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To cite this article: Maria Grazia Bonelli *et al* 2019 *IOP Conf. Ser.: Earth Environ. Sci.* **289** 012002

View the article online for updates and enhancements.

Lead collection after automatic components removal from printed circuit boards as a "novel" process for noble metals recovery from WEEE

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Abstract. In recent years, the recovery of noble metals from WEEE (Waste Electrical and Electronics Equipment) has received great attention in the academic and industrial community since it highly contributes to decrease the cost of the recycling and/or disposing of the short life cycle of electronic devices. Noble metals are mainly present in Printed Circuit Boards (PCBs) which are normally sold in bulk to specialized companies or sent to "recycling sites" where they may be open burned creating a great environmental concern. An alternate route is to further subject the PCB to a manual or automatic dismantling of the integrated circuits and chips. After a study conducted on more than 20.000 kg of WEEE, it has been shown that easily removable parts will account for 13,01% of the PCB w/w (0,75% of the whole sample) but will contain 89,50% of gold (2109 ppm). Since the removed parts are low in weight but highly enriched, lead collection could become a viable process for noble metal recovery. The main components of the above parts are the Silicon wafers. Since no bibliographic information is available on this kind of "gold matrix" the aim of the present study has been to assess the best quantity of the flux primary components (litharge, sodium bicarbonate, anhydrous borax) to enhance gold recovery. Results greater than 90% have been assessed.

1. Introduction

According to the European Commission, the waste stream of electronics and electrical equipment (WEEE) has been identified as one of the fastest growing waste streams in the EU, currently being less in quantity than Municipal Solid Waste (MSW) but increasing, annually by more than the growth of MSW. Each European inhabitant produces about 20 kg each year.

The Waste Electrical and Electronic Equipment Directive (WEEE Directive) 2002/96/EC, issued by the European Commission aims to minimise the impact of end-of-life electrical and electronic goods on the environment, by increasing re-use and recycling and then reducing the amount of WEEE used for landfill.

A decision of the Commission stated that, within December 2006, 4 kg WEEE/inhabitant should have been collected yearly. Nevertheless, at present, more than 14,7 kg/inhabitant are collected in

Sweden, but only 1,6 kg/inhabitant in Romania. Furthermore, the WEEE Directive 2012/19/EU introduced an new annual collection target defined as the ratio between the collected amount and the average weight of EEE put on the market in the three preceding years. The collection target is set at 45% in 2016 and will rise to 65% in 2019. According to the data, only 1 EU Member States (Bulgaria) over 22 has already reached the target [1].

Virtually all electrical and electronic equipments contain printed circuit boards (PCB) that are currently incinerated in order to recover metals from the ashes, leading to the formation of toxic organohalogen compounds and heavy metal vapors which cause considerable health problems to the workers and to the human communities surrounding the workplaces. These problems are very eminent in developing countries where non-formal operators are extracting precious metals through crude means for easy money. The extraction of metals in non-formal units is carried out by dipping PCBs in the acidic/alkaline solutions or by PCB's heating/burning. These processes are flourishing in India, Ghana, Nigeria, Vietnam as well as in China through the network involving collectors, traders and unorganized recyclers [2][3]. As consequence increased levels of pollutants soil, sediments and body fluids has been reported; in particular PAHs and BrPAHs [4] [5], Polychlorinated Biphenyls, DDT, HCB, HBCD [6] PBDE, Cd, Pb, Hg, As [7] [8] dioxin [9] and dechlorane [10]. It is felt that just enacting laws and routine vigilance, the growing business of non-formal sector cannot be stopped. It is appropriate to provide an alternative source of income to nearly millions of people, involved in this profession. One of the aims of the present work is to find an alternative process easy enough to be used from unskilled people and creating less environmental concerns.

WEEE are currently sorted and disassembled and PCB are separated as an isolated waste stream [11]. It has been estimated that printed circuit boards comprise approximately 4-6 wt% of all WEEE. They contain mainly metals (40 wt%), ceramic materials (30%) and plastics (30 wt%). Recycling of printed circuit boards is difficult due to the complex structure of the boards and wide material composition. They also contain precious metals such as gold, silver and palladium which increase the interest to find economically viable recycling technologies to recover such metals. In this paper, the use of fire assay as a means to recover gold from printed circuit boards of waste electrical and electronic equipment after a manual sorting procedure [12] or the use of an automatic components removal procedure is assessed. The main components of the above parts are Silicon wafers. Since no bibliographic information were available on this kind of "gold matrix" the aim of the present study has been to assess the best quantity of the flux primary components (litharge, sodium bicarbonate, anhydrous borax) to enhance gold recovery.

2. Materials and methods

2.1. Sample preparation

"Easy to remove" (ETR) integrated circuits and computers processors were manually dismantled from PCB (printed circuit boards) from 3 WAEE's categories, namely computers, TV monitor and computers monitors.

The total sample, worked out in 14 days, accounted to 20961 kg. The categories mentioned above were respectively 0,77%, 0,37% and 4,4% by weight. Precious metals contents are reported in table 1 modified after Delfini et al, 2011 [12]. Weights and grades of recoverable gold from the easy-to-remove components of three different types of printed circuit boards found in a 14 days sample.

It is noteworthy that ETR components did contain more than 95% of all PCB's gold, but they only weighed a small fraction of the total sample's weight (0,114%), namely 1,71 kg/day.

A 230g sample, composed by ETR chips and integrated circuits, was crushed to -5 mm in a laboratory jaw crusher (Denver Inc., USA type H); chemical analysis are shown on Tab. 2.

In order to establish the gold liberation grade, the sample was milled into a bar mill (Jar mill, Denver Inc., USA) with different time intervals and analysed. The bar mill was cleaned at the end of every test with silica powder; the latter has been analysed and gold amount found into it was added to

the sample concentration. Results are shown in figure 1. Good recovery was already obtained after 6 minutes milling. Size distribution at this time is shown in Tab. 3. Longer milling time was not employed in order to avoid loss of gold due to the adhesion of the metallic grains on the surface of the mill. This procedure did generate a poorly representative sample related to the size distribution, due to the small volume of material employed in the fire assay, and in the rest of the work it forced us to separately analyze either the bullion, the slag and the crucible in order to reconstitute the metals content in each sample.

Table 1. Amount of ETR components in a 20961 kg sample

Easy-to-remove components[1]	Weight[2]	Au	
Computer PCB	(%)	(mg/kg)	(mg/day)
-Processors	0,027	7004	2831
-Integrated Circuits	0,073	701	766
Monitor PCB			
-Integrated Circuits	0,006	154	14
TV PCB			
-Integrated Circuits	0,008	315	38
Total ETR[3]	**0,114**	**2137**	**3649**
Total ETR kg	**23,9**		
Total ETR kg/day	**1,71**		

1)   subjectively evaluated by the operators;
2)   respect to 20961 kg (total WAEE collected in 14 days);
3)   ETR: easy-to-remove components.
(Modified after Delfini et al, 2011)

Table 2. Chemical analyses of an "ETR components" 230 g sample

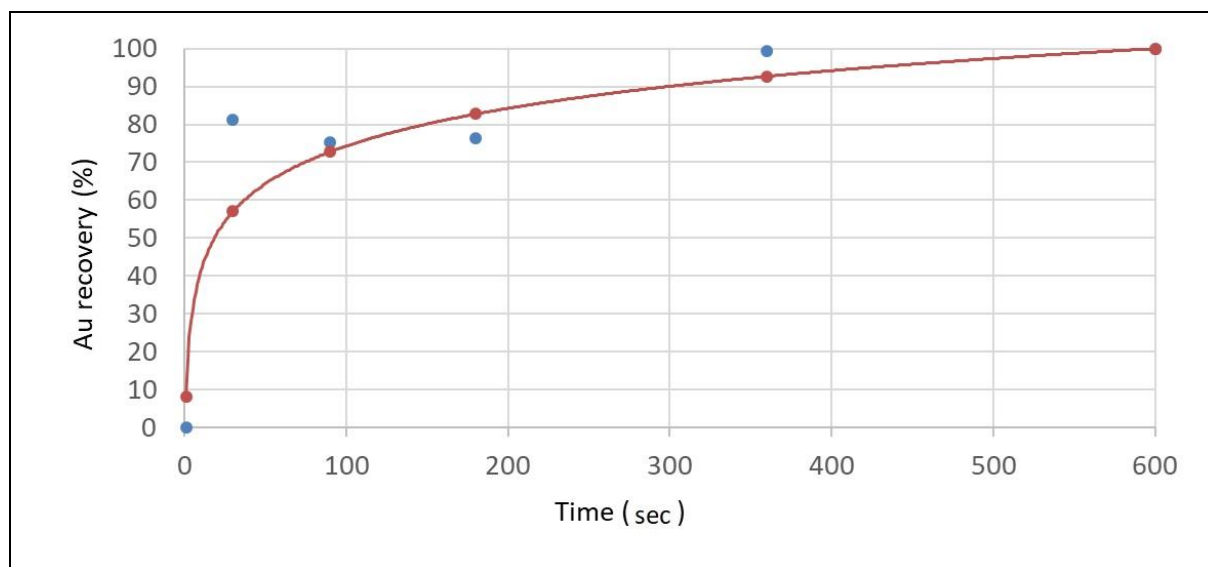| Au	Fe	Cu	Ni	Pb	Sn
(mg/kg)	(%)	(%)	(%)	(%)	(%)
701	4,9	13,5	3,3	1,6	3,2

Figure 1. Extractable gold of ETR components after bar milling at different time intervals

Table 3. Size distribution of the 230 g ETR components sample used in the rest of the work

Size	Weight	Weight	Cumulative passing
(μm)	(g)	(%)	(%)
+2000	9,75	11,86	88,14
-2000+1000	9,51	11,57	76,57
-1000+500	11,53	14,03	62,54
-500+250	16,77	20,40	42,14
-250+125	13,90	16,91	25,23
-125+75	7,45	9,06	16,17
-75+38	12,70	15,45	0,72
-38	0,59	0,72	0,00
Total	82,20	100,00	

2.2. Pyrometallurgy and analytical chemistry assessment

In order to investigate the applicability of the lead collection to recover gold and precious metals from ETR, two preliminary tests were performed according to the method described by Treadwell [13]. The first test was employed to determine the reducing power of the sample. 1,0062 g of sample was carefully mixed in a porcelain crucible with 16,00 g of PbO, 4,00 g of $NaHCO_3$, 1,00 g of Sodium tetraborate decahydrate. The crucible was placed in a muffle furnace (Megatron Inc., USA model ZE) and the temperature raised from room to 1000 °C in 2 hours; melted sample was maintained at this temperature for 30 minutes.

The second test was employed to verify the possibility of the recovery of precious metals from a significative quantity (5 g) of sample: the amount of the reagent to employ in this second assay was calculated from the weight of the lead "bullion" got in the first test. The assay was performed in the same condition of time and temperature of the first test. The weight of the "bullion" obtained was

higher than the weight expected for this test and it was probably due to the bad representativity of the second sample.

Subsequent assays were performed in order to find out a suitable method of precious metal extraction together with the volume reagents minimization. 5 g of dried sample was weighted in beaker on a 0.1 milligram readability balance and the fluxes were added according to the table specified in experimental section of this paper. Sample and reagents were stirred in the beaker to obtain a homogeneous mix, transferred into a Morgan crucible and ignited at the same conditions reported above. After the fusion in muffle furnace at 1000 °C for 30 min, the crucible was extracted, cooled and broken along the longitudinal axis; the bullion of lead containing the precious metals was extracted and cleaned and the slag separated from the crucible.

Both bullion and slag were treated with diluted nitric acid to solubilise metals forming insoluble chlorides ($PbCl_2$ and $AgCl$); the residue was dissolved in aqua regia to analyse gold.

Crucible, containing only a small quantity of slag was directly dissolved in aqua regia, as the solubility of AgCl in concentrate hydrochloric solutions was sufficient at the sample silver concentration [14]. Both nitric and aqua regia solutions obtained were analysed to determinate Au, Ag and Cu.

Pd, Ag, Cu, Sb, Zn and Co were also determined.

The bullion was solved in beaker on hot plate after the addition of diluted HNO_3. After sample breakdown, deionised water was added and temperature raised to boiling point to dissolve the nitrates formed. The solution was filtered and the filter containing the residue was ignited in muffle furnace at 550°C and, after cooling, digested in aqua regia (1:3 HNO_3:HCl).

The slag and the crucible were weighted, crushed in a jaw crusher under 2 mm and then undergone the same process reported for the bullion.

Measurements of all solutions were carried out, in triplicate, by means of ICP-OES (Perkin-Elmer Plasma 400) equipped with a monochromator with a spectral range of 160-800 nm covered by two gratings. After calibration with NIST traceable standards (O2SI Llc, Charleston, SC, USA), the elements were analysed at the wavelength showing the best signal/noise ratio. No noteworthy interferences were noted. In order to prevent AgCl precipitation, HCl 1:1 (v/v) was employed to prepare standard, blank and flushing solutions.

3. Results

Fire assay is a very old method to determine the metal content of an ore containing noble metals such as gold, platinum and silver. In the mining industry a typical sample of 30 grams is used for fire assaying. Fluxes such as borax, soda, silica are added to the ore, mainly constituted by SiO_2, in order to decrease the melting point and imparting a homogeneous fluidity to the melted oxide impurities. Lead oxide is added to the ore. The solubility of precious metals in lead, as well as the insolubility of base metals is the basis of the process. The ore sample with the fluxes and lead are then added to a crucible, placed in a furnace, heated to 1370 K, and left there to melt for up to 1 hour. Then the crucible is removed from the assay furnace and allowed to cool. The lead, containing the gold, being the heaviest material in the slag will be on the very bottom. When the slag cools, the lead button is separated from the lighter material and recovered. Accuracy in sampling, preparation, assaying, handling, weighing is extremely important in fire assaying, due to the very small absolute gold quantity in the starting material.

In case of WEEE materials, as reported above, the main constituent of "the ore" is Silicon chips. Metals are mainly present in their elemental form and not as derivatives (sulfides, carbonates, silicates, etc.)
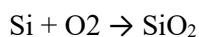
The chemistry of the lead collection is therefore different than gold mining and can be described in the following equations:

1) Silicon oxidation and PbO reduction to metallic Pb
Silicon oxidation by lead dioxide

$Si + 2PbO \rightarrow 2Pb + SiO_2$ [15]
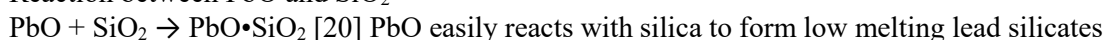
Silicon oxidation by Oxygen

$Si + O2 \rightarrow SiO_2$

PbO reduction by metals (M) with relative reduction potential less than -0,13 E°/V

(React. collector: Pb(II) +2e- = Pb0) [21]

$M + PbO \rightarrow MO + Pb$ [16]

2) Silica reaction with litharge flux

Reaction between PbO and SiO_2

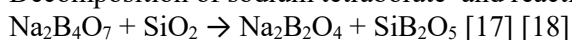$PbO + SiO_2 \rightarrow PbO \cdot SiO_2$ [20] PbO easily reacts with silica to form low melting lead silicates

3) Silica reactions with other fluxes

Decomposition of sodium carbonate by reaction with silicon dioxide to form sodium silicate

$Na_2CO_3 + SiO_2 \rightarrow Na_2SiO_3 + CO_2\uparrow$ [18]

Decomposition of sodium tetraborate and reaction with silicon dioxide

$Na_2B_4O_7 + SiO_2 \rightarrow Na_2B_2O_4 + SiB_2O_5$ [17] [18]

4) Reaction of metals oxides with B_2O_3

$MeO + B_2O_3 = Me(BO_2)_2$ [17] [18]

Most important covalent oxides have oxygen bonded to form three-dimensional networks: the complex structure of the obtained glass may involve a considerably larger variety of basic structural oxides units [19].

All tests were performed in duplicate and the results reported in table 4 are the average of two measurements.

Table 4. Feed and Au recovery for the test performed

Test	Sample	PbO	Na_2CO_3	$Na_2B_4O_7$	Au recovery
(number)	(g)	(g)	(g)	(g)	(%)
00	1,6800	16,0000	2,5232	0,0000	96,11
1	8,4456	133,9550	21,1337	8,3680	98,74
2	5,0245	79,8820	0,0000	0,0000	93,48
3	5,3197	80,5470	20,0740	0,0000	96,33
4	5,0632	60,4480	12,5530	5,0020	95,66
5	5,0703	40,2450	12,5547	4,9870	95,12
6	5,0434	20,0476	12,6551	5,0171	99,24
7	5,0039	9,9529	12,5469	4,9738	98,80
8	5,0437	5,0187	12,6498	5,0184	99,09
9	5,0902	2,6362	12,6574	5,0184	94,41
10	5,0483	5,0605	0,0000	0,0000	57,39

Recovery of other metals in the bullion has been assessed on test 6. Results are reported on table 5.

Table 5. Recovery of other metals from the bullion

Pd	Ag	Cu	Sb	Zn	Co
(%)	(%)	(%)	(%)	(%)	(%)
58,95	99,20	84,49	8,07	4,29	0,57

4. Discussion

The experimental plan has been statistically analysed (JMP software from SAS, ver.13.2.1, USA). Sample and reagents weights were used as input variables; bullion weight, Au recovery was used as output parameter.

Input data has been normalised by considering each of them as the proportion of total amount of the feed. The corresponding date are shown in Table 6.

Table 6. Model input and output variable after normalization

Test (number)	Sample (%)	PbO (%)	Na_2CO_3 (%)	$Na_2B_4O_7$ (%)	Au recovery (%)
00	8,32	79,20	12,49	0,00	96,11
1	4,91	77,93	12,29	4,87	98,74
2	5,92	94,08	0,00	0,00	93,48
3	5,02	76,03	18,95	0,00	96,33
4	6,10	72,77	15,11	6,02	95,66
5	8,07	64,03	19,97	7,93	95,12
6	11,79	46,88	29,59	11,73	99,24
7	15,41	30,65	38,63	15,31	98,80
8	18,19	18,10	45,62	18,10	99,09
9	20,04	10,38	49,83	19,76	94,41
10	49,94	50,06	0,00	0,00	57,39

Data have been studied applying the standard least square fitting model. It has been demonstrated that data are in good agreement with the linear equation:

$$\text{Au recovery (\%)} = 10{,}94*Sample + 11{,}75*PbO + 11{,}95*Na_2CO_3 + 12{,}01*Na_2B_4O_7 - 1077{,}37$$

showing a R-Square of 0,98 and RMSE of 2,38 at p-value <0,0001. Then, the fitting model is statistically significant. Figure 2 shows the actual/model predicted gold recovery values.
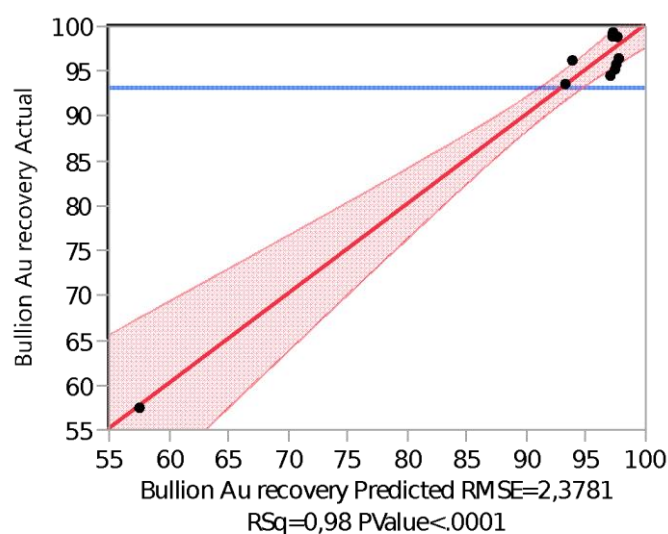

Figure 2. Actual/Predicted Au values by least square predicting model for Au recovery from lead collection reagents.

Feed reagents maximum desirability has been demonstrated to be 56% PbO, 22% Na_2CO_3, 14% Sample, 8% $Na_2B_4O_7$, as shown in figure 3.
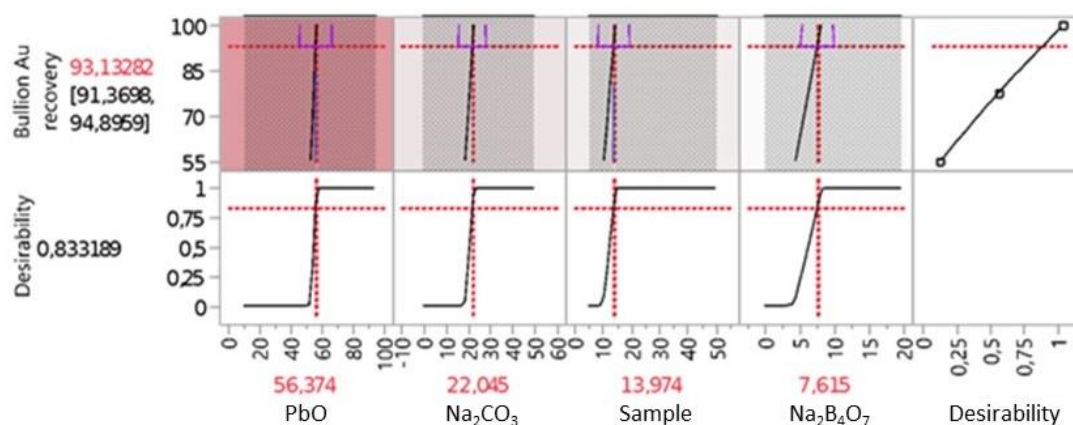

Figure 3. Feed components desirability

Considering the Pearson's correlation matrix (table 7), multicollinearity between independent variables has been observed.

Multicollinearity is usually a problem, because it can increase the variance of the coefficient estimates and make the estimates very sensitive to minor changes in the model. The result is that the coefficient estimates are unstable and difficult to interpret. A possible solution can be to remove highly correlated predictors from the model by a stepwise regression.

Table 7. Correlation matrix

	Sample	PbO	Na_2CO_3	$Na_2B_4O_7$	Au_rec
Sample	1	-0,464	-0,046	0,055	-,883**
PbO	-0,464	1	-,859**	-,887**	0,017
Na_2CO_3	-0,046	-,859**	1	,942**	0,481
$Na_2B_4O_7$	0,055	-,887**	,942**	1	0,384
Au_rec	-,883**	0,017	0,481	0,384	1

**Correlation is significative at level 0,01 (two tails)

In fact, stepwise regression is a way to set up a model by adding or removing predictor variables, depending on statistic tests (F-test or T-test) of the estimated coefficients. Unlike the standard least square regression, the stepwise regression can detect how the variables removed or added to the fitting model can provide valuable information about its quality.

In this study, a stepwise regression has been conducted, in order to determine the most significant input variables to Au recovery.

13 possible models (tab. 8), in forward selection method, has been analyzed: in each step, a predictor to the equation has been added.

Table 8. Stepwise regression results: all possible models

Model	Number	RSquare	RMSE	AICc	BIC
Sample	1	0,7798	5,9455	77,6558	75,4209
Na2CO3	1	0,2314	11,1089	91,4082	89,1733
Na2B4O7	1	0,1475	11,6994	92,5477	90,3128
PbO	1	0,0003	12,6695	94,3001	92,0652
Sample, PbO	2	0,9764	2,0631	58,3130	53,2379
Sample,Na2CO3	2	0,9740	2,1668	59,3916	54,3165
Sample,Na2B4O7	2	0,9674	2,4255	61,8731	56,7980
PbO,Na2CO3	2	0,9369	3,3756	69,1451	64,0700
PbO,Na2CO3,Na2B4O7	3	0,9765	2,2040	65,6306	55,6201
Sample,Na2CO3,Na2B4O7	3	0,9765	2,2043	65,6341	55,6236
Sample,PbO,Na2B4O7	3	0,9765	2,2044	65,6351	55,6246
Sample,PbO,Na2CO3	3	0,9765	2,2044	65,6352	55,6247
Sample,PbO,Na2CO3,Na2B4O7	4	0,9765	2,3781	76,6075	57,9948

To choose the best model between all them, the maximum R-Square, the minimum corrected Akaike Information Criterion (AICc) and the minimum Bayesian Information Criterion (BIC) has been used.

Therefore, the best of all possible models has two predictive variables, Sample and PbO, with a R-square of 0,976 and Root Mean Square Error (RMSE) of 2,06, and the stepwise linear equation is:

$$\text{Au recovery (\%)} = 119,8 - 1,025*\text{Sample} - 0,220*\text{PbO}$$

It is noteworthy that the four variables model is exactly the same already described in least square fitting model.

Results mentioned above show that Silicon chips and PbO could be considered as a self-fluxing matrix being able to form a suitable slag for Au recovery maximization.

Findings from this work could be applied to setup a laboratory scale gold automatic recovery facility from WEEE printed circuit boards (PCBs).

Automation will be obtained from the coupling of an automatic component's removal from WEEE PCBs (stage 1) to an automatic lead collection phase (stage 2). In the last part of the process (stage 3), Au, as well as all other precious metals, will be recovered from anode muds produced by lead electrowinning [22].
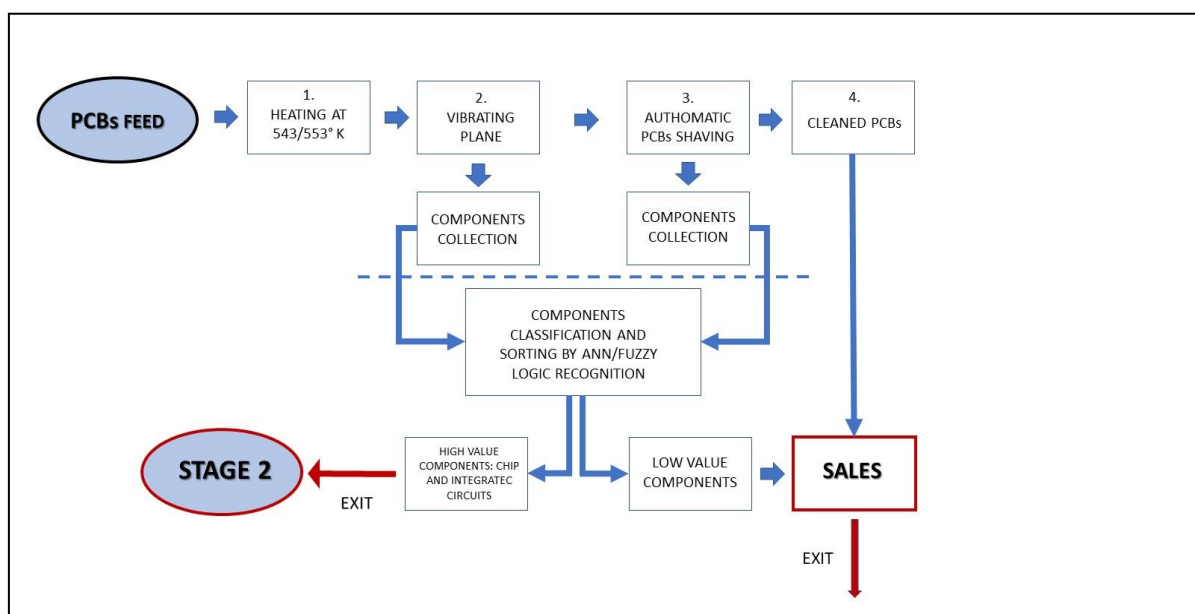
Figure 4. Stage 1: automatic component's removal from PCBs [23]

During stage 1, as shown in figure 4, PBCs are heated to 543/553 K in order to remove the soldering. Tin is recovered. Heat generation happens through the employment of blowing apparatus and electric resistances controlled by thermocouples. Most of the components are simply removed by means of vibration. All remaining components are mechanically shaved from the PCBs [23]. Integrated circuits and chips are classified ("sensed") and sorted ("gripped") on a moving conveyor belt [24] by 3D vision technique coupled to artificial neural network/fuzzy logic recognition technique and then separated by a robotic system. They are then fed to Stage 2. Low value components and cleaned PCBs maintain a residual value and they are sold out without any further manipulation. In the present paper the flux blend has been optimized for rapid fusion, insignificant metal entrainment and effective quantitative transfer of Au to the lead collector phase; Stage 2 can be achieved when furnace and slag separator are integrated and designed for robotic manipulation and materials handling as already described from McIntosh et al. [25].

Lead bullion electrowinning will be performed in agreement with the Betts process. Lead will be recycled.

5. Conclusions

WEEE PCBs chips and integrated circuits account for less than 1% in weight of the total WEEE but around 90% of the gold contained in them. Under these circumstances, "Lead collection" represents an efficient recovery method. The main purpose of the present work has been to find the best flux characteristics being able to allow phases separation (lead on the bottom, slag on top), to control the viscosity throughout the fusion (no residual metal in the slag and a sharp metal/slag interface) and lower the melting point of the sample. Interactions between sample weight and flux primary components (litharge, sodium bicarbonate and anhydrous borax) have been studied. Results show that this "gold matrix" is self-fluxing and gold recovery higher than 95% can be achieved by simply adding litharge to it. This kind of finding can be used to set up an automated process constituted by a WEEE PCBs components removal and sorting followed by lead collection and electrowinning. Gold, as well as the other precious metals, will be recovered from the anode muds.

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