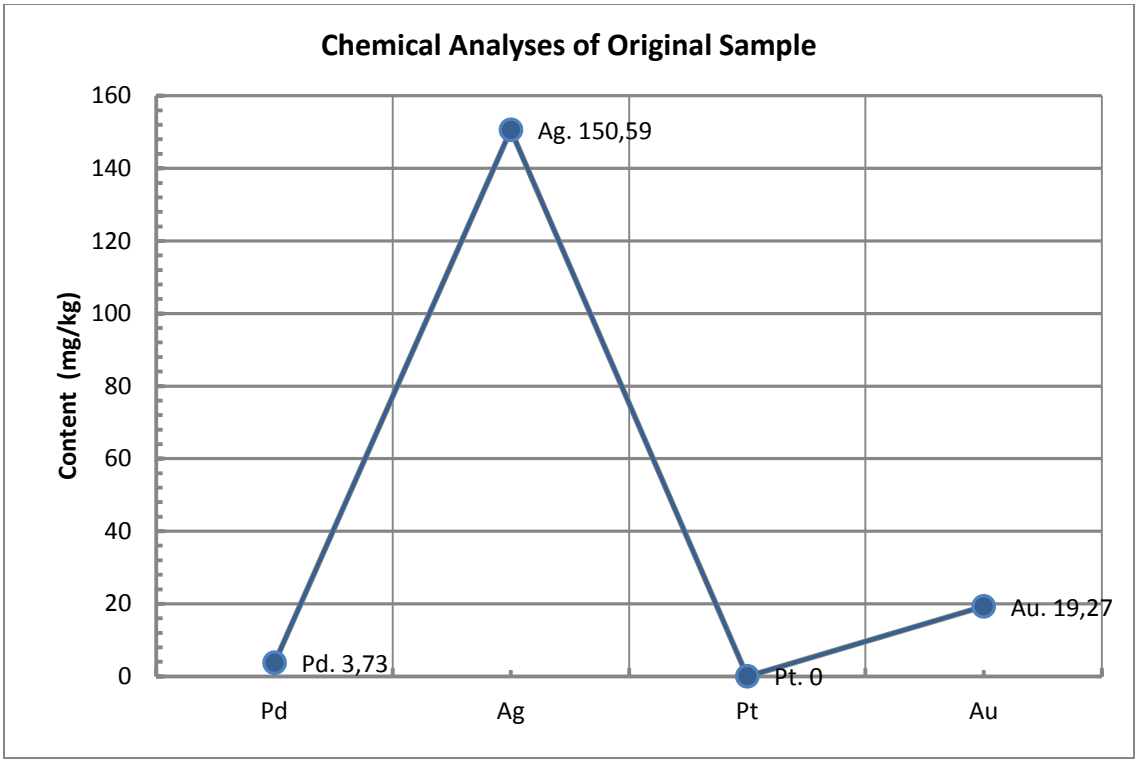

Figure 1.3-2: Precious metals content (mg/kg) of the original sample.

1.3.2. Flotation Tests - Stages

The flotation tests were conducted using a Denver "Sub-A" flotation machine of the Laboratory of Mineral Processing (NTUA), Figure *1.3-3*.

Figure 1.3-3: Denver "SUB-A" Laboratory flotation machine

The designed flotation tests were conducted in three different stages successively. The various process parameters (e.g. the slurry density, the stirring speed, the stirring time and the time of removal of the "float" product) were maintained constant. The test procedures applied are represented in Figure 1.3-4.

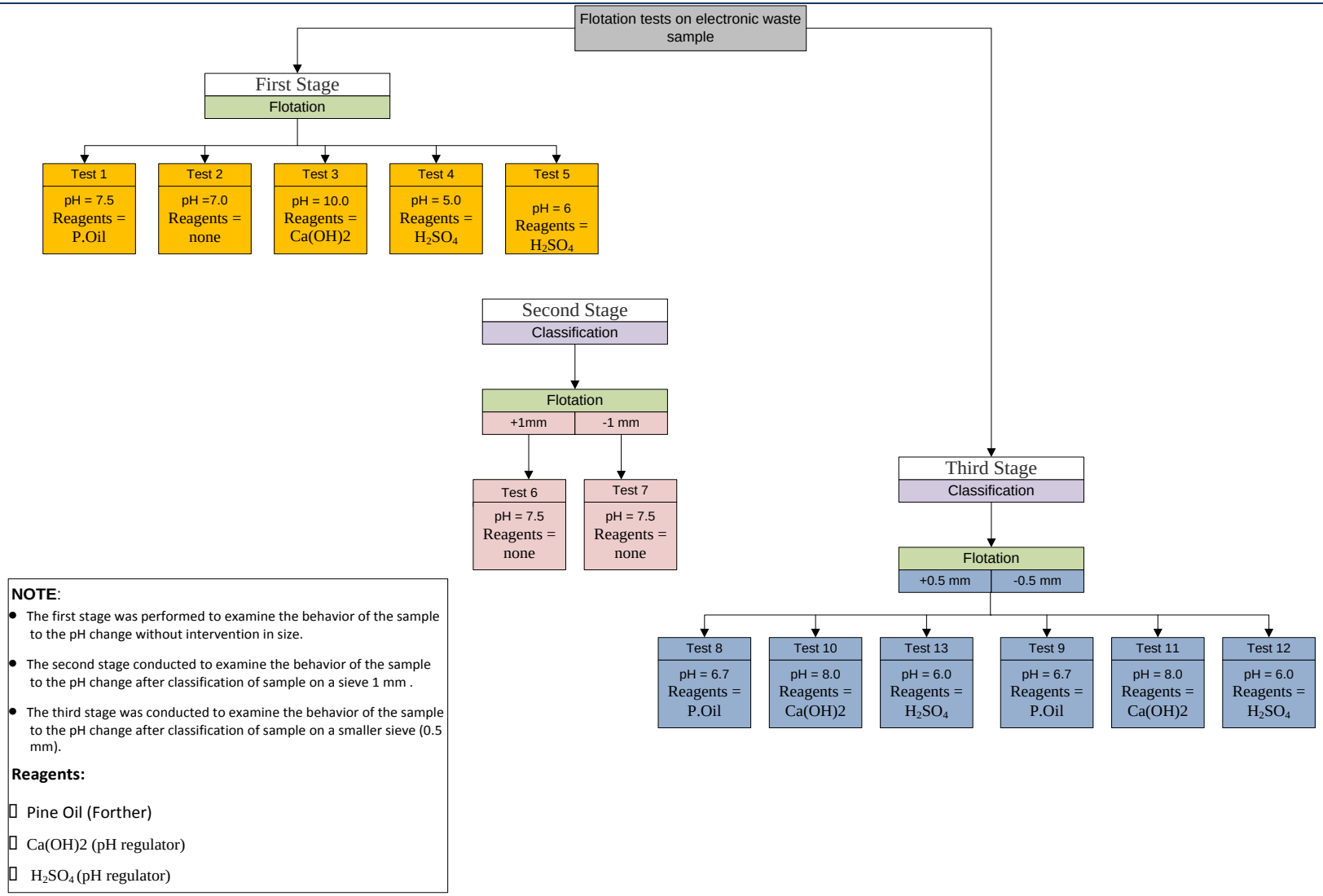

Figure 1.3-4. Different stages of the various laboratory flotation tests.

Chapter 2. Results from Beneficiations

2.1. First Stage Tests and Results

The five (5) tests of this stage, were conducted under normal flotation conditions on original material feed, by changing solely the pH of the pulp. All other process variables (e.g. slurry/pulp density, machine rotor speed, stirring time) were maintained constant during the tests. The experimental results of each test are given in Tables 2.1-1 and 2.1-2, while the experimental conditions are shown in Tables 2.1-3, 2.1-4, 2.1-5, 2.1-6 and 2.1-7, respectively. From the above 5 tests, two of them (No 1 and 2 tests), considered as the most "promising", were analyzed in detail for the "floats" and the "sinks" and assessed for the metals presenting economic interest.

The flotation tests of the 1st stage were preliminary ("trial" tests) in order to study the behavior of the metal values and the non-metallic material associated with the PCBs fragmented material.

The parameters "c", "t", refer to the content (% or mg/kg) of the various metals in the feed, "floats" and "sinks", respectively, while R refers to the % recovery of the useful metal values in the products ("floats" and "sinks"), or their % distribution in the "coarse" (oversize) and the "fine" (undersize) products, after the size classification of the original feed.

Some primary comments, as deduced from the results are:

1. The precious metals, Au and Pd showed a tendency to report in the "floats", while high percentage of the other precious (Ag) reports to the "sinks" (Tables 2.1-1 and 2.1-2). The rest "high-concentration" metals Cu and Fe, reports in the "sinks" and the "floats", respectively.
2. Since, the chemical analysis of such complex flotation products is not only time consuming but expensive as well, it was decided to select the most representative tests, from the following two different experimental stages (2nd stage and 3rd stage), to perform complete chemical analysis of their products ("floats" and "sinks").

Table 2.1-1: Experimental results of the "float" product of the 1st stage (5 tests)

Element	Original sample	Test 1		Test 2		Test 3	Test 4	Test 5
		mean c % ("float")	R %	c % ("float")	R %	c % ("float")	c % ("float")	mean c % ("float")
As	-	-		-		-	-	n.a.
Cd	-	0.0008		0.0006		0.0005	0.0005	
Cu	3.19	0.72	8.8	0.61	7.6	0.43	0.89	
Mn	1.00	2.02		2.23		2.20	2.39	
Pb	0.67	0.89		0.72		0.52	0.61	
Fe	4.40	8.15	71.2	8.28	74.1	7.71	7.76	
Ni	0.11	1.64		0.85		1.87	1.83	
Cr	0.01	0.01		0.01		0.17	0.02	
Zn	0.85	1.55		1.66		1.55	1.83	
Element	Original sample mg/kg	c ("float") mg/kg	R %	c ("float") mg/kg	R %	c ("float") mg/kg	c ("float") mg/kg	c ("float") mg/kg
Pd	3.73	5.96	61.4	5.87	61.9	4.72	5.41	5,27
Ag	250.59	221	33.7	196.03	30.8	172.14	177.94	207.5
Pt	<0.05	<0.05		<0.05		<0.05	<0.05	<0,05
Au	19.27	36.5	72.9	39.43	80.5	30.06	37.73	32,80
Weight %		38.48		39.36		38.24	27.89	43.39

Table 2.1-2: Experimental results of the "sink" product (tailing) of the 1st stage

Element	Original Sample, %	Test 1		Test 2	
		t % ("sink")	R %	t % ("sink")	R %
As	-	0.0015		0.0006	
Cd	-	0.0041		0.0016	
Cu	3.19	4.73	91.2	4.86	92.4
Mn	1.00	0.33		0.20	
Pb	0.67	1.04		0.64	
Fe	4.40	2.06	28.8	1.89	25.9
Ni	0.11	0.31		0.20	
Cr	0.01	0.01		0.03	
Zn	0.85	0.72		0.32	
Element	Original Sample mg/kg	t ("sink") mg/kg	R %	t ("sink") mg/kg	R %
Pd	3.73	2.34	38.6	2.34	38.1
Ag	250.59	270.1	66.3	286	69.2
Pt	<0.05	<0.05		<0.05	
Au	19.27	8.49	27.1	6.18	19.5
Weight %		61.52		60.64	

Table 2.1-3: Experimental results of Test 1

Test 1

Test conditions:
Sample: Electronic waste from the original feed
Reagents : Pine Oil (Frother)
Particle size fraction: Original sample
Stirring Time: 2 min
Pulp % solids: 15%
pH: 7.5
Time of float removal : 1min
RPM : 900
Flotation cell volume: 1 liter

Content %					
Element	Original Sample	"Float"			"Sink"
		1	2	Mean	
As	-	-	0.0015	-	0.0015
Cd	-	0.0008	0.0006	0.0008	0.0041
Cu	3.19	0.74	0.68	0.72	4.73
Mn	1.00	2.22	1.50	2.02	0.33
Pb	0.67	1.02	0.55	0.89	1.04
Fe	4.40	8.85	6.26	8.15	2.06
Ni	0.11	1.83	1.11	1.64	0.31
Cr	0.01	0.01	0.02	0.01	0.01
Zn	0.85	1.70	1.14	1.55	0.72
Content (mg/kg)					
Pd	3.73	7.32	2.32	5.96	2.34
Ag	250.59	236.88	178.43	221	270.1
Pt	<0.05	<0.05	<0.05	<0.05	<0.05
Au	19.27	46.33	9.92	36.5	8.49
Weight %	100.00	28.01	10.47	38.48	61.52

Table 2.1-4: Experimental results of Test 2

Test 2 Test conditions: Sample: Electronic waste from the original feed Reagents : none Stirring Time: 2 min Pulp % solids: 15% pH: 7.0 Time of "float" removal : 1min RPM : 900 Flotation cell volume: 1 liter			
Content %			
Element	Original Sample	"Float"	"Sink"
As	-	-	0.0006
Cd	-	0.0006	0.0016
Cu	3.19	0.61	4.86
Mn	1.00	2.23	0.20
Pb	0.67	0.72	0.64
Fe	4.40	8.28	1.89
Ni	0.11	0.85	0.20
Cr	0.01	0.01	0.03
Zn	0.85	1.66	0.32
Content (mg/kg)			
Pd	3.73	5.87	2.34
Ag	250.59	196.03	286
Pt	<0.05	<0.05	<0.05
Au	19.27	39.43	6.18
Weight %	100.00	39.36	60.64

Table 2.1-5: Experimental results of Test 3

Test 3 Test conditions: Sample: Electronic waste from the original feed Reagents : Ca(OH)2 (pH regulator) Stirring Time: 2 min Pulp % solids: 15% pH: 10.0 Time of "float" removal : 1min RPM : 900 Flotation Cell volume: 1 liter			
Content %			
Element	Original Sample	"Float"	"Sink"
As	-	-	n.a.
Cd	-	0.0005	
Cu	3.19	0.43	
Mn	1.00	2.20	
Pb	0.67	0.52	
Fe	4.40	7.71	
Ni	0.11	1.87	
Cr	0.01	0.17	
Zn	0.85	1.55	
Content (mg/kg)			
Pd	3.73	4.72	n.a.
Ag	250.59	172.14	
Pt	<0.05	<0.05	
Au	19.27	30.06	
Weight %	100.00	38.24	61.76

Table 2.1-6. Experimental results of Test 4

Test 4 Test conditions: Sample: Electronic waste from the original feed Reagents: H2SO4 (pH regulator) Stirring Time: 2 min Pulp % solids: 15% pH: 5.0 Time of 'float" removal : 1min RPM : 900 Flotation Cell volume: 1 liter			
Content %			
Element	Original sample	"Float"	"Sink"
As	-	-	n.a.
Cd	-	0.0005	
Cu	3.19	0.89	
Mn	1.00	2.39	
Pb	0.67	0.61	
Fe	4.40	7.76	
Ni	0.11	1.83	
Cr	0.01	0.02	
Zn	0.85	1.83	
Content (mg/kg)			
Pd	3.73	5.41	n.a.
Ag	250.59	177.94	
Pt	<0.05	<0.05	
Au	19.27	37.73	
Weight %	100.00	27.89	72.11

Table 2.1-7. Experimental results of Test 5

Test 5

Test conditions:
Sample: Electronic waste from the original feed
Reagents : H2SO4 (pH regulator)
Stirring Time: 2 min
Solids: 15%
pH: 6.0
Time of "float" removal : 1min
RPM : 900
Flotation Cell volume: 1 liter

Content %					
Element	original sample	"Float			"Sink"
		1	2	Mean	
As	-	n.a.	n.a.	n.a.	n.a.
Cd	-				
Cu	3.19				
Mn	1.00				
Pb	0.67				
Fe	4.40				
Ni	0.11				
Cr	0.01				
Zn	0.85				
Content (mg/kg)					
Pd	3.73	5.43	4.35	5.27	n.a.
Ag	250.59	216.90	154.08	207.5	
Pt	<0.05	<0.05	<0.05	<0.05	
Au	19.27	35.45	17.61	32.80	
Weight %	100.00	36.94	6.45	43.39	56.61

2.2. Second Stage Tests and Results

The flotation tests of the 2nd stage were conducted on the two products (+1 mm and -1 mm) produced after size classification of the original feed sample on a laboratory sieve of 1 mm aperture, producing two size fractions +1 mm and -1 mm, respectively.

The experimental results and their assessment are given in Table 2.2-1 and the conditions of the tests in Tables 2.2-2 and 2.2-3, respectively.

Table 2.2-1: Experimental results of the "Floats" and "Sinks" of the 2nd stage

Element	Original sample	Feed -1 mm	Test 6	Test 7 (-1 mm)			
			c % ("float")	c % ("float")	R %	t % ("sink")	R %
As	-		n.a.			-	
Cd	-			0.0005		0.0007	
Cu	3.19	3.55		0.70	8.8	6.38	81.1
Mn	1.00	1.06		2.24		0.39	
Pb	0.67	1.55		0.91		2.16	
Fe	4.40	5.32		8.29	75.8	2.37	21.8
Ni	0.11	0.99		1.64		0.33	
Cr	0.01	0.012		0.01		0.014	
Zn	0.85	1.58		1.64		1.51	
				c ("float") mg/kg		t ("sink") mg/kg	
Pd	3.73	4.32		6.28	67.8	2.38	25.9
Ag	250.59	250.8		207.73	33.4	293.5	47.5
Pt	<0.05	<0.05		<0.05		<0.05	
Au	19.27	22		38.64	80.7	5.5	11.6
Weight %	100	80.83		40.25		40.57	

Table 2.2-2: Experimental results of Test 6

Test 6 Test conditions: Sample: Size classified of the original Electronic waste feed Reagents : none Particle size fraction: +1mm Stirring Time: 2 min Pulp % solids: 15% pH: 7.5 Time of "float" removal : 1min RPM : 900 Flotation cell volume: 1 liter				
Content %				
Element	Original sample	Feed +1 mm	"Float"	"Sink"
As	-		n.a.	n.a.
Cd	-			
Cu	3.19			
Mn	1.00			
Pb	0.67			
Fe	4.40			
Ni	0.11			
Cr	0.01			
Zn	0.85			
Content (mg/kg)				
Pd	3.73		n.a.	n.a.
Ag	250.59			
Pt	<0.05			
Au	19.27			
Weight %	100.00	19.15	1.85	17.3

Table 2.2-3. Experimental results of Test 7

Test 7 Test conditions: Sample: Classification by size of the original Electronic waste feed Reagents : none Particle size fraction: -1 mm Stirring Time: 2 min Pulp % solids: 15% pH: 7.5 Time of "float" removal : 1min RPM : 900 Flotation Cell volume: 1 liter				
Content %				
Element	Original sample	Feed -1 mm	"Float"	"Sink"
As	-	-		-
Cd	-	-	0.0005	0.0007
Cu	3.19	3.55	0.70	6.38
Mn	1.00	1.06	2.24	0.39
Pb	0.67	1.55	0.91	2.16
Fe	4.40	5.32	8.29	2.37
Ni	0.11	0.99	1.64	0.33
Cr	0.01	0.012	0.01	0.014
Zn	0.85	1.58	1.64	1.51
Content (mg/kg)				
Pd	3.73	4.32	6.28	2.38
Ag	250.59	250.8	207.73	293.5
Pt	<0.05	<0.05	<0.05	<0.05
Au	19.27	22	38.64	5.5
Weight %	100.00	80.83	40.25	40.57

2.3. Third Stage Tests and Results

Detailed tests conducted by adjusting solely the pH of the pulp, on samples from the two products (+0.5 and -0.5 mm), which obtained after classification of the original sample in a finer, than previously, sieve aperture size (0.5 mm). The experimental conditions of these flotation tests are shown in the respective tables. Table 5.12 shows the size distribution of the original feed in the two fractions and the distribution % of the useful metal values between the oversize (**+0.5 mm)** and the undersize (-0.5 mm) material. It is obvious that over 80% percent of the various useful metals (Cu, Fe, Pd, Ag and Au) report to the fine fraction -0.5 mm.

Table 2.3-1: Size classification results of the original feed on sieve aperture 0.5 mm and % distribution (R %) of metal values.

Test 8 Test conditions: Conventional laboratory sieving (Ro-tap machine) Sample: Original Electronic waste feed Size classification of the original sample on sieve 0.5 mm (two products, +0.5 and -0.5 mm)					
Content %					
Element	Original sample	+0.5mm	R(+), %	-0.5 mm	R(-), %
As	-	-		-	
Cd	-	0.0005		0.0015	
Cu	3.19	1.71	18.9	3.99	80.1
Mn	1.00	0.062		1.51	
Pb	0.67	0.03		1.02	
Fe	4.40	0.19	1.52	6.71	98.48
Ni	0.11	0.04		0.15	
Cr	0.01	0.0005		0.02	
Zn	0.85	0.32		1.14	
Content (mg/kg)					
Pd	3.73	0.32	3.0	5.59	97.0
Ag	250.59	118.5	16.5	323.2	83.5
Pt	<0.05	<0.05		<0.05	
Au	19.27	8.75	16.0	25	84.0
Weight %	100.00	35.26		64.74	

Table 2.3-2: Experimental results of "floats" of the 3rd stage (+0.5 mm) and recovery of useful metal values in the "floats of the "coarse" (+0.5 mm) size fraction.

Element	Original sample	Feed +0.5 mm	Test 8		Test 10	Test 13
			c % ("float")	R %	c % ("float")	c % ("float")
As	-	-	-			
Cd	-	0.0005	0.0002			
Cu	3.19	1.71	0.30	0.19		
Mn	1.00	0.062	0.41			
Pb	0.67	0.03	0.17			
Fe	4.40	0.34	1.98	0.9		
Ni	0.11	0.04	0.36			
Cr	0.01	0.0005	0.01			
Zn	0.85	0.32	0.46			
Element	Original sample	Size fraction +0.5 mm	c ("float") mg/kg	R %	c ("float") mg/kg	c ("float") mg/kg
Pd	3.73	0.32	1.29	0.7	1.30	0.48
Ag	250.59	118.5	48.17	0. 4	42.31	17.60
Pt	<0.05	<0.05	<0.05		<0.05	<0.05
Au	19.27	8.75	12.25	1.28	11.35	12.93
Weight %	100	35.26	2.02		15.01	35.99

Table 2.3-3: Experimental results of the "sinks" of the 3rd stage (+0.5 mm) and recovery R %.

Element	Original sample	Feed +0.5 mm	Test 8		Test 10	Test 13
			t % ("sink")	R %	t % ("sink")	t % ("sink")
As	-	-	0.0003		0.0005	
Cd	-	0.0005	0.0004		0.0002	
Cu	3.19	1.71	1.82	19.0	1.75	
Mn	1.00	0.062	0.04		0.03	
Pb	0.67	0.03	0.09		0.05	
Fe	4.40	0.34	0.24	1.81	0.28	
Ni	0.11	0.04	0.06		0.05	
Cr	0.01	0.0005	0.02		0.02	
Zn	0.85	0.32	0.37		0.34	
Element	Original sample	Size fraction +0.5 mm mg/kg	t ("sink") mg/kg	R %	t ("sink") mg/kg	t ("sink") mg/kg
Pd	3.73	0.32	0.26	2.32		
Ag	250.59	118.5	121.8	16.15		
Pt	<0.05	<0.05	<0.05			
Au	19.27	8.75	8.45	14.6		
Weight %	100	35.26	33.24		29.97	22.57

Table 2.3-4. Experimental results of the "floats" of the 3rd stage (-0.5 mm) and recovery R %.

Element	Feed -0.5 mm	Test 9		Test 11		Test 12	
		c % ("float")	R %	c % ("float")	R %	c % ("float")	R %
As	-						
Cd	0.0015			0.0008			
Cu	3.99			0.56	6.4		
Mn	1.51			1.88			
Pb	1.02			0.52			
Fe	6.71			8.53	76.3		
Ni	0.15			1.33			
Cr	0.02			0.01			
Zn	1.14			0.88			
Element	Feed -0.5 mm (mg/kg)	c mg/kg	R %	c mg/kg	R %	c mg/kg	R %
Pd	5.59	5.72		7.87	83.0	6.63	
Ag	323.2	194.53		236.1	37.1	183.90	
Pt	<0.05	<0.05		<0.05		<0.05	
Au	25	38.06		39.4	80.5	36.48	
Weight %	64.74	36.21		39.36		38.72	

Table 2.3-5: Experimental results of the "sinks" of the 3rd stage (-0.5 mm) and recovery R %.

Element	Feed -0.5 mm	Test 9		Test 11		Test 12	
		t % ("sink")	R %	t % ("sink")	R %	t % ("sink")	R %
As	-	-		-			
Cd	0.0015	0.0006		0.0027			
Cu	3.99	8.2		9.3	74.0		
Mn	1.51	0.61		0.92			
Pb	1.02	2.61		4.02			
Fe	6.71	2.78		3.89	22.5		
Ni	0.15	0.54		0.77			
Cr	0.02	0.04		0.06			
Zn	1.14	1.84		1.95			
Element	Feed -0.5 mm (mg/kg)	t mg/kg	R %	t mg/kg	R %	t mg/kg	R %
Pd	5.59			2.03	13.8	n.a.	
Ag	323.2			458.2	46.4		
Pt	<0.05			<0.05			
Au	25			2.67	3.52		
Weight %	64.74	25.2		25.4		26.02	

Table 2.3-6: Experimental results of Test 8

Test 8 Test conditions: Sample: Size classification of the original sample on sieve 0.5 mm Reagents : Pine Oil (frother) Particle size fraction: +0.5mm Stirring Time: 2 min Pulp % solids: 15% pH: 6.7 Time of "float" removal : 1min RPM : 900 Flotation cell volume: 1 liter				
Content %				
Element	Original sample	Feed + 0.5 mm	"Float"	'Sink"
As	-	-	-	0,0003
Cd	-	0.0005	0.0002	0,0004
Cu	3.19	1.71	0.30	1.82
Mn	1.00	0.062	0.41	0,04
Pb	0.67	0.03	0.17	0,09
Fe	4.40	0.19	1.98	0,24
Ni	0.11	0.04	0.36	0,06
Cr	0.01	0.0005	0.01	0,02
Zn	0.85	0.32	0.46	0,37
Content (mg/kg)				
Pd	3.73	0.32	1.29	0.26
Ag	250.59	118.5	48.17	121.8
Pt	<0.05	<0.05	<0.05	<0.05
Au	19.27	8.75	12.25	8.45
Weight %	100.00	35.26	2.02	33.24
			35.26	

Table 2.3-7: Experimental results of Test 9

Test 9

Test conditions:
Sample Size classification of the original sample on sieve 0.5 mm
Reagents : Pine Oil (frother)
Particle size fraction: -0.5mm
Stirring Time: 2 min
Pulp % solids: 15%
pH: 6.7
Time of "Float" removal : 1min
RPM : 900
Flotation cell volume: 1 liter

Content %					
Element	Original sample	Feed -0.5 mm	"Float" 1	"Float" 2	"Sink"
As	-	-	n.a.	n.a.	-
Cd	-	0.0015			0.0006
Cu	3.19	3.99			8.2
Mn	1.00	1.51			0.61
Pb	0.67	1.02			2.61
Fe	4.40	6.71			2.78
Ni	0.11	0.15			0.54
Cr	0.01	0.02			0.04
Zn	0.85	1.14			1.84
Content (mg/kg)					
Pd	3.73	5.59	5.72	n.a.	n.a.
Ag	250.59	323.2	194.53		
Pt	<0.05	<0.05	<0.05		
Au	19.27	25	38.06		
Weight %	100.00	64.74	36.21	3.38	25.15

Table 2.3-9. Experimental results of Test 10

Test 10

Test conditions:
Sample: Size classification of the original sample on a sieve 0.5 mm
Reagents : Ca(OH)2 (pH regulator)
Particle size fraction: +0.5mm
Stirring Time: 2 min
Pulp % solids: 15%
pH: 8
Time of "float" removal : 1min
RPM : 900
Flotation cell volume: 1 liter

Content %					
Element	Original sample	Feed +0.5 mm	"Float" 1	"Float" 2	"Sink"
As	-	-	n.a.	n.a.	0.0005
Cd	-	0.0005			0.0002
Cu	3.19	1.71			1.75
Mn	1.00	0.062			0.03
Pb	0.67	0.03			0.05
Fe	4.40	0.19			0.28
Ni	0.11	0.04			0.05
Cr	0.01	0.0005			0.02
Zn	0.85	0.32			0.34
Content (mg/kg)					
Pd	3.73	0.32	1.30	0.43	n.a.
Ag	250.59	118.5	42.31	25.54	
Pt	<0.05	<0.05	<0.05	<0.05	
Au	19.27	8.75	11.35	1.88	
Weight %	100.00	35.26	1.62	3.67	29.97

Table 2.3-10: Experimental results of Test 11

Test 11

Test conditions:
Sample: Size classification of the original sample on a sieve 0.5 mm
Reagents : Ca(OH)2 (pH regulator)
Particle size fraction: -0.5mm
Stirring Time: 2 min
Pulp % solids: 15%
pH: 8
Time of "float" removal : 1min
RPM : 900
Flotation cell volume: 1 liter

Content %						
Element	Original sample	Feed -0.5 mm	"Float" 1	"Float" 2	Mean "Float" c %	"Sink"
As	-	-	-	-		-
Cd	-	0.0015	0.0008	0.0007	0.0008	0.0027
Cu	3.19	3.99	0.61	0.27	0.56	9.3
Mn	1.00	1.51	2.08	0.68	1.88	0.92
Pb	0.67	1.02	0.55	0.32	0.52	4.02
Fe	4.40	6.71	9.65	2.02	8.53	3.89
Ni	0.11	0.15	1.48	0.46	1.33	0.77
Cr	0.01	0.02	0.01	0.009	0.01	0.06
Zn	0.85	1.14	0.95	0.48	0.88	1.95
Content (mg/kg)						
Pd	3.73	5.59	8.5	4.37	7.87	2.03
Ag	250.59	323.2	246.4	176.52	236.1	458.2
Pt	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
Au	19.27	25	45.08	6.4	39.4	2.67
Weight %	100.00	64.74	33.56	5.79		25.4
			39.36		39.36	25.4

Table 2.3-11: Experimental results of Test 12

Test 12

Test conditions:
Sample: Size classification of the original sample on a sieve 0.5 mm
Particle size fraction: -0.5 mm
Reagents : H2SO4 (pH regulator)
Stirring Time: 2 min
Pulp % solids: 15%
pH: 6.0
Time of "Float" removal : 1min
RPM : 900
Flotation Cell volume: 1 liter

Content %					
Element	Original sample	Feed -0.5 mm	"Float" 1	"Float" 2	"Sink"
As	-	-	n.a.	n.a.	n.a.
Cd	-	0.0015			
Cu	3.19	3.99			
Mn	1.00	1.51			
Pb	0.67	1.02			
Fe	4.40	6.71			
Ni	0.11	0.15			
Cr	0.01	0.02			
Zn	0.85	1.14			
Content (mg/kg)					
Pd	3.73	5.59	6.63	6.33	n.a.
Ag	250.59	323.2	183.90	204.39	
Pt	<0.05	<0.05	<0.05	<0.05	
Au	19.27	25	36.48	29.32	
Weight %	100.00	64.74	32.93	5.79	26.02

Table 2.3-12: Experimental results of Test 13

Test 13

Test conditions :
Sample: Size classification of the original sample on a sieve 0.5 mm
Particle size fraction: + 0.5mm
Reagents : H2SO4 (pH regulator)
Stirring Time: 2 min
Pulp % solids: 15%
pH: 6.0
Time of Concentrate removal : 1min
RPM : 900
Flotation cell volume: 1 liter

Content %					
Element	Original sample	Feed +0.5 mm	"Float" 1	"Float" 2	"Sink"
As	-	-	n.a.	n.a.	n.a.
Cd	-	0.0005			
Cu	3.19	1.71			
Mn	1.00	0.062			
Pb	0.67	0.03			
Fe	4.40	0.19			
Ni	0.11	0.04			
Cr	0.01	0.0005			
Zn	0.85	0.32			
Content (mg/kg)					
Pd	3.73	0.32	0.49	0.48	n.a.
Ag	250.59	118.5	18.15	17.60	
Pt	<0.05	<0.05	<0.05	<0.05	
Au	19.27	8.75	3.34	22.93	
Weight %	100.00	35.26	1.37	11.33	22.57

2.4. Enviromental Characterization of Pulps

In order to proceed with the environmental characterization process, the pulps obtained, after filtration of the flotation products, were investigated for the presence of metals and metalloids (As, Cd, Cu, Mn, Pb, Fe, Ni, Zn and Cr). After sampling, all liquids were immediately stored below 4◦C, for purposes of adequate preservation and before any chemical analysis.

Namely six (6) samples were examined, according to DIN EN ISO 11885 and DIN EN ISO 17294 by utilizing Inductively Coupled Plasma Spectrometry (ICP – AES / Prodigy – Teledyne, Leeman Labs) and Atomic Absorption Spectroscopy (AAS – Hitachi Z2000). Results are presented in the following table (Table 2.4-1)

Table 2.4-1: Chemical Analysis of Pulps for purposes of environmental characterization (all values in mg/l)

Pulp Code	As	Cd	Cu	Mn	Pb	Fe	Ni	Cr	Zn
EpH 5	<0.01	0.01	<0.005	0.58	<0.01	<0.01	<0.005	<0.005	5.12
EA	<0.01	<0.005	<0.005	0.014	<0.01	<0.01	<0.005	<0.005	0.21
EpH 10	<0.01	<0.005	<0.005	<0.005	<0.01	<0.01	<0.005	<0.005	<0.005
E8	<0.01	<0.005	<0.005	<0.005	<0.01	<0.01	<0.005	<0.005	0.011
Ex	<0.01	<0.005	<0.005	0.014	0.018	<0.01	<0.005	<0.005	0.22
Eo	<0.01	<0.005	0.023	0.083	<0.01	<0.01	<0.005	<0.005	0.52

For purposes of adequate results interpretation, is critical to identify the conditions (pH and solvent) the flotation products were subjected to, prior to filtration. In Table 2.4-2, those conditions are illustrated. As it is shown in Table 2.4-2, pH values are consistent with the solvent used for each sample (e.g acidic pH for when H2SO4 is used).

Table 2.4-2: pH and Solvent used for elaborating flotation products, prior to filtration

Pulp Code	Average pH	Solvent Used
EpH 5	5.0	H2SO4
EA	7.0	Tap Water
EpH 10	10.0	Ca(OH)2 solution
E8	8.0	Ca(OH)2 solution (plus foaming)
Ex	7.0	Tap Water
Eo	6.0	H2SO4 (plus foaming)

Generally, metals concentrations are presented low in all tested samples. Especially in EpH10 pulp, all metals concentrations (including Zn and Mn) are non-detectable. That was expected, due to the strongly alkaline pH conditions. Very low concentrations are also illustrated in alkaline sample E8, where only a small concentration of Zn (11 ppb) is detected.

Zinc and Manganese are the only metals with almost constant presence in all tested samples. As shown from Table 2.4-1, sample EpH5 possessing an acidic pH (= 5). That is the reason for relatively high concentrations of Zn and Mn in the liquid, since both metals present high dissolution rates under those pH conditions (Vogel et al., 2000). For both metals, their concentrations in the pulp are at least one order of magnitude higher than all other tested samples. A small portion of Cadmium (10ppb) is present in that sample, also attributable to the low pH environment (Vogel et al., 2000). Nevertheless, a small increase to pH value (from 5 to 6 for sample E0) decreases significantly both Zn and Mn concentrations. Copper is detected only in sample E0 (23 ppb) and Pb only in sample Ex (18 ppb). Iron, nickel, chromium and arsenic are not detected in any tested sample.

Greek legislation (Ministerial Decision 145116 / Official Gazette 354B'/8-3-2011: Determination of measures, terms and procedures for treated wastewater reuse) provides limit values for the presence of certain metals and metalloids in treated wastewater for purposes of possible reuse. Those values are presented in Table 2.4-3:

Table 2.4-3. Maximum allowable concentrations of metals and metalloids for treated wastewater prior any possible reuse

Element	Max Concentration (mg/l)
As	0.1
Cd	0.01
Cu	0.2
Mn	0.2
Pb	0.1
Fe	3.0
Ni	0.2
Zn	2.0
Cr	0.1

Comparing values presented in Tables 2.4-1 and 2.4-3, it is observed that only sample EpH5 may considered slightly problematic in terms of each further management, since Mn and Zn concentrations are exceeding the proposed limit values.

2.5. Conclusions from the float tests

From the preliminary work performed in the Laboratory of Mineral Processing (NTUA) under the frame of the present research work, it was verified that a natural hydrophobicity exists, a stable froth was observed even without the addition of any frother reagent.

The "report" of the useful metal values to the "floats" or the "sinks" could be effectively controlled during the flotation procedure, by pH alteration or the use of a flotation reagent. Thus, many of the metals were found to report to the foam (float) phase, while some other metals demonstrated a distinct preference for the sink product. Plastics and lightweight material are easily removed with the "floats", without the addition of any reagent, just by stirring and aeration of the pulp.

From the precious metals, Au and Pd showed an explicit "tendency" to report in the "floats" and Ag to the "sink", while the other metals of economic value (Cu and Fe) go to the "floats" or the "sinks", respectively.

The classification of the original sample into two size fractions (+0.5 mm and -0.5 mm) is helpful for the flotation, since the majority of the plastics and the lightweight material report in the "coarse" (+0.5 mm) fraction, while the metals report in the "undersize" or "fine" fraction (-0.5 mm), Table 2.3-1.

The distribution of the metals with economic value in the "fine" (-0.5 mm) fraction is Cu 80.1%, Fe 98.48%, Pd 97.0%, Ag 83.5% and Au 84.0%. After flotation of the "fine" fraction, the recovery of the metals is as follows: Au 80.5%, Pd 83.0%, Ag 37.5% and Fe 76.3% in the "floats", while for Cu 74.0% and Ag 46.4% in the "sinks".

It was noted that Ag presents an indifferent behavior between the "floats" and the "sinks". The higher values for Au 39.4 mg/kg and Pd 7.87 mg/kg were noted in the "floats" of the -0.5 mm size fraction, while the higher values for Cu and Ag were 9.3% and Ag 458.2 mg/kg, respectively, in the sink product of the same test (Test 11, Tables 5.15, 5.16 and 5.20).

The experimental results of the -1 mm treatment agree with the above findings (Tables 2.1-1 and 2.1-3). It is expected that, removing the ultrafine material (-0.045 mm, -45μm) prior of flotation, might be supportive to the success of the flotation procedure.

Finally, it was concluded that it is necessary to investigate the flotation more extensively as a method of recovery of the useful metals (Cu, Au, Pd and Ag) from e-wastes. Perhaps, applying a factorial design investigation of the tests, could clarify the "effect" of the various operating parameters on the process. This would lead to the optimization of the flotation process applied on the PCBs processing.

Chapter 3. Difficulties - Deviations

The major difficulty that was encountered was the absence of e-waste quantities from the landfill excavated waste. Thus, the results obtained and presented in the above paragraphs were estimated using e-waste from other sources obtained especially for beneficiation process, in an attempt to assess the most promising method to recover/reuse the valuable materials.