




Fabian Diaz



**Process concept based on
pyrolysis for integration of
Shredder light fractions (SLF)
in the Recycling of Waste
Electrical and Electronic
Equipment (WEEE)**

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light fractions (SLF) in the Recycling of Waste Electrical and
Electronic Equipment (WEEE)”**

The Faculty of Georesources and Materials Engineering of the
RWTH Aachen University

in respect of the academic degree of
Doctor of Engineering

approved thesis

Submitted by
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“I have not even a little control over you.
Except You, in this world, nothing else is mine.”
Sant Ajaib Singh Ji

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Symbols and Abbreviations

ASR	Auto shredder residue
BFRs	brominated flame retardants
BMs	Basic Metals
CFCs	Equipment containing chlorofluorocarbons
CTRs	Cathode ray tubes
decaBDE	decabromodiphenyl ether
DTA	Differential thermal analysis
EEE	Electrical and electronic Equipment
ElektroG	Elektro- un Elektronikgerätgesetz
ELVs	End-of-Life vehicles
e-waste	Electronic waste
FTIR	Fourier-transform infrared spectroscopy
HCFCs	hydrochlorofluorocarbons
HFCs	hydrofluorocarbons
HHV	High heating value
ICT	Information and Communications Technology
LHV	Lower heating value
PBDEs	polybrominated diphenyl ether group
PCB	Polychlorinated biphenyl
PCBs	Printed circuit boards
PCDD	Polychlorinated dibenzodioxins
PCDFs	Polychlorinated dibenzofurans
PGMs	Platinum Group Metals
PM	Precious metals
PP	Polypropylene
PSLF	Pyrolysed Shredder light fraction
PUR	Polyurethane
PVC	Polyvinyl chloride
RCRA	Resource conservation and Recovery Act
REE	Rare earth elements
RoHS	Restriction of Hazardous Substances Directive
SHF	Shredder heavy fraction
SLF	Shredder light fraction
SR(s)	Shredder residue(s)
TBBA	Tetrabromobisphenol A
TBRC	Top Blown Rotary Converter
TG	Thermogravimetric analysis
TSL	Top Submerged Lance
WEEE	Waste Electrical and electronic Equipment

Extended Abstract

Introduction

The Production of shredded residues (SR) during the pre-processing of Waste Electric and Electronic Equipment (WEEE) is still a matter of concern, as around 2.5 billion tonnes of this “dangerous” waste was produced in 2012 that too in Europe alone. This problem increased the research activities towards the developments to solve the accumulation and wrong treatment of SR (especially Shredder Light Fraction SLF) like deposition in landfills, which in turn is prohibited by the regulations today¹ [1,2]. One of the most common method for the recovery is through the energy production from this materials mainly because of its considerable amount of intrinsic heat (LHV 18830 kJ/kg). But the problem regarding this method is that, recovery of valuable metals cannot be done properly. It should be noticed that, if this material has come from electrical and electronic industry, this one contains many valuable metals in considerable amount for example copper (2.74%), tin (0.05%), lead (1.05%), zinc (0.33%), silver (119.4ppm), gold (13.8ppm), and others.

The developments towards solving the accumulation and wrong treatment of SR (specially SLF) has cover multiple pathways to avoid deposition of the same in the landfills [1]. From these, at least three strategies can be distinguished: 1) Mechanical separation of metals 2) “energy recovery” in a co-incineration plant and 3) pyrolysis of SR and further mechanical separation. The first one has been always a topic of discussion as this process requires enormous efforts both economically and technologically in order to extract even a small concentration of valuable metals and in addition to this, even if mechanical separation is applied, co-incinerations can't be avoided due to the high concentration of organic matter [3]. The Second one, can be quite challenging, as this involves the extraction of valuable metals from small sized target materials like cables, joints, soldering rests etc., which could be generally found in case of SLFs [4]. The third one, has been extensively studied for ASR and very limited information could be found for SLF from WEEE. In addition, most of the research has been focused on pyrolysis as a separated process, but no metallurgical assessment of pyrolysed products has been registered. This, of course is a matter of discussion, since separation of metals, especially copper and Precious Metals (PM), are difficult to accomplish if the material is used elsewhere other than metallurgical recycling of copper bearing materials. Therefore, this study has focused on pyrolysis of SLF and tried to focus on the link between pre-processing and end-processing in metallurgical applications.

Limits and challenges in the Metallurgical Processing of WEEE: SLF

In the copper recycling, despite of the good recovery efficiency of main elements, some issues has been reported regarding metallurgical processing of secondary copper sources. Some of them are as follows: 1) heterogeneous metal composition and nature of the material fractions being treated; 2) variation of chemical composition requires modifications in the operating conditions [3,5]; 3) limited use of high organic materials, (6% of the feeding material in the Top Submerged Lance (TSL) reactor) [6]; 4) mixed

¹ Bundesgerichtshof Beschl. v. 26.09.1996, Az.: III ZR 244/95

types of organics/plastics with different concentrations and sorts of flame retardants, since they are challenging materials in terms of safety due to presence of halides (Cl, Br, Br, etc.) [5,6]; 5) incomplete combustion of organic materials leads to low temperature in the melt and increased oxygen demand [7]; 6) high concentrations of halides can lead to strong volatilization of silver in the smelter (up to 12% of the available silver in the feeding material). Therefore, concentration of halides in the produced dust can be a challenge if re-fed in the smelter [8]; 7) formation of dioxins and furans, since they should be controlled by proper off gas handling, which normally requires fast quenching due to the rapid cooling rate of the off-gas to hinder their formation [8].

Pyrolysis and its applications for the recycling of WEEE and SRs

Pyrolysis, also called cracking process, is a thermochemical process, where organic material decomposes at elevated temperatures (300-900°C) in the absence of oxygen. Here the structure of polymers breaks down into smaller intermediate products at different temperatures [9,10]. The process is performed under a vacuum condition or inert atmosphere to produce oil, gas and char [9]. The general degradation of the polymeric structure can be represented by equation (18) as follows:

$$\text{Organic(s)} = \text{Cokes(s)} + \text{gaseous Components} \quad (1)$$

The redistribution of elements during pyrolysis is one of the advantages that could be offered by this method. Critical elements like halogens are volatilized from the solid material. Therefore, this method is also known as viable dehalogenation process. Electric and Electronic Equipment (EEE) contain Brominated Flame Retardants (BFRs), as a measure to reduce their potential of flammability. It is worth noting that these compounds are also of concern during the pre-processing stages. As they might become a sources of high toxicity during heating. Pyrolysis applied to e-waste has been documented already in many publications and books. The most common tested material has been printed circuit boards (PCBs) and microelectronic components. Cui et al. stated that pyrolysis appears to be an emerging option in WEEE recycling technology, facilitating the recovery of high value, potentially accessible products such as precious metals, fuel and chemicals [11]. During pyrolysis of PCBs, it is not only possible to break the organic part in order to obtain fuel or useful chemicals, but also ensures a more effective processing of the solid product which enables the recovery of valuable metals easily and efficiently [12].

Pyrolysis of SRs have been studied in the past. Nevertheless, most of the studies has been focused in characterization of pyrolysis products like oils, syngas and chars, and very limited information can be found about proper metallurgical recycling of pyrolysed SLF.

Investigative approach and research needs

Pyrolysis can be the link between mechanical pre-processing and Metallurgical recovery of SRs, mainly because of the presence of valuable metals in SLF. Using pyrolysis the SLFs which are considered as “waste” can, not only be brought back to the metal production chain in the WEEE recycling, but also provide technical benefits to the metallurgical process itself. Some of those benefits are: production of a valuable

syngas with relevant potential as a source of energy and could also be used as a substitute for fossil reducing agents in gas form, production of an effective alternative of solid reducing agent from the pyrolysed solid product, recovery of valuable metals from Cu-slugs and SLF in a single process.

This work contains relevant information on pyrolysis of WEEE streams, upscaling pyrolysis of SLF from lab to pilot, evaluation of pyrolysed SLF as alternative energy source in the copper industry as well as evaluation of pyrolysed SLF as reducing agent. The last one has been studied in a mini-scale (few grams) to semi industrial application in a Top Blown Rotary Converter (TBRC), where the material has shown its biggest potential if injected with a high speed inside the molten slag and under proper reducing conditions. Some of the main research gaps considered in this work are indicated as follows:

- Better understanding on the degradation process of the organic material contained in WEEE under different parameters like temperature, heating rate, and low oxygen levels. This along with the previous knowledge makes it easy to understand the nature of pyrolysis products and helps to predict the adjustments required to achieve the best quality products.
- Full characterization of pyrolysis products: pyrolysis char, Syngas and pyrolysis oil. A good characterization of products can guide their applications at the industrial level. It is a key factor to increase the sustainability of the process by minimizing the waste production.
- Metallurgical evaluation of pyrolysed SLF as alternative fuel for Cu-smelting applications. This evaluation covers kinetic analysis, thermal degradation of Pyrolysed Shredder Light Fraction (PSLF), efficiencies, definition of benefits and pains for the process.
- Metallurgical evaluation of pyrolysed SLF as alternative reducing agent for Cu-containing slags in the copper sector. This evaluation covers kinetic analysis, reduction mechanism, efficiencies and definition of benefits and pains for the process.
- Best results in lab scale should be brought to the demo/pilot level (in 1/4 ton scale) for the real assessment of products. This is a key factor since most lab scale data can strongly varies under industrial applications.

Degradation of organics during pyrolysis of WEEE:

The degradation process experienced by the organic material contained in WEEE can be influenced by different parameters like temperature, heating rate, and low oxygen levels. In Table 1, the main highlights from the results obtained during this study are summarized. It is worth mentioning that this lab scale study was carried out mainly with PCBs, and hence PCBs are considered as the reference material. In addition, the investigation on the influence of the amount of organic in different WEEE streams covered four types: PCBs from domestic appliances (category 1a and 1b), PCBs used in IT system, Plastic-mixed fraction and shredder light fraction (SLF) from pre-processing of WEEE. The appearance of this target materials can be seen in Figure 1.

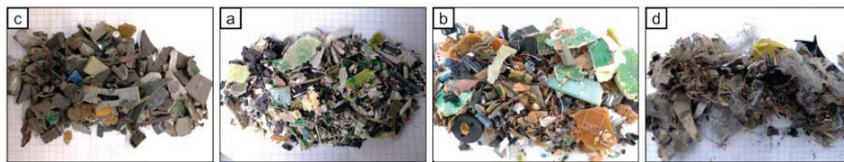


Figure 1: studied input materials: a) PCBs (domestic appliances 1a and 1b), c) PCBs (IT systems), d) Plastic-mixed fraction, e) Shredder Light Fraction (SLF)

Table 1: highlights from the degradation mechanism study of WEEE during pyrolysis

Parameter	Highlights
Temperature (under low heating rate $\sim 300^{\circ}\text{C/h}$)	<ul style="list-style-type: none"> - Drying - Stage I ($200\text{--}245^{\circ}\text{C}$): First depolymerisation and oxidation reactions of hydrocarbons by hydroxyl radicals; formation of CO_2, CO and H_2O, phenols and primary tar. formation of hydrogen probably due to reverse methanation reaction; first formation of HCl and HBr - Stage II ($245\text{--}576^{\circ}\text{C}$) Cracking of primary tar and formation of secondary tar; formation of long chain hydrocarbons; cracking of ethane to form CH_4 and H_2; formation of HCl and HBr - Stage III ($>576^{\circ}\text{C}$): cracking of secondary tar and formation of CH_4 from phenols; formation of long hydrocarbons like cresols, acrolein, ethylene, styrene, which are degraded, forming CO, H_2 and CH_4.
Heating rate	<p>Increased heating rates ($>10^{\circ}\text{C/s}$) take some variations in the degradation mechanism like:</p> <ul style="list-style-type: none"> - Increased formation of butane and limited formation of ethane - Reverse methanation reaction above 700°C leading to formation of CO and H_2 - Increased formation of other hydrocarbons - Increased formation of HBr - Dehydrogenation of organics - Catalytic steam/dry reforming reaction leading to formation of H_2 and CO - Other catalytic reactions like water-aluminium can takes place
Low oxygen	<p>Pyrolysis of PCBs has been done under different concentration of oxygen in the carrier gas (0, 2, 4 and 8%). From this, the following could be remarked:</p> <ul style="list-style-type: none"> - Gasification reactions might be beneficial as less production of long chain hydrocarbons leads to minimized formation of Oils and easy handling of the offgas. However, if the presence of oxygen is beyond the limit then the reactions might change the environment from a reducing condition to a more neutral or even oxidizing atmosphere. This can lead to undesired metal oxidation. - From all detected gases, CO_2 represents more than 70% of the produced gases with 4% O_2. Strong minimization of CH_4 and C_xH_y, whereas CO formation is favoured. - Possible water-gas shift reaction and partial oxidation reforming reaction might promote formation of hydrogen, CO_2 and CO.

<p style="text-align: center;">WEEE streams</p>	<p>Pyrolysis of PCBs (domestic appliance), PCBs (IT systems), plastic mixtures and SLF has been carried out and as result the following can be concluded:</p> <ul style="list-style-type: none"> - The halogen removal efficiency increases with its initial concentration in the input material. For all material streams Br and Cl could be removed in at least 75% and 65%, respectively. - Plastics and SLF showed an important increase in the intrinsic heat loss, minimum being 40%. - SLF showed the highest mass loss with almost 50%. - A high concentration of metals like Cu, Ag, Au, Fe, Si, etc. are found in the pyrolysis solid product, which is also called as the pyrolysis char.
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Pyrolysis of SLF: From lab to pilot

The pilot scale pyrolysis was conducted at the pilot plant in the company Kunststoff- und Umwelttechnik GmbH in Forst, Germany. The material was charged into an endless screw, and then it was taken to a drying oven in order to prevent the moisture from entering the pyrolysis reactor. The input material was then put into the reactor and then it was heated up to a temperature of 700°C, at the same time another endless screw constantly brings material towards the top of the reactor to ensure a continues decomposition of the material. Once the material reach the bottom of the main reactor, it was brought into a second reactor in which the off gas is injected back after being cleaned. This ensures further decomposition, and further cracking of the long chain hydrocarbons from the off gas. Then the off-gas was cleaned again inside three different scrubbers. The non-condensable (also called permanent gases) gases were then burnt outside the plant. The coke was also collected regularly at the end of the plant.

This experiment was conducted with 250kg of SLF, charged at around 2kg/min. The temperature of the furnace was fluctuating between 700°C and 800°C depending on the intensity of the decompositions and the heterogeneity of the material. The pyrolysis was conducted for a total duration of 3 hours. Pyrolysis oil Samples were taken from each scrubber at the beginning, middle and end of the experiment. In addition, samples of the permanent gas after the scrubbers were taken for chemical composition determination.

SLF experience a remarkable visual transformation after pyrolysis which is as shown in Figure 2. Plastics, textiles, foils and wood have been degraded, and the copper wires as well as metal pieces are now evident. SLF is characterized a very low bulk density. After the experiment an estimation of the bulk density has been conducted and this showed, an increase from 0.215 kg/L for SLF to 0.396 kg/L for PSLF. The black colour of the solid residue was because of the coke content after pyrolysis and this seems relatively homogeneous in the entire sample.

The above mentioned characteristics helps in understanding the SLF as a very heterogeneous material in terms of chemical composition. From the obtained results, it could be observed that after pyrolysis, SLF turns into a more homogeneous material because of the degradation of organics. Most elements in metallic and oxide form experienced some increase in concentration for both pyrolysis scales e.g. Si, Al, Ca,

Cu, Pb, Fe, etc. and only volatile elements like C, N, and H experienced strong reduction in concentration after the thermal process. In addition, a considerable amount of intrinsic heat was removed, and this was found to be 7 037.5 kJ/kg for the lab scale and 6 150 kJ/kg for the pilot one. The slight difference between the LHV and PSLF from the pilot to that of the lab scale trial is related to the increased degradation yield in the pilot scale trial. This can be explained due to the increased surface area which in turn is justified by the material is being mixed, partially crushed and re-circulated inside the pilot pyrolysis reactor by means of a backwards moving screw. It could be seen from the ultimate result that degradation of organics works much efficient in the pilot scale compared to the Labscale, mainly because of the formation of smaller molecules.

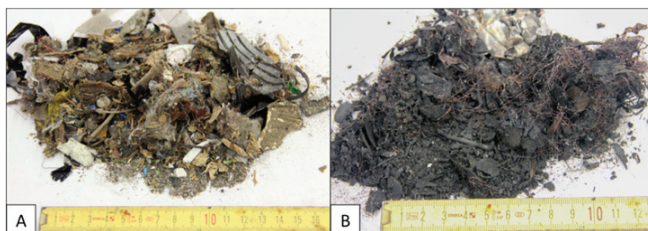


Figure 2: visual comparison of SLF before (A) and after (B) pyrolysis

Pilot scale pyrolysis showed the enormous potential of pyrolysis to produce combustible gases like CH₄ (23 vol. %), H₂ (24 vol. %), CO (18 vol. %), Ethylene, Ethane and others. The heating value estimated during pyrolysis is 48.6 MJ/kg. Moreover, pyrolysis oil was found to be a combination of three main constituents, paraffins, naphthenes and aromatics, and the heat calorific value of these components sums up to 26.3 MJ/kg and 22.8 MJ/kg for the lab and the pilot scale pyrolysis, respectively. This clearly shows an important potential of pyrolysis for the generation of fuel from electronic wastes. Nevertheless, halogens (Br, Cl) should also be safely removed as they get concentrated in the condensates.

Pyrolysed SLF (PSLF) still contains a considerable amount of carbon, which can be used in metallurgical applications in the WEEE recycling route. In general such a carbonaceous material can be used as an alternative energy source or as a reducing agent of copper containing slags. Both Options has been investigated in this study. In the following chapter a more detailed information is given for these two cases.

Energetic potential of solid pyrolysis products in the copper metallurgy

The energetic potential of solid pyrolysis products in the metallurgical applications has been evaluated. The key findings regarding the results are listed below:

- Pyrolysed matter has an increased the energy barrier (activation energy E_a) for the degradation of the organics during combustion. Moreover, the determined pre-exponential factor suggests that the collision frequency of molecules are strongly minimized due to minimized formation of volatile matter during combustion. This kinetic parameter indicate that pyrolysed matter will require

an increased temperature to burn and the oxidation process will occur slowly, as evidenced by the combustibility index S.

- Autothermic smelting of PSLF is observed. Nevertheless, as the intrinsic heat is being minimized, the final temperature is also low, which in turn increases the viscosity of the melt. This suggests that this material should be combined with other organics to balance temperature and improve the melting conditions.
- Combustion of PSLF combined with SLF and PCB experience two main stages during the process. The first one is an oxidizing stage, where carbon is burned out and at the same time the target metals are concentrated in the slag as oxides. The second stage is a reducing period, which is driven by the unburned pyrolysed material. During the last one, metal in oxide form will mobilized to the metal phase e.g. Copper. The same effect was observed by using only PCBs due to limited distribution of oxygen in the material leading to pyrolysis in areas where oxygen cannot reach while the material is heated.

The Use of pyrolysis coke as reducing Agent

Pyrolysed SLF was also evaluated as reducing agent in lab trials as well as in demo/pilot scale in a Top Blown Rotary Converter (TBRC). From the results, it could be concluded that:

- Reduction with PSLF start at a low temperature (495°C) and involves at least two reaction stages. The first one is found between 495°C and 1000°C and the second one at the temperature range above 1000°C. The first reduction stage involve secondary cracking of organics caused by catalytic reactions generating carbon monoxide and hydrogen as main reducing agents. Besides this, other hydrocarbons could also be generated below 750°C. Temperatures above 650°C showed increased concentration of CO and hydrogen as a result of the boudouard and “water gas” reactions.
- The apparent activation energy (E_a : 17.21 kJ/mol) and pre-exponential factor (A : $6.99E+09$ S⁻¹) obtained from the kinetic analysis indicate that reduction with pyrolysed SLF requires low energy barrier and involve increased collision frequency during reduction. This means lower temperature requirement and increased volatile matter involved in the reduction process.
- Hydrogen and carbon monoxide increases drastically with increased concentration of PSLF. This could be supported by catalytic reactions as the metallic copper fractions is increased in the sample during the process. The presence of copper, nickel and aluminium could lead to a catalytic condition for the further degradation of organics, which ultimately generate reducing gases. Nevertheless, at this stage of the research, it was not possible to determine the degree of influence for each metals.

Recycling concept for integration of SLF in the WEEE Recycling: Upscaling

The idea with the proposed methodology is to evaluate the use of PSLF in the metallurgical WEEE recycling process. Therefore, the main attempt is not to create a

complete new process chain for recycling of shredder light fraction, but to evaluate its potential use in a common metallurgical stage at any Cu-recycling company. For this particular case, and based on the obtained results, the potential use of PSLF as reducing agent in industrial applications are evaluated.

Metallurgical recycling of WEEE always involve an oxidation/combustion stage where organic materials are being burned to liberate energy for its own smelting process. This along with other conventional fossil combustibles are commonly used. This process has shown outstanding results regarding energy recovery of the intrinsic heat in the material itself. However, due to increased activity of oxygen during combustion of organics or during slag converting, valuable metals are lost during the process and the lost is because of the undesired oxidation reactions of the metals. Therefore, it is fairly common to include a reduction stage where metals are recovered from the slag after the oxidative smelting process. Based on this, the recycling concept for shredded light fraction from WEEE has been proposed as shown in the Figure 3 A.

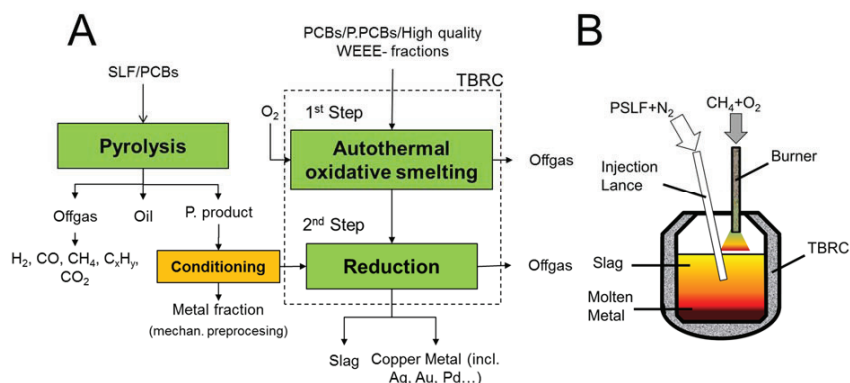


Figure 3: A) process concept for metallurgical utilization of SLF as reducing agent based on pyrolysis; B) Injection concept of PSLF in a Top Blown Rotary Converter (TBRC)

For this process concept, SLF is being pyrolysed in a separate unit to generate Syngas (H₂, CO, CH₄, C_xH_y and CO₂) as main volatile products and some oils. PSLF are then feed into the reactor at the reduction stage to reduce Copper from the slag. Copper contained in the SLF is also recovered in the same reactor under reducing conditions.

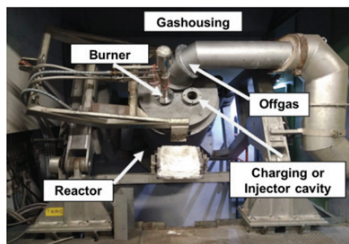
In order to assure good kinetic performance and reduction efficiency, the reducing agent should be in contact with the slag and turbulence should be provided to avoid floating of the reducing material on the melt surface. Therefore, PSLF is prepared to be injected inside the melt with nitrogen gas to avoid oxidation and to control the atmosphere inside the reactor. Nitrogen as carrier gas provide also good turbulence to the melt and inhibit agglomeration and post combustion of the PSLF at the surface.

If SLF is produced from the WEEE sector, it is expected that metallic copper should be presented in the material as main metallic constituent. However, if it is coming from the automobile industry, this can have a considerable amount of other ferrous and non-ferrous metals. This recycling strategy offers the possibility of mechanically processing the PSLF and to recover metals e.g. iron and aluminium from the material stream before smelting in the TBRC, which otherwise cannot be recycled due to economic considerations. This conditioning is presented in Figure 3 A, before injection of the PSLF in the TBRC.

At the end of the process, a copper metal and a copper poor slag can be produced in the TBRC which could be achieved under a well-controlled combustion and reducing conditions.

PSLF as alternative reducing agent in the Cu-sector: Demo scale trial

The demo scale Top Blown Rotary converter (TBRC) used for the upscaling trial is shown in Figure 4. The Unit corresponds to a cylindrical shape reactor of 240L volume, which has a capacity to process up to 100L of molten material. The furnace is heated up with an Oxyfuel burner, which uses only natural gas and pure oxygen as the fuel. The burner is water cooled. This offers a huge advantage since adjustment of Lambda (λ 0.7-1.3) relatively changes the atmosphere inside the reactor at any time during the experiment.



Rotation:	0 - 10 U/min
Tilting angle:	0 – 110°
Volume:	240L (max. 100 L melt)
Burner:	Oxyfuel, max. 400 kW
λ (adaptable):	(0.7-1.3)

Figure 4: Demo scale Top Blown Rotary Converter (TBRC)

The TBRC have a variable rotating speed from 0 to 10 rpm and correspond to a tiltable furnace which could be tilted at an angle between 0 to 110°. This is a great advantage as vertical placing is possible and beneficial for the submerged injection, and moreover, direct casting in a mould which is placed in front of the furnace. The TBRC has a Cr-magnesite (MgCr) lining material which can hold Cu-base materials and is resistant to corrosion until 1600°C, which makes TBRC optimum for this kind of applications.

The TBRC includes a state of the art offgas cleaning system. The maximum suction capacity is 10.000 Nm³/h and the system has got two main pathways, one of which is so called hygienegas or housing suction and the second is called process gas. The first one takes all fumes from the melting hall and takes the gases into a fabric filter, which is critical specially at the time of casting and charging of organic materials. The second one takes the offgas directly from the TBRC, it is cooled down with air quenching

to around 130-240°C and transferred into an electrostatic filter for dust collection. Both offgases (hygienegas and process gas) are transported to the scrubber, which is set to a pH value of 10 with NaOH. This is essential specially for halogen removal and deposition of untrapped heavy metals like As, Cd, Pb and others. The scrubber has a volume capacity of around 5100 liters. The cleaned gas is finally taken to the chimeney and is realised to the environment.

120 kg of Cu-slag is charged inside the preheated TBRC reactor at a temperature of around 800°C. After charging the slag, the furnace is heated to 1350°C with the Oxyfuel burner (natural gas and oxygen) which is set to 102 kW/h and λ of 1.02. The TBRC is set to a rotation speed of 2 rpm. The way pyrolysed material is fed into the TBRC can strongly influence the reduction efficiency. Therefore, after the complete melting of Cu-slag, the reduction experiment takes place in two phases according to the art of charging: which are the manual charging and Injection of the PSLF. It is important that the Copper in the slag is analysed periodically during the whole trial.

The calculation of the stoichiometric amount of carbon to reduce the copper oxide measured in the slag is done by assuming carbon as the only reducing agent, which is equal to 12.6 Kg of PSLF for each 100Kg of Cu-slag. Based on this ratio, PSLF is charged manually in three periods: 72.5%, 100% and 145% of the required amount of PSLF to treat the 120 kg of Cu-slag. For this period, the rotation was set to 8rpm to increase the turbulence in the melt. At the end of the reduction process with manual charging, copper concentration in the slag is found to be in similar to the one that is initially measured. Therefore, the injection trial is performed subsequently using the same molten slag in the TBRC.

For the injection, the TBRC is placed vertically (90°), the rotation speed is initially set to 2rpm, and the lance is placed at the top of the TBRC and is hold by hand. A flushing period with nitrogen gas for 1 min takes place before the PSLF is being injected. The material is injected using nitrogen as the carrier gas until the material has been completely injected. After this, gas flushing operates for about a minute while the lance is removed from the molten bath and place safely outside the TBRC reactor. This procedure is repeated every time an injection period takes place. The first injection period takes place with the same λ of 0.89 and rotation speed of 8 rpm. Firstly, 50% of the PSLF required to reduce the copper oxide in the slag is injected with an injection speed of ~2.75kg/min. The lance is removed directly after the injection of the material is finished, which means that no gas stirring takes place. After one hour of holding time the copper concentration in the slag is found to be similar to that of the registered copper concentration value before the trial.

For the second injection setup, λ in the burner is set at 0.7 in order to increase the reduction condition in the furnace. In addition, it is planned to perform an extra stirring period after finishing the injection of the material. This is done in order to increase the turbulence in the melt and avoid flotation of the material, which ultimately hinders reduction and promotes surface combustion. In addition, this injection period takes place in two main blocks. In each block a total of 72.5% of the required PSLF is injected, so in total 145% of the required PSLF is charged. Once it is finished, subsequent injection periods with small quantities takes place, with the same

conditions but small different quantities. This means that, in the next injection periods, the equivalent quantity will be 15% and then 3% of the required amount are charged to the molten slag. Once reduction of the material is finished, casting of the melt in a mould takes place. The metal–slag separation occurs with the density difference at the mould.

The resulting reduction efficiency for copper from the slag is plotted in Figure 4 against the incremental addition of PSLF in the system. As shown in the graph, manual charging of PSLF showed very poor efficiencies for reduction of copper. A maximum of 7.1% of efficiency has been registered after the process, which could indicate that manual charging on the surface had considerable challenges such as insufficient turbulence to provide proper mixing of the slag with the reducing agent and surface burning. On the contrary, injection trials indicated improved performance registering up to 48 % during the first injection period. This efficiency is then drastically improved by performing controlled dosification of the PSLF and increased stirring period. Only by varying this two parameters the reduction efficiency could be improved up to 82% and this in turn is obtained by using PSLF equivalent to 93% of the required PSLF.

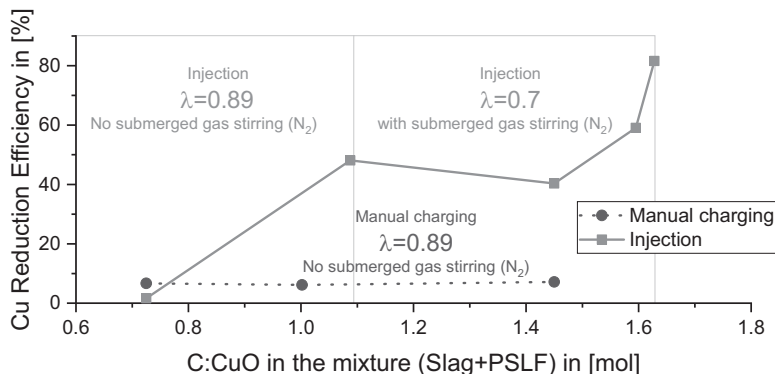


Figure 4: Cu reduction efficiency Vs C:CuO ratio in the system according to the art of charging in the TBRC

It can be observed in Figure 4 that the process efficiency is limited to less than 50% at increased λ , low turbulence and rapid charging PSLF. These results indicate that injection technology and submerged gas stirring are the key factors to be implemented if pyrolysed materials want to be used as reducing agents of Cu-slugs.

The same operations have been experimented for other accompanying elements like Ag, Pb, Zn, Ni, Sn and Sb. In general, accompanying elements from the Cu-slag can be hardly reduced if copper oxide is concentrated in the slag. Therefore, poor reduction efficiencies are shown in the manual charging trial, where only silver and tin indicated reduction but in poor efficiencies with values below the 25%. Completely different scenarios are registered in trials with injection and specifically with that of submerged gas stirring. As copper is being reduced, other metals can be finally reduced to e.g. Sb (100%), Sn (63%), Ag (100%), Pb (75%), Zn (53%) and Ni (17%).

Conclusion and future work

Pyrolysis demonstrate to be a good link between mechanical pre-processing and Metallurgical recovery for SRs. SLF which is considered as hazardous material could be successfully transformed into solid product with about 50% less volume and concentrated amount of valuable metals, which is suitable for metallurgical application. As evidenced, valuable metals contained in SLF can not only be brought back to the metal production chain in the WEEE recycling, but also provide technical benefits to the metallurgical process itself. Some of these benefits are: production of a valuable syngas during pyrolysis with relevant potential as energy source and could also be used as a substitute for fossil reducing agents in gas form (H_2 , CO , CH_4 , $C_xH_y...$); production of an effective alternative for solid reducing agent from the pyrolysed solid product; recovery of valuable metals from Cu-slugs and SLF in a single process stage. It was also evidenced that pyrolysis oil can also be minimized at increased heating rate or catalytic conditions.

Future research work should be performed in the following key areas to improve the pyrolysis process itself, as well as, the performance of pyrolysed material in metallurgical applications:

- Creation of a combustion-reduction model, to undergo an autothermic smelting process with simultaneous addition of reducing agent (PSLF). This could lead to a reduced processing time inside the smelter.
- Investigate the use of halogens to volatilize critical metals in the pyrolysis gas could improve the sustainability of the pyrolysis process and increased the overall recycling quota of critical elements like In, Ga, Sb, and others.
- Further investigation at the industrial level regarding optimum injection parameters to improve the reduction yield of target elements.
- Investigate further catalytic reactions during pyrolysis that improves hydrogen production.
- Investigate the use of Syngas from the pyrolysis process in metallurgical applications as reducing gas. This might have a potential to replace nitrogen as carrier gas for the pyrolysed char; or being used directly as reducing agent. This could be beneficial, as the minimization of greenhouse gases are overmuch necessary and hence needs to decrease the usage of carbon-based reducing agents with hydrogen.