Mass Flow Analysis and Metal Losses by the Degradation Process of Organic-Containing WEEE Scraps

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In the past years the topic of WEEE recycling has gained more relevance due to increased production and reduced effectiveness in metal recovery. Therefore, new processing technologies are evolving today as result of the increasing heterogeneity of WEEE. Such is the case of pyrolysis as an upgrading and conditioning method for different types of complex scraps, which also facilitate further mechanical separation of metal as well as production of an alternative fuel source. In this work, it has been concluded that pyrolysis can be easily integrated as a preprocessing step in a resource efficient recycling route.

Keywords: Autothermic smelting, Mechanical separation, Pyrolysis, Pyrometallurgy, Recycling route, WEEE

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1 Preface

The electronic industry provides devices which in the recent years have become essential in modern life. However, strong competition encourages the industry to produce improved performance of devices, increase number of features and reduced production costs in each generation of products, which bring the balance between production, waste generation and recycling processes to its unsustainability. It was estimated for the year 1998 that Europe produced about 6 million tons of waste electrical and electronic equipment (WEEE), in 2005 the WEEE arising was about 8.3 and 9.1 million tons being 4 % of the municipal waste and expecting to grow annually between 2.5 and 2.7 % reaching about 12.3 million tons in 2020. In Europe, there are several directives and regulations that aim to stimulate WEEE production, recycling and disposal such as the WEEE Directive [1]. The existence of such directives has clarified the horizon to develop a new generation of products and to develop more safe recycling processes in Europe. However, the path is still long to cover non-European electronic devices and have reliable recycling processes.

The world has moved from relatively simple devices with few elements to incredible complex technologies including a large variety of elements. These elements are used as chemical compounds, as metal alloys and in some special cases as pure metal. Therefore, the new electronic devices represent due to their complexity and miniaturization a real challenge for the end-of-life product processers.

The wide spectrum of elements in WEEE goes from base metals, precious metals, critical metals, different types of plastics, to some harmful elements. The so-called critical metals are used mostly in scarce quantities and are distributed in different components like printed circuit boards PCBs (e.g., platinum group metals (PGMs), precious metals (PMs), Sb, Ta, rare earth elements (Ta, Nd), Fe, Al, Cu, Pb, Ni, Sn, As, Ba, Br, Bi); liquid crystal displays LCD screens (e.g., indium as indium tin oxide ITO), light emitting diode LED (e.g., Ga, In and REs (Gd, Ce, Tb, Eu, Y, La, Sm, Lu, Tm, Dy), getters (e.g., W, Ta), fluorescent powders (e.g., La, Tb, Eu, Y, Ce), hard disks (e.g., PGMs), flame retardants (e.g., Sb), CRT glass (e.g., Sb) and batteries (e.g., Co, REs like Ce, LA, Nd, Pr) [2]. Quantities of base metals and precious metals vary from time to time according to their applications.

2 Challenges in WEEE Recycling

There are many attempts to stablish a certain path for WEEE recycling. This is however not easy since WEEE is a mixture of different components which require special preprocessing techniques for their recycling and recovery. The general mechanical preprocessing begins with hand sorting and removal procedures of hazardous containing elements such as mercury switches, capacitors, etc. The material follows then a conditioning stage through size reduction and screening steps. Size reduction can be conducted through shredders, hammer-mills or sphere-mills. The cri-

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terion on which equipment is more appropriate depends on the desired selectivity and particle size. The separation of ferrous from non-ferrous metals normally takes place in conveyor belts with an initial magnetic separator followed by an eddy current separator [3].

Typical metallurgical recycling facilities using a common smelter have a processing capacity of about 1000 t of input material per day from which only 10 % correspond to WEEE [4]. Previous work at IME has demonstrated that the top blown rotary converter TBRC is a feasible unit capable to recycle electronic scrap autothermically using 100 % of WEEE as feedstock material. The enormous potential of this unit for recycling of complex organic containing scraps is obvious [5]. Without making any distinction from the melting unit, this requires an intensive offgas treatment system, which includes waste heat boilers to recover heat from the offgas and an electrostatic separator (ESP) to recover fine dust, sulphur and other environmentally hazardous substance.

The efficiency in Europe (with BAT) for metallurgical recovery of precious metals, especially gold, is 95 %, which is considered to be relatively high compared with the efficiency during collection (~60 %) and during the mechanical preprocessing (~25 %). From literature, it is known that elements like Ta, In, Te, Ga, Se and rare earth elements (REs) account for recovery rates smaller than 1 %. Whereas base metals and precious metals are being recovered in more than 50 %, which technologically speaking it is feasible to recover them from WEEE [6].

Probably for WEEE, the mechanical preprocessing has the biggest impact in the recycling rate of the base metals as well as precious metals. Metals ending in the wrong fraction will hinder its recovery. Data suggest that for precious metals the recovery of silver is only 11.5 %, for gold is 25.6 %, and for palladium is 25.6 %. Precious metals are used in PCBs in contacts, connectors, solders, and hard disk drives with capacitors, integrated circuits, plastics in PCBs tracks, interboard layers, etc. Therefore, after shredding the PMs are mainly dispersed in the small pieces still containing a magnetic part, which are pulled out during the strong magnetic separation (Fe-fraction), as well as dispersed in the dust produced during the strong shredding process. In the case of copper, iron and aluminum, the estimated recovery is about 60 %, 95.6 %, and 75 %, respectively [7].

3 Recycling Concept

The new recycling concept developed at IME seeks the optimization in both the preprocessing and metallurgical recycling of worthy metals from WEEE. This recycling concept is realized taking the following statements:

1) Purely mechanical preprocessing increases the metal losses. Therefore, manual dismantling combined with mechanical preprocessing increases the metal recycling rate.
2) Stronger shredding for more size reduction of PCBs will lead to distribution of precious metals in all output fractions.
3) Implementation of a thermic process for PCBs like pyrolysis will permit easier separation of metals and non-metals, which ultimately would encourage the development of new intermediate processes for recovery of some metals in minor concentration like Ta and some RE metals.
4) Pyrolyzed fines would have to undergo an agglomeration process through pelletizing or briquetting for feeding in the smelter.
5) Avoid unnecessary material separation process to prevent dissemination of precious metals in other streams.

The standard mechanical preprocessing of WEEE would be applied to devices that do not contain a major portion of organics and for which the standard mechanical preprocessing fulfils the required recycling quote. However, for devices that contain considerable amount of organics, plastics and non-recyclable valuable metals a separation is necessary either at the manual separation stage or after preshredding to avoid intensive grinding of, e.g., PCBs and to produce a rich fraction of them. For the scope of this work a low organic content scraps (LOC scrap) and a high organic content scraps (HOC scrap) are of relevance. For both fractions pyrolysis is used as a preprocessing method, allowing a better separation of the metallic and non-metallic fraction which ultimately will favor the recycling quote of the different valuable metals in WEEE.

As shown in Fig. 1, the approach used for this study aims to determine the impact of pyrolysis in the materials flow of some valuable base metals from WEEE. The present study begins with the study of the degradation of organics in the scrap, respective halogen removal and elemental distribution in the different pyrolysis products. In the following sections, the impact of pyrolysis applied to low organic content scrap as a preprocessing method will be evaluated. The whole recycling steps will be taken into account, which means that mechanical preprocessing as well as metallurgical assessments of products will be presented.

4 Pyrolysis of Organic-Containing Scraps

Pyrolysis is a process that involves chemical and thermal decomposition, where the principal objective is to break down the macromolecular structure of polymeric materials into smaller molecules known as monomers or oligomers. The degradation of the polymeric structure can be explained by Eq. (1) as follows:

$$\text{organic(s)} \rightarrow \text{cokes(s)} + \text{gaseous components} \qquad (1)$$

The gaseous components, however, can be farther divided in non-condensable gases and condensable gases. The later can be transformed into oil (normally constituted of naph-

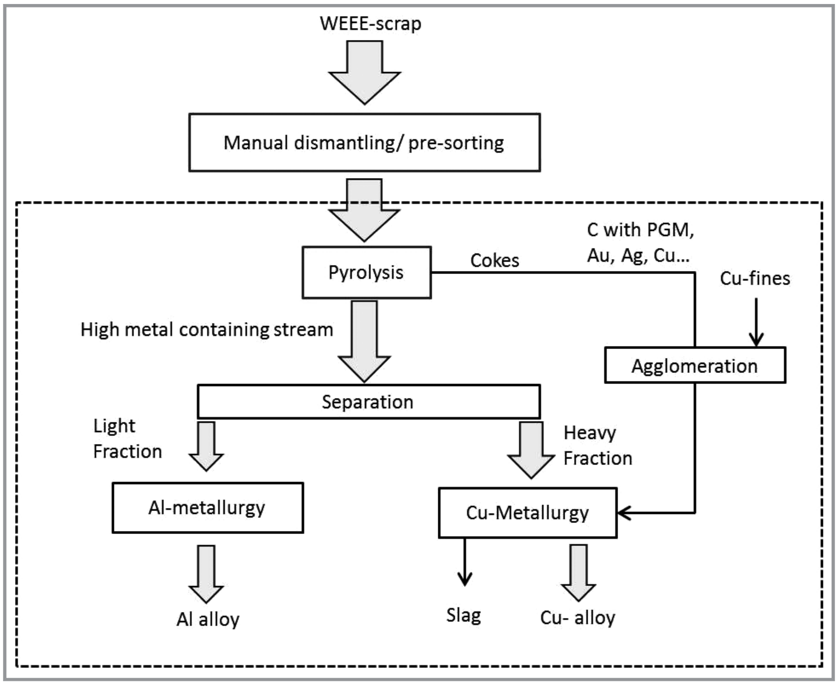

Figure 1. High recovery recycling route (dotted line: IME research approach).

thenes, aromatics, paraffins and olefins). The way in which a polymer decomposes during the pyrolytic reaction has several mechanism to proceed that in most of the cases involve the scission of the chain (by its end or randomly along it) and the stripping of side groups or elements not inherent to the polymeric chain. Yet, the way in which the polymer is decomposed and the products generated are to a certain extent related to the bond dissociation energies, the chain defects of the polymer and the presence of additives in the chain such as halogens and heteroatoms. In Fig. 2 the thermal degradation of the organic material upon temperature is shown [8, 9].

The redistribution of elements during the pyrolysis is one of the advantageous characteristics of pyrolysis, as it is known to be a viable dehalogenation process. Electric and electronic equipment (EEE) contain brominated flame retardants (BFRs) to reduce their potential of flammability. Though, the presence of halogenated flame retardant compounds is a concern during the preprocessing stages as they might become sources of high toxicity during heating.

During the pyrolysis process, halogens (Br and Cl) as well as antimony (alternative to halogenated flame retardant) are collected in the gases, oil and solid residue according to the substrate and on pyrolysis conditions. Despite the advantage of strong reduction of halogens from the solid materials there is still a major concern of appropriated treatment of oil and gases due to the added value for these complex treatments to the total recycling process. [8]

4.2 Experimental Setup

As already mentioned, the experiments were designed for a set of two waste materials that are distinguishable from each other by the high and low content of organic material. The material with the highest content of organic material is naturally the most attractive when it is desired to visualize the degrading process of pyrolysis over the organic matter. However, for the case of LOC scrap it can be said that the pyrolysis will have a degrading effect over the small organic fraction, while the metallic part will be upgraded in the product.

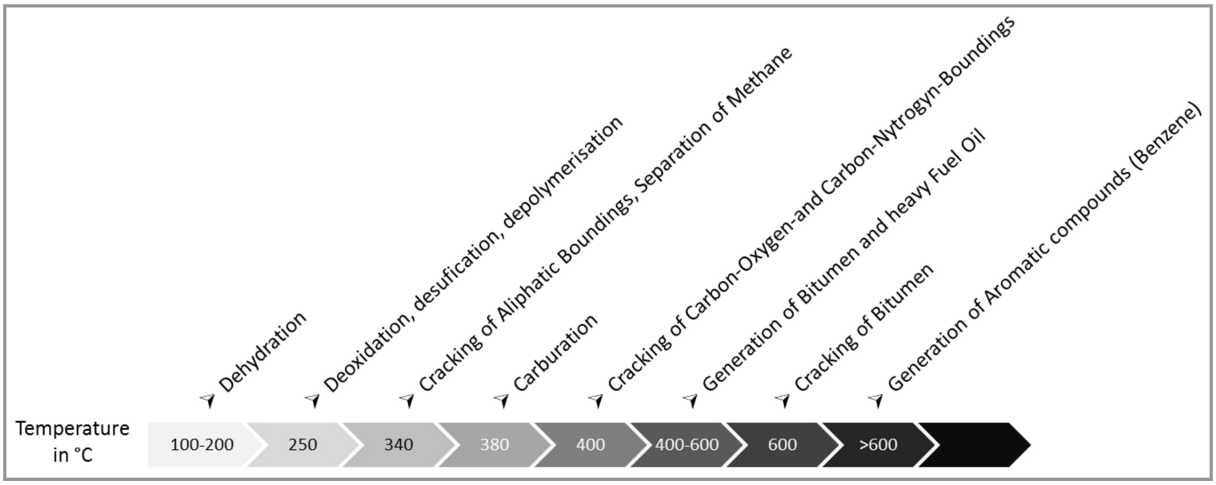

Figure 2. Thermal decomposition of organic material to temperature [10].

The pyrolysis experiments for the HOC scraps were divided into two main setups. Experiments dedicated for analysis of solid and condensates were conducted at temperatures of 500 and 700 °C, under a protective atmosphere with nitrogen and atmospheric pressure. In contrast, the experiments for the analysis of the evolution of gases were conducted at 600 °C and under constant flow of 3 L min^{-1} of argon. The produced gases were analyzed with an online Fourier transform infrared spectroscopy (FTIR) measuring device. With the above conditions it was possible to study the time, temperature and state dependency of HOC scrap over the onset of the pyrolysis reaction and the evolution of gases and solid residue. The final product after the pyrolysis of the HOC scrap is characterized later through grinding and sieving in order to obtain a metallic and a non-metallic fraction.

4.2.1 Organic Degradation and Halogen Distribution

A process of cryogenic milling was utilized in order to characterize the non-metallic content of the input material, such as O, H, C, N and halogens since these elements will be the most modified after the pyrolysis. The input material is composed of epoxy resin particles together with glass fiber material. As can be seen in Tab. 1, additional to carbon, oxygen is also found. It is probable that it derives from SiO_2, Al_2O_3 and other oxides which make up the glass fibers used to re-inforce the polymeric matrix in printed circuit boards and are not degraded by the pyrolysis process. Among the halogen elements, Br is the one with the highest contribution to the composition. The calorific value of the input material is around 13 MJ kg^{-1}, which is relatively high when compared to the calorific value of a common solid fuel such as coal (27 – 31 MJ kg^{-1}).

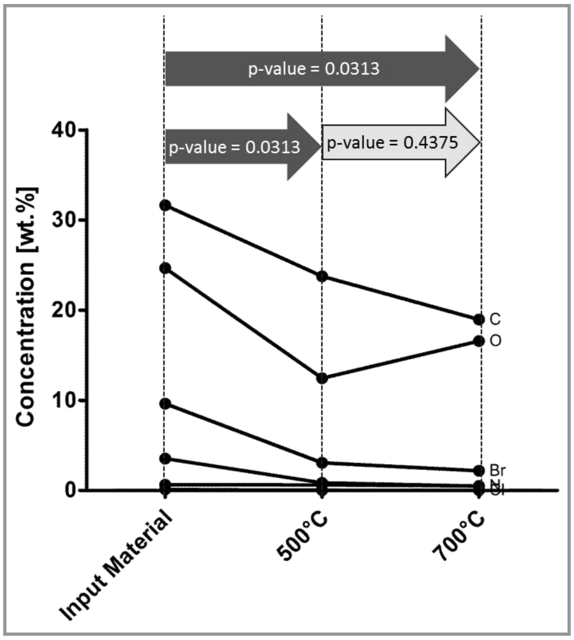

Figure 3. Comparison between input material and resulting solid residue after pyrolysis at 500 and 700 °C (dark grey: statistically significant change, p-value < 0.05; light grey: not significant change, p-value > 0.05).

The pyrolysis of the HOC scrap produces a non-condensable gas, a condensable liquid/oil and a friable solid. The composition of C, O, H, N and halogens (such as Cl and Br) in the solid product is shown in Fig. 3. In overall it can be seen that carbon is the element that possess the highest concentration followed by oxygen. It is clear that in all cases the concentration after pyrolysis decreases with respect to the concentration of the input material. In any case, it is not clear if there is a relationship or a significant change between the values of the input material, the solid residue at 500 °C and the solid residue at 700 °C.

For this reason, a very simple statistical method to demonstrate the significance between two measured phenomena is based upon the *p*-value. The first step is the selection of a null hypothesis, which is a statement that there is no relationship between two measured phenomena. The validity of this statement will be proved with the evidence given by the data and the statistics that go along with it. In order to test the hypothesis, a *p*-value is used which measures the strength of the evidence or in other words what the data is telling about the population. A small *p*-value (typically ≤ 0.05) indicates strong evidence against the null hypothesis, that means rejection of the null hypothesis. In contrast, a large *p*-value (> 0.05) indicates weak evidence against the null hypothesis, implying a failure to reject the null hypothesis while, a *p*-value close to the reference (0.05) is considered to be marginal, meaning they could go either way.

After running the statistical results with the program GraphPad Prism 5, the *p*-value was determined. For the first two cases where the input material is compared to pyrolyzed material it is clear that the measurements are significant between each other. In the graph the grade of significance is depicted with a dark grey arrow which means that this change is statistically significant. However, judging for the case where the results of the two solid residues are compared, the *p*-value indicates that

Table 1. Organic degradation and halogen removal from HOC scrap after pyrolysis.

	Cl [wt %]	Br [wt %]	C [wt %]	O [wt %]	H [wt %]	N [wt %]	C_p [kJ kg^{-1}]
Input Material	0.12	9.62	31.65	24.66	3.54	0.64	13687.6
Solid product (500 °C)	0.03	3.06	23.76	12.44	0.84	0.62	10222.2
Solid product (700 °C)	0.03	2.19	18.97	16.57	0.49	0.50	8054.9

there is no significant change and is depicted with a light grey arrow.

The liquid (condensate) obtained after the pyrolysis was constituted of an aqueous compound and oil. From Tab. 2, it can be seen that from the liquid condensate 126.72 mL kg^{-1} HOC scrap and 132 mL kg^{-1} HOC scrap of oil were produced during pyrolysis at 500 and 700 °C, respectively, while 113.28 mL kg^{-1} HOC scrap and 118 mL kg^{-1} HOC scrap accounted for the aqueous compound at 500 and 700 °C, respectively. Note that the 60 wt % of carbon in the oil accounts for a calorific value of 27 MJ kg^{-1}, revealing its enormous potential as fuel. The aqueous compound has a calorific value of less than 1000 kJ kg^{-1}, proving that water is its main constituent.

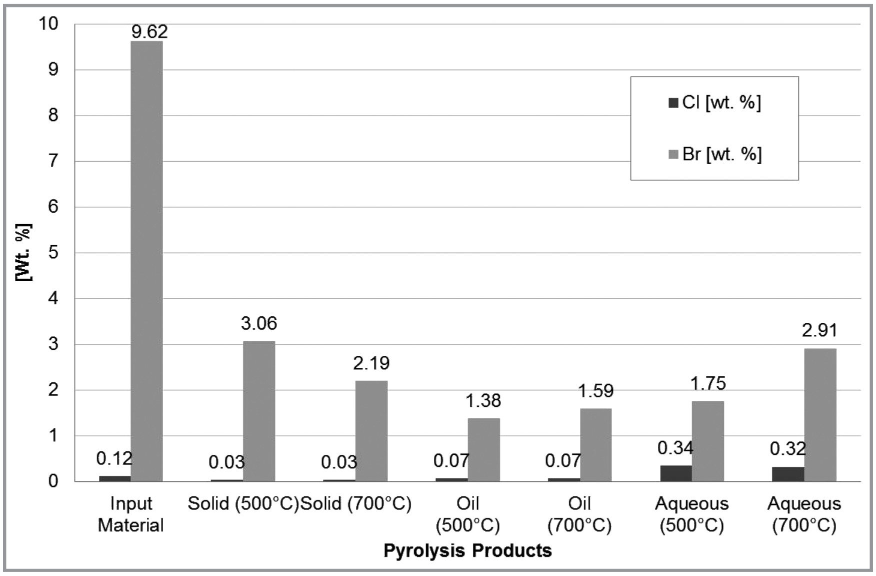

Figure 4. Halogen distribution in the pyrolyzed products at 500 and 700 °C: solid and liquids.

The existence of an aqueous compound can be due to reactions among oxygen containing functional groups and the oxidation of hydrogen. In contrast, it is very likely that the oil is composed of functional groups like aromatic and aliphatic hydrocarbons, phenolic compounds and complex compounds with C_5 to C_{15} structures. Another fact that supports this assumption is the C/H atomic ratio for the oils (500 and 700 °C) which in both cases approached 0.7. Note that values between 0.70 – 0.8 indicate that aromatic compounds are the dominant fraction in the liquid yield. These characteristic makes the oil as a potential chemical or fuel feedstock in industry.

As seen in Fig. 4 increasing pyrolysis temperature makes the dehalogenation process (mostly Br and Cl) more extensive. The non-metallic fraction of HOC scrap before pyrolysis exhibits a concentration of 9.62 % of Br and 0.12 % of Cl. After the pyrolysis at 500 °C the Br concentration is decreased by 68 % and the concentration of Cl by 78 %. At 700 °C the decrease is more apparent, showing 77 % reduction for Br and 79% for Cl. Naturally, the reduction of halogens in the organic fraction will lead to condensation in the liquid and consequently increased concentration of these elements in the aqueous compound and oil.

Table 2. Composition of the condensate obtained after pyrolysis of HOC scrap.

	C [wt %]	H [wt %]	N [wt %]	Water [wt %]	Volume [mL kg^{-1}]	C_p [kJ kg^{-1}]
Oil (500 °C)	59.60	7.54	1.44	10.20	126.7	28410.0
Oil (700 °C)	60.10	7.52	1.56	16.60	132.0	26660.0
Aqueous (500 °C)	4.53	9.41	1.74	91.10	113.3	< 1000
Aqueous (700 °C)	4.62	9.41	2.06	86.00	118.0	< 1000

The gas evolution during the pyrolysis of HOC scrap exhibits a behavior which might be related to its physical properties. As this material is highly composed of printed circuit boards, the characteristically compact layer structure might be responsible for the evolution of a compact gas profile as shown in Fig. 5. In other words, the layered structure of the material influences the way in which the sample heating initially starts at the surface and moves progressively into the inner layers before a stable temperature is reached through the whole material.

In agreement to Fig. 2 and as seen in Fig. 5, the thermal decomposition of HOC scrap exhibits a deoxidation and desulfurization due to the formation of CO at 275 °C and the later formation of SF_6 and SO_2 around 290 °C, respectively. The existence of CO_2 and CO is most likely due to the decomposition of epoxy groups or calcium carbonate in the polymer. It is also clear that for the majority of the aliphatic and aromatic compounds the maximal concentration peaks are reached between 290 and 300 °C forecasting already the cracking of their bonds around 320 – 340 °C. It is the cracking of these that produces free hydrogen atoms and a hydroxyl (–OH) group that will join to form water. For this reason the dehydration of water does not take place between 100 – 200 °C, but around 320 °C.

In regard to the halogen compounds, no brominated compounds were detected except for HBr, which started to form around 310 °C and reached a concentration peak (60 ppm) at 320 °C. It was also found that the concentration of compounds containing fluorine was higher than for bromine compounds. Judging from the results, it can be said that a pyrolysis conducted at 400 °C is sufficient to start the thermal decomposition of HOC scraps.

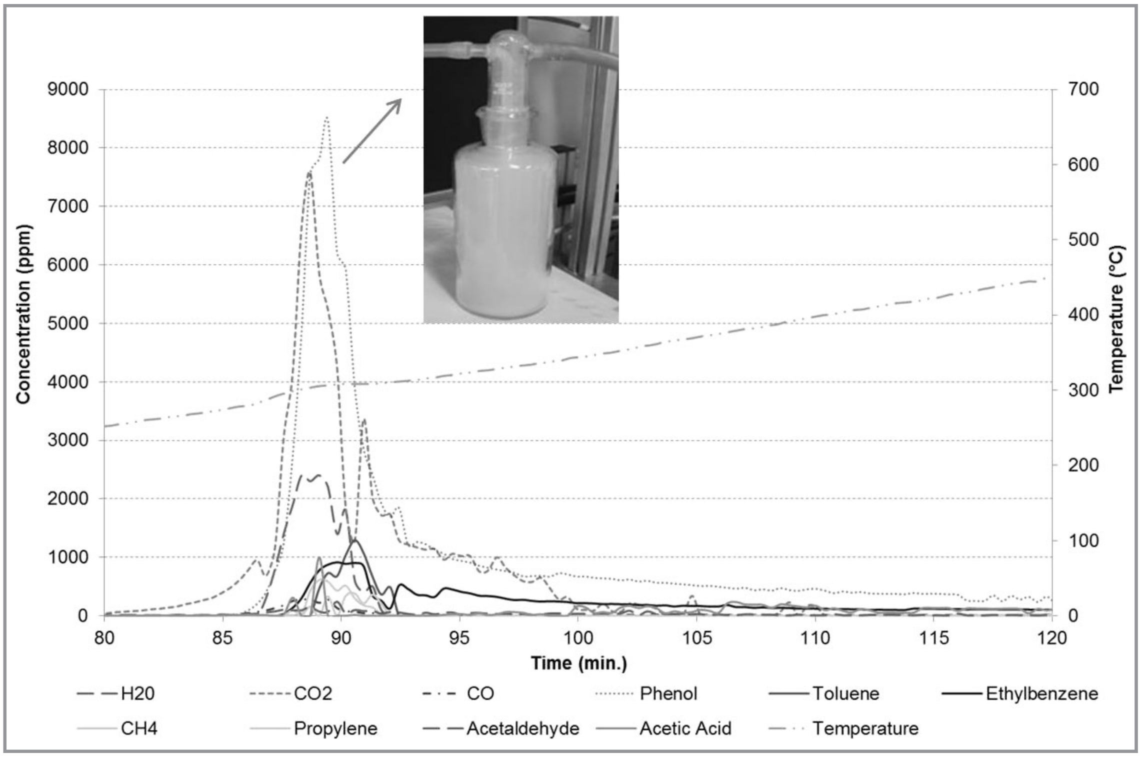

Figure 5. Evolution of the syngas during pyrolysis of HOC.

4.2.2 Material Analysis of the Solid Residues

The metal upgrading of HOC scrap after pyrolysis is shown in Tab. 3. Consequently Fig. 6 compares the metal content (wt %) for the input material and the solid residue resulting from 500 and 700 °C. It is evident that copper is the metal with the highest concentration with almost 17 wt %, followed by silicon and calcium. An important feature from the figure is the tendency of metals to exhibit an increase of concentration after the pyrolysis. So is the case for copper whose concentration is increased about 10 wt % after the pyrolysis. This phenomenon can be explained since during the pyrolysis only elements like C, H, O and halogens are affected, but in principle the metallic structure should remain unaffected.

The statistical significance was measured for the metal concentration values for the input material and the solid product after 500 and 700 °C. It was found that the values for the input material and solid residue at 500 °C are highly significant. The same behavior is observed for the case of the input material and the solid residue at 700°C. For the values of 500°C and 700°C no statistical significance was found. This can be interpreted that pyrolysis has a direct relation over the concentration of the metal elements in the HOC scraps, no matter if the pyrolysis is conducted at 500 or 700 °C. However, the fact that there is no statistical significance between metal concentration in the solid between 500 and 700 °C probably suggest that a pyrolysis at 500 °C is sufficient in order to increase the metal concentration at least 10 wt %.

5 Mechanical Separation After Pyrolysis

LOC scraps are characterized by their high metallic content, mostly aluminum and copper plus a reduced content up to 20 % of organic material. The last one is derived in many of the cases by plastic pieces that remain attached to the metallic portion as is common in electrical applications. For this reason, the treatment of this kind of scrap results in a more

Table 3. Metal upgrading of HOC scraps after pyrolysis.

	Ag [ppm]	Au [ppm]	Cu [wt %]	Zn [wt %]	Sn [wt %]	Pb [wt %]	Ni [wt %]	Sb [wt %]	Al [wt %]	Si [wt %]	Ca [wt %]	Fe [wt %]
Input material	226	6.52	15.26	0.12	1.73	0.77	0.02	0.22	1.61	5.30	3.87	0.10
Solid product (500 °C)	235	12.58	27.14	0.14	3.18	1.45	0.00	0.39	2.57	8.24	6.29	0.17
Solid product (700 °C)	567	10.25	26.38	0.28	2.88	1.25	0.06	0.39	3.10	10.43	7.32	0.19

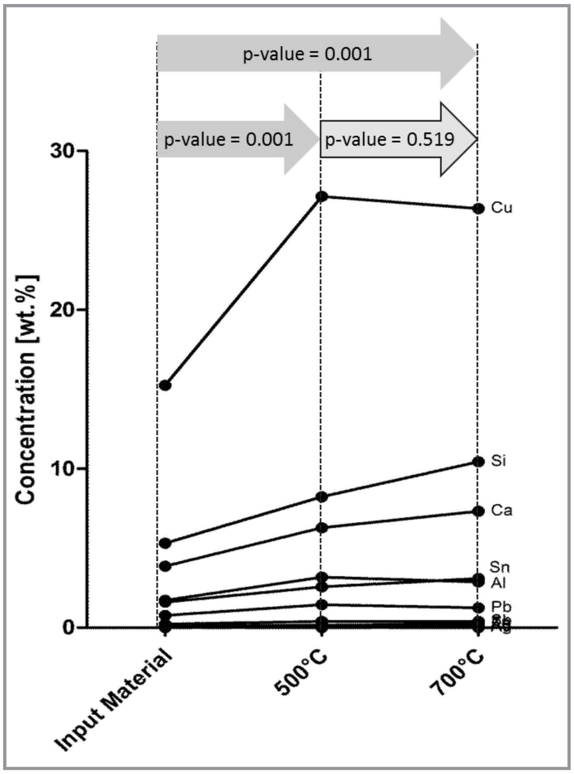

Figure 6. Comparison between the metal contain in the input material and the resulting solid residue after pyrolysis at 500 and 700 °C (dull grey: statistically highly significant, *p*-value << 0.05; light grey: not significant, *p*-value > 0.05).

complex process that involves the integration of several techniques whose only purpose is to obtain at the end separate fractions rich in Cu and Al. Notice that, based upon the observations found on pyrolysis of HOC scraps, it was decided to conduct the pyrolysis of LOC scraps at 500 °C and under argon atmosphere to ensure a complete removal of the volatile matter.

5.1 Separation Strategy

The metallic fraction was described as a mixture of mainly copper and aluminum (40:30). As it is known, aluminum should be mechanically separated from copper before melting since the metallurgical processing of copper does not allow recovery of metallic aluminum due to strong oxidation tendency, thus, ending up in the slag. This fact makes recovery of aluminum not economically viable.

As the aluminum must be separated from the copper, a sink/flotation procedure is a viable way to remove metals based upon the difference of their density in a fluid media. For this purpose a sodium-polytungstate solution ($3Na_2WO_4 \cdot 9WO_3 \cdot H_2O$, $\rho = 2.82\,g\,cm^{-3}$) was utilized. It is expected that the heavier metals will sink (fraction rich in copper) while the lighter will float in the surface of the liquid (light metal fraction rich in aluminum). However, before subjecting the material to a mechanical separation process, it has to undergo a pyrolysis since it will permit an easy separation of organics from the metals. This fact is of importance otherwise the density separation would not work as expected due to an alteration of the buoyancy force of heavier metals. In other words, the buoyancy force of the plastic covering the metal is higher than the gravity force of the heavy metal necessary to settle in the bottom of the liquid.

5.2 Results of the Separation Tests for LOC Scraps

After pyrolysis of the LOC scraps, it was seen that almost 85 % of the material after pyrolysis is metal, 5.71 % accounts for coke while the volatile matter sum up to approximately 8.9 %. The weight loss is attributed to the decomposition of the organic matter through the pyrolysis, which yields volatile gases, combustible gases and gases that upon condensation will form the liquids. The pyrolyzed coke produced from this LOC scrap has a carbon concentration of 25 wt % which accounts for the calorific value of 9.5 MJ kg^{-1}. This value can be compared to other solid fuels such as coal (27.2 – 33.5 MJ kg^{-1}) or wood (18.4 – 18.6 MJ kg^{-1}).

After pyrolysis and subsequent removal of the remaining pyrolyzed cokes the residual material underwent the sink-float separation process. Fig. 7 compiles the main results of the separation process in scale of 100 kg of LOC scraps to assess the material potential in big mass scale. As it can be seen, the mechanical separation of the pyrolyzed LOC scraps resulted in a good separation of the different fractions, accounting for 69.58 wt % heavy fraction, 29 wt % light fraction and only 1.42 wt % material losses.

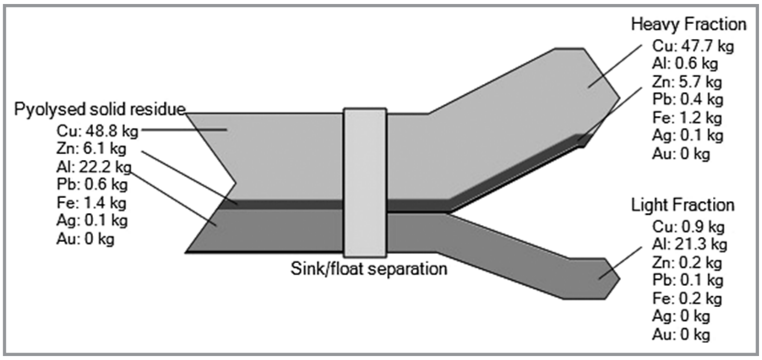

Figure 7. Elemental flow diagram during sink-float separation of pyrolyzed LOC scrap.

6 Metallurgical Assessment for the Light and Heavy Metal Fraction

As the mechanical separation step yields two different fractions, namely a heavy one rich in copper and a light one rich in aluminum, it is clear that different recycling techniques need to be used in order to recover aluminum and copper portions. In the case of the light fraction a molten salt bath typical for aluminum recycling is the most appropriate technique. However, for the heavy fraction a straight melting procedure is not beneficial since Zn content needs to be recovered. For this reason, a vacuum distillation step becomes a visible alternative to recover a foil rich in zinc and a metal portion rich in copper. The metal fraction obtained can be surely treated through a melting procedure using borax as slag.

6.1 Experimental Strategy

The light fraction was treated by a molten salt bath process in a resistance furnace with a melting temperature of 660 °C, using a metal to salt ratio of 1:2 (salt mixture = 70:30 NaCl:KCl). Additionally based on the amount of salt 2 wt % of CaF_2 was used in order to improve the cohesion of the metal droplets in the melt.

In contrast the heavy fraction was treated initially with a vacuum distillation process conducted in an induction furnace with temperature holding steps of 950 and 1200 °C and a variation step of argon pressure in the furnace from 600 mbar to 0.1 mbar. After obtaining the metallic zinc foil and metal piece rich in copper the metal was finally melted with borax as slag using a ratio metal:borax of 1:1.

6.2 Mass Flow Analysis and Metal Losses

The light fraction that was treated through a molten salt bath process yielded a metal (91 wt % Al) and slag. The resulting products obtained from the heavy fraction after vacuum distillation and subsequent re-melting with borax were a metallic foil having a concentration of 95.52 wt % Zn and 4 wt % Pb and a metal block. The metal was rich in Cu (94.5 wt %). In overall, the Cu yield for this process was 98.3 %, for Al it was 93.1 % and for Zn was 96 %.

To evaluate the recycling quote applied to the whole process it is necessary to consider the metal losses during every single step. Fig. 8 depicts the flow of main metals during mechanical upgrading and metallurgical processing of LOC scraps from WEEE. Regarding the pyrolysis, separation of cokes from the solid product would be always a challenge. As it is seen, the cokes collect part of the metals such as Cu and Al, thus, they can be used in the Cu industry to minimize its loss and the same time can act as alternative fuel since they can contain up to 30 % C. The following step, density separation, is characterized by two main results: Firstly, even though the final purpose of separating light from heavy metal was met, the presence of remaining carbon particles affects the efficiency of the process. Secondly, it was found that due to the physical characteristics of the material (strong presence of cables) it is necessary to

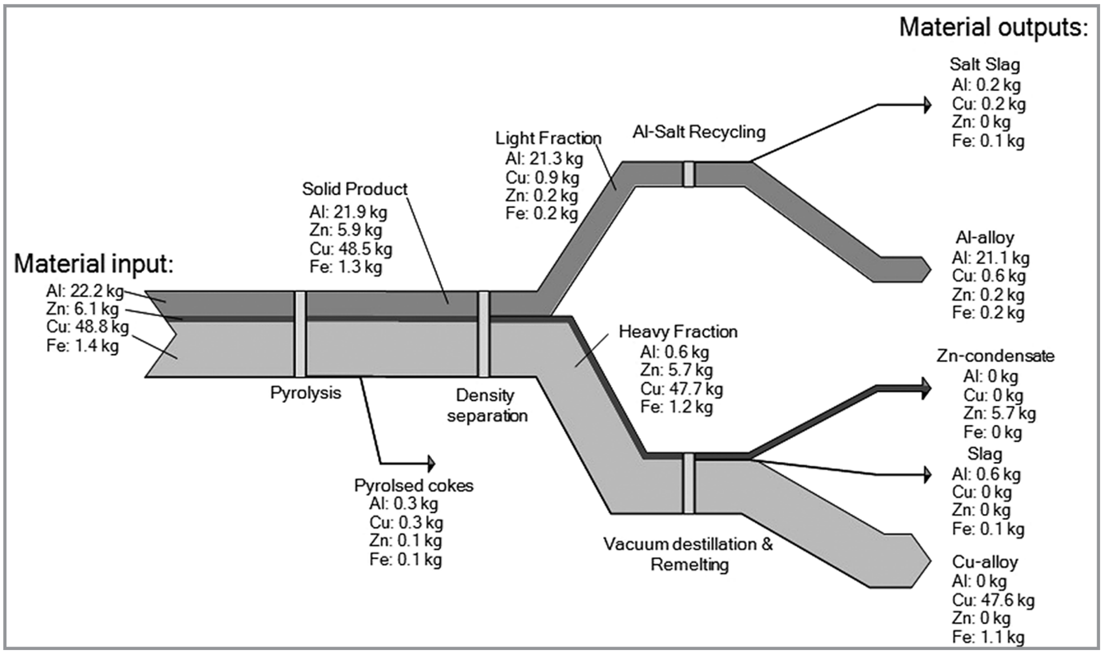

Figure 8. Flow of main metals during mechanical upgrading and metallurgical processing of LOC scraps from WEEE (values are scaled to 100 kg of input material).

ensure that during the density separation step the particles are free enough to allow an easy separation in the liquid media.

Regarding the metallurgical assessment of products, it was observed that the Al salt recycling process fits the requirements for this kind of materials. Metal losses in the salt are minimized allowing an easy reuse after the state of the art cleaning process. Finally, the integration of the vacuum distillation and remelting step for the heavy fraction has in overall satisfactory results. However, implementation of the vacuum distillation to recover zinc is practically not viable from an economic point of view. In any case, this method contributes to an easy characterization and recovery of copper and zinc products.

7 Conclusions and Outlook

Pyrolysis is a process that involves chemical and thermal decomposition which converts WEEE in three main products: non-condensable gas fraction, liquid fraction (made up of naphthenes, aromatics, aliphatics, paraffin and olefins) and solid residue. Oils and gases can be used as chemical feedstock or fuels due to their high calorific value, whereas metals, inorganic fillers, organic carbon and glass fibers are accumulated in the solid fraction. The physical properties of the resulting solid material makes the separation of organics, metals and glass fiber fractions much easier and consequently the recycling of each fraction more viable.

In regard to HOC scraps it was concluded that a pyrolysis is a viable process with no material losses that produces a liquid fuel and combustible gases, while the solid product due to its friability and the inherent mass reduction after pyrolysis allows a relatively easy upgrading of the metals. It was also concluded that pyrolysis permits removal of about 77 % of the bromine and more than 79 % of the chlorine from HOC scraps, which otherwise by treating in the smelter would be fumed producing acidic gases that harm the refractory material of the furnace at high temperatures. However, accumulation of halogens in the condensate makes its treatment rather complex and expensive. An alternative would be to perform combustion of the produced syngas before condensation takes place. The liberated energy could be used as a part of the consumed energy during the pyrolysis itself which would decrease strongly the operating cost of the process.

Based on this work, it was found that a recycling process of complex metallic waste involving a pyrolysis followed by a density separation allows recovery of aluminum with 93 % effectiveness. If the same complex metallic waste was treated by traditional methods for copper-containing scraps, aluminum would be lost in the slag during the metallurgical process. In addition, the process permits implementation of the pyrolyzed cokes as marketable good for the pyrometallurgical recycling process of copper.

Tab. 4 shows a parallel between a standard pyrometallurgical process involving a direct smelting and the high recovery recycling route proposed in this work given in Fig. 9. In the future, the idea of implementing a pyrolysis will take even more relevance if by this mean a rich fraction of critical metals is obtained after post-treatment of the produced pyrolyzed cokes.

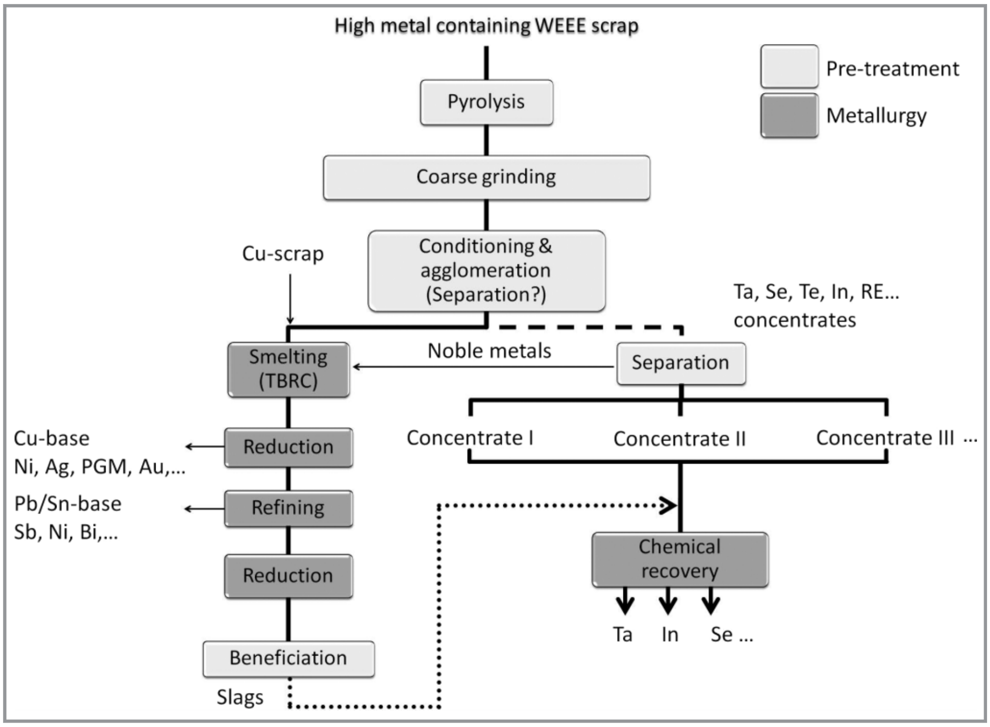

Figure 9. Flowchart of the standard process and high recovery recycling route (IME).

Table 4. Standard process vs. high recovery recycling route (IME).

Standard process	High recovery recycling route (IME)
+ simplicity of process	+ high recycling rate of Al
+ single unit	+ controllable slag formation
+ wide range of feedstock materials	+ better quality of Cu-alloy
	+ minimized metal losses
	+ autothermic pyrolysis possible
– no Al recovery	– more processing steps
– increased slag formation	– syngas handling during pyrolysis
– halogens in the smelter harm the refractory material in the smelter	
– complex handling of slags	
– Uncontrollable combustion rate	

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Abbreviations

WEEE	waste electrical and electronic equipment
LOC	low organic containing scrap
HOC	high organic containing scrap
PCBs	printed circuit boards
TBRC	top blown rotary converter
FTIR	Fourier transform infrared spectroscopy

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