

Autotherme Wertmetallgewinnung aus Elektronikschrott im TBRC

Von der Fakultät für Georessourcen und Materialtechnik
der Rheinisch -Westfälischen Technischen Hochschule Aachen

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vorgelegt von **Dipl.-Ing.**

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Verwendung von Abschlussarbeiten

In dieser Arbeit sind Versuchsserien eingeflossen, die Studierende im Rahmen ihrer Abschlussarbeit durchgeführt haben oder Großversuche mit begleitet und detailliert dokumentiert haben. Alle Abschlussarbeiten sind am IME Institut für metallurgische Prozesstechnik und Metallrecycling an der RWTH Aachen University unter meiner Betreuung entstanden und sind Bestandteil des BMBF Projektes im Rahmen des r^2 -Förderschwerpunktes. Im Folgenden sind diese aufgeführt und in welchen Kapiteln dieser Arbeit die Inhalte verwendet worden sind.

A. Lenz	(2010, Diplomarbeit): Schlackendesign für das E-Schrott-Recycling zur Metallgewinnung; Kapitel 8.1
S. Kruse	(2010, Studienarbeit): Untersuchung zum Abbrandverhalten von Elektronikschrott; Kapitel 9.1.3
S. Kruse	(2011, Diplomarbeit): Rückgewinnung strategischer Metalle aus Elektronikschrott; Kapitel 9.2.3
A. Trentmann	(2011, Bachelorarbeit): Einfluss von Schlackenzuschlägen auf die – metallausbeute beim Direkteinsmelzen von Elektronikschrott; Kapitel 9.1.2
S. Gül	(2011, Diplomarbeit): Beurteilung von Vorbehandlungsmethoden und Sauerstoffangebot beim Elektronikschrottrecycling; Kapitel 9.1.1
R. Meier	(2012, Diplomarbeit): Untersuchung zur Feststoffverbrennung und der Abgaszusammensetzung beim Direkteinsmelzen von Elektronikschrotten; Kapitel 9.1.3
F. Kaußen	(2012, Diplomarbeit): Einschmelzen von Elektronikschrott im Technikums-TBRC; Kapitel 9.2.4 und 9.2.5

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Verwendete Symbole und Abkürzungen

a	Aktivität
AAS	Atomabsorptionsspektroskopie
CMR	frz. Convention relative au contrat de transport international de marchandises par route"; Beförderungsdokument für den Straßentransport
D	Durchmesser
EAR	Stiftung Elektro-Altgeräteregister
EU	Europäische Union
FCKW	Fluorchlorkohlenwasserstoffe
G	freie Enthalpie
γ	Aktivitätskoeffizient
H	Höhe
ICP-OES	optische Emissionsspektrometrie mit induktiv gekoppeltem Plasma
K	Massenwirkungskonstante
K	Geschwindigkeitskonstante eines Gasstrahls
KRF	kupferreiche Fraktion
KrWG	Kreislaufwirtschaftsgesetz
$L^i_{X,Y}$	Verteilungskoeffizient des Elementes i zwischen der Phase X zu Y
LPF	Leiterplattenfraktion
M	Mischfraktion aus LPF und KRF im Verhältnis von 50 zu 50
M	Impuls
PAK	polyaromatische Kohlenwasserstoffe
PCB	polychlorierte Biphenyle
PGM	Platingruppenmetalle
PP	Polypropylen
R	ideale Gaskonstante
RFA	Röntgenfluoreszenzanalyse
ρ	Dichte
Re	Reynoldszahl
S.NE.S	Stiftung Entsorgung Schweiz

SWICO	Schweizerischer Wirtschaftsverband der Informations-, Kommunikations- und Organisationstechnik
T	Temperatur
TBRC	Drehkippkonverter (Top Blown Rotary Converter)
TOC	Gesamtheit des Kohlenstoffs in organischen Verbindungen (Total Organic Carbon)
u	Geschwindigkeit
WEEE	Waste of Eletronical and Electronic Equipment (Elektronikschrott)
x	Anteil eines Stoffes am der Gesamtstoffmenge

Extended Abstract

Introcuccion

End-of-life Electrical and Electronic Equipment (EEE) is an important raw material for Germany. Its composition is roughly 1/3 plastics, 1/3 metal and 1/3 ceramics. Not only base metals like iron, copper and aluminum can be found in EEE but also precious metals like silver, gold and palladium and strategic metals like antimony, nickel or tin. That is why recycling of Waste of EEE (WEEE) is an important step towards a sustainable society. The concentration of valuable materials in primary ores is lower compared to WEEE which is shown in figure 1. It is to say that for the raw material potential of 1 t of WEEE 50 t ore has to be moved and treated. [1], [2], [3], [4], [7], [8]

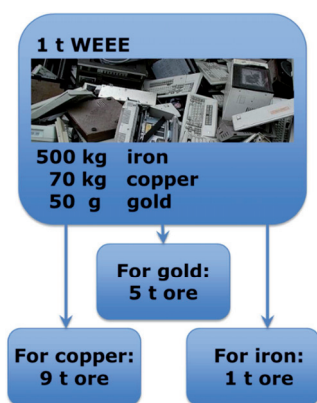


Figure 1: Metal potential in WEEE [4]

In this paper an autothermal process for WEEE recycling with an innovative slag design and sustainable zero waste metallurgy is developed from lab to demonstration scale. As the demonstration scale furnace, a top blown rotary converter (TBRC) is used.

WEEE arising and mechanical treatment

End-of-life EEE were an inconvenient waste for a long time. This changed with the implementation of the WEEE directive. The raw material prices increased and the focus of WEEE changed from the hazardous materials towards the valuable metals. A side effect of this is the gold rush fever which leads to unofficial recycling and exports out of the European Union. In developing countries, WEEE is recycled without protection for health and environment in an inefficient way. For example the gold yield of such processes is at only 25%. The damage to the EU by these processes and illegal export are higher than 2 t silver, 500 kg gold and 300 kg PGM per year. [7], [11], [13], [14]

Figure 2 shows that the arising of WEEE in total and per capita for Germany and the EU was constant in the years 2008 to 2013. In Germany a lot of small EEE like mobile phones, USB-sticks and small kitchen devices are disposed together with the municipal waste and incinerated without any problems in a technical or environmental point of view. A large numbers of households have an intermediate storage in cellars or attics of in total 350,000 t. In addition, the economic pressure by high raw material prices forces illegal exports. [11], [14], [36]

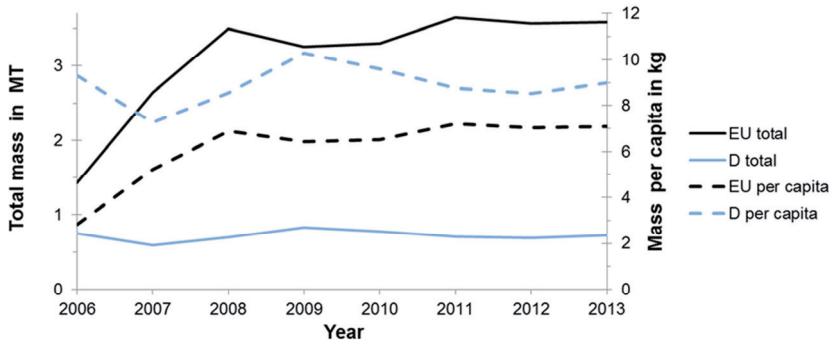


Figure 2: Collected EEE in the EU and Germany in mass total and mass per capita [36], [37], [38]

The design of a product shapes its chosen material, complexity and joining technology. A “design for recycling” or “design for disassembly” is not a common practice. After its lifecycle, the product is collected, mechanically treated and the containing raw materials are recovered. The treatment of WEEE determines which material is going to a recycling process and which elements can be recovered. Figure 3 shows the correlation between the effort of the mechanical treatment and metallurgical recovery in a qualitative way. [30], [43], [44], [45], [46]

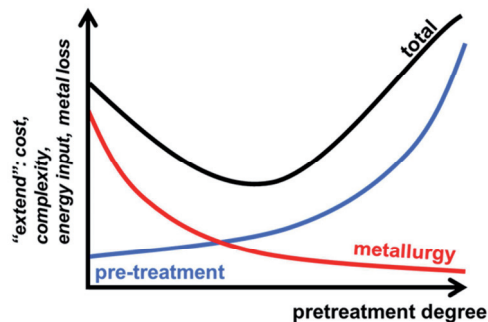


Figure 3: Correlation of the mechanical treatment and metallurgical recovery in the matter of costs, metal and energy losses [44]

Through mechanical treatment, it is possible to separate and sort 90% of the different materials in WEEE in a technological way. But invest and operation of machines are too expensive to reach such an accuracy. There is a direct link between the combination and joining of materials and the quality of the produced secondary raw material for the metallurgical recovery. This also influences the recycling rate. With an unfinished mechanical treatment, the only way of separation is the metallurgical process. In a metallurgical process all elements can only be separated into the metal, slag and gas phase. The separation efficiency and hence the losses of every element is predicted by thermodynamics, which is depending on temperature and composition of different phases, elements and compounds. [50], [45], [76]

In average, the mass flow is divided into 27% manual separated parts, 33% iron fraction, 26% plastics fraction and 13% copper rich blend. Looking at the distribution of some elements in the mechanical treatment, e. g. gold is largely collected in the iron phase (about 40%). Only 25% is transferred into a phase, were it can be separated. For aluminum the rate is 75%, for iron 89% and copper 60%. [45], [46]

Top Blown Rotary Converter (TBRC) technology and processes

The TBRC is a special kind of converter which is rotatable and a gas jet is blown on top of the melt via a lance. It was invented by Bo **KAL**ling for the steel industry and a fist demonstrator was built in **DOM**narvet in Sweden. That is why a TBRC is also called Kaldo-furnace. A TBRC was not used in the steel industry but was successfully implemented into the secondary lead metallurgy in the 1970s. Nowadays TBRC are also used in the nickel industry where it usually has a capacity of 110 t. [75], [76], [77], [78]

A TBRC, shown in Figure 4, has one opening for charging and tapping the furnace. The furnace body is rotatable around the longitudinal axis and tiltable around the cross axis. Due to the one opening, emissions can be collected easily through a lid. This lid mostly has three openings for the off-gas, a lance or burner and one opening for material feed. The furnace can be tilted into a charging position, tapping and working position. In charging position, the opening is tilted horizontally. In working position, the off-gas is collected through a water cooled hood where remaining CO or metal vapor can be oxidized by false air. [6], [58]

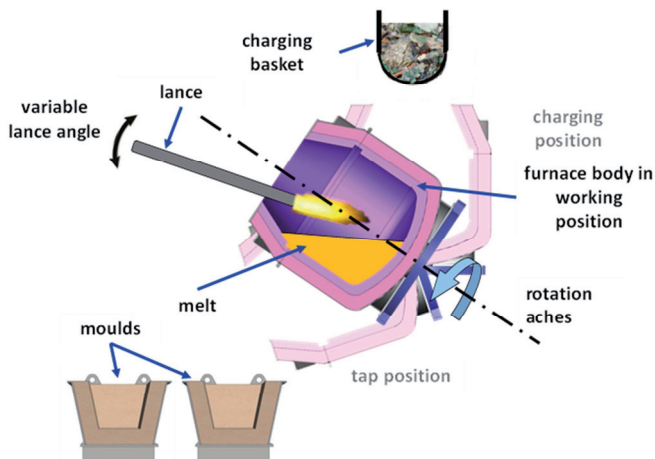


Figure 4: Schematic drawing of a TBRC in working, charging and tapping position

A big advantage of this type of furnace is the adjustment of temperature, atmosphere and turbulences independently from each other. Another advantage of this furnace is the rotation of the furnace vessel. A high rotation speed induces a good mixing of the melt which leads to small gradients in concentration or temperature throughout the melt. The process is close to the thermodynamic equilibrium. The rotation also leads to not overheating the furnace wall because the wall is always moved away from the lance or burner induced hotspot. Hence, the heat input proceeds via heat conduction. The temperature in recycling processes should not be higher than 1200 °C. During heating up the furnace, the wall takes energy from the gas area and transfers it directly into the melt. Thus bigger blocks can be melted down faster compared to not moving furnaces. Furthermore, the wall is wetted by the melt which leads to dust particle collection from the gas phase and thus it is feasible to charge fine material. The rotation speed is determined by the vessel size and mounting. Small vessels up to a diameter of 750 mm can be held and powered via the rotational axis. Such vessels can rotate with up to 60 rpm. Industrial furnaces are limited by their size up to 20 rpm and need a supporting ring. An operation for simple melting processes needs a slow rotation speed. High rotation speed improves the yield in treatment processes with a necessary mass transfer. [75], [77], [79], [39], [81], [82]

For converting processes in a TBRC, oxygen is blown through a lance into the furnace chamber. There is no difference in converting speed or efficiency between blowing on top of or into the melt. Important is that the oxygen reaches the metal phase and penetrates through the slag phase. Used material for uncooled lances are steel or alumina, for cooled lances copper is used. [80], [79], [84]

The chosen slag system should be suitable for the refractory lining to reduce corrosion. Also, the slag system should not be overheated, because the reactivity of the slag increases with the overheating rate. In basic to neutral brick linings like chromiummagnesia (basic), chromiualumina (slightly basic) and alumina (neutral), the alumina content in the slag should not be lower than 10%. Besides, the acidic components in the slag must not be too high, nevertheless for recycling processes the silica content in the slag is needed at 25%. [76], [79]

A TBRC can be used for recycling of WEEE fractions with a high organic content, where normal bathmelting processes are not practicable. For operating this process there are two strategies: a batch and a semi continuous operation.

In the batch process the material is charged in the charging position. The charging speed is 70 to 100 t per day. After charging, the furnace is tilted into working position and heated up to a temperature between 500 and 700 °C. In this period the organics are cracked by pyrolysis and combustion. The off-gas has to be post combusted because of the high organic content. The off-gas volume after the post combustion is 30,000 m³/h and contains 3 to 5 kg/h dust. The amount of produced gas can be controlled by the rotational speed of the furnace vessel. The faster the rotation speed of the TBRC, the more gas is produced. After combustion of all organic components, the material is heated up to a temperature of 1050°C and a molten slag and metal phase is produced. [6], [58]

For the semi continuous process the particle size needs to be small. The furnace is charged in the working position and the feeding speed is dependent on the temperature, off-gas volume and composition. Through this feeding technique, the organics inside the feed material are cracked by pyrolysis or combustion, hence the need for a post combustion outside the furnace. In comparison to the batch wise feeding strategy, the off-gas stream cannot be controlled through the rotational speed. But the rotation during feeding prevents an accumulation of unburned particles. The cracking of the organics is supported by the fact, that the particles are falling on to a hot slag surface with a high viscosity and the feeding is continuous. An advantage of the continuous charging is the easy control of the combustion gases in the reactor and accordingly in the off-gas. By adding oxygen into the furnace and combusting the organic compound, energy is brought into the process. [69], [70]

The flue dust and slag of both processes are treated in a slag fuming process and the metal phase is fed into the converter of the primary copper production. [58], [70]

The heat input into a TBRC can be done in two ways. In one case a burner which heats up a wall of the furnace. In another case a lance which initializes an exothermal reaction and brings energy into the furnace chamber. Figure 5 shows the heat transfer inside the furnace for these different heating systems. The heat transfer through the wall is negligible for the heat balance in the oven. Through using a lance, the heat transfer is directly into the melt. Through the burner in operation, indirect

heat transfer takes place. First the wall is heated up and transfers the heat via conduction into the melt.

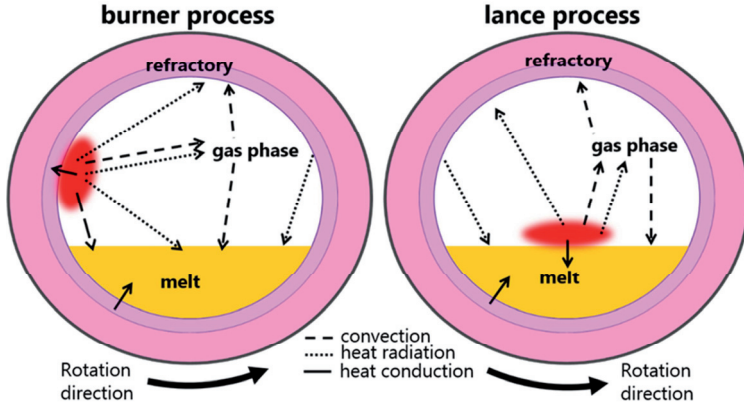


Figure 5: Heat transfer in a TBRC with energy input by burner and lance (according to) [86]

Metal-slag-equilibrium

In the nonferrous industry a basic slag consist of iron, calcium and silicon oxides. During the process, impurities of the input material (e.g. MgO , Al_2O_3) and slagging of valuable metals (e.g. PbO , Cu_2O) add to this base slag. Slagging happens through oxygen diffusion through the slag metal phase boundary. The metal phase is saturated with oxygen, which diffuses through the metal phase and reacts with the matrix metal and impurities. The oxidized matrix metal itself reacts with less noble impurities, due to their higher oxygen affinity. These so composed oxides are adding to the slag phase. [80]

The distribution coefficient between slag and metal can be linked with the law of mass action which is shown in equation I. It is to see that the activity of every single element influences the distribution as well as the temperature and the oxygen partial pressure. The activity of an element in a phase is determined by the element, its concentration and composition. In a slag phase the composition is the most important factor.

$$L_{Schlacke, Metall}^{Me} = \frac{x_{MeO_n}}{x_{Me}} = \frac{(p_{O_2})^{\frac{n}{2}} K \gamma_{Me}}{\gamma_{MeO_n}} = (p_{O_2})^{\frac{n}{2}} \cdot e^{-\frac{\Delta G}{RT}} \frac{\gamma_{Me}}{\gamma_{MeO_n}} \quad (I)$$

L_{ij}^{ME} : partition coefficient of element ME between phases i and j; x: ratio of ME in the phase; K: law of mass action constant; p_{O_2} : oxygen partial pressure; ΔG : change in free Gibbs energy by the reaction; R: ideal gas constant; T: absolute temperature; γ_i : activity coefficient of species i

Nakajima et al. calculated the element distribution for different elements in a copper converting process. They did not only focus on the partition between slag and metal but also between metal and gas phase. This type of element mapping clarifies in what way the elements are distributed in metallurgical process between the three phases. [89]

Material characterization

For the experiments, two different kinds of scrap material was used. One type was a hand sorted and crushed printed circuit board fraction called LPF (**L**ight **P**rinted Circuit Board **F**raction). The processor chips were removed from the boards before crushing and treated separately. The other type consist of different sorts of WEEE with disassembled circuit boards. These WEEE was crushed and magnetic sorted to remove iron and afterwards eddy current sorted to remove metallic aluminum. This fraction is called CRF (**C**opper **R**ich **F**raction).



Figure 6: Pictures of both fractions with the same scale, CRF copper rich fraction on the left and LPF light printed circuit board fraction on the right

Both fractions were homogenized and a representative samples was taken. For CRF four different samples and for LPF six samples were taken. The samples were analyzed with different physical and chemical analytical methods. In addition, the calorific value was identified. Table 1 shows the average, minimum and maximum analyses for both fractions.

Table 1: Composition of CRF and LPF and calorific value with information of the average, minimum and maximum content

fraction	copper rich			printed circuit board		
element	min	max	av.	min	max	av.
Cu in %	16,8	18,0	17,5	10,2	22,8	18,7
Fe in %	2,3	3,4	3,0	1,7	6,8	5,0
Sn in %	0,8	1,2	1,0	0,1	2,7	1,6
Pb in %	0,8	2,4	1,9	0,6	1,9	1,1
Zn in %	1,0	1,4	1,2	0,9	1,8	1,3
Sb in %	0,20	0,24	0,23	0,05	0,70	0,42
Ni in %	0,26	0,60	0,35	0,25	0,71	0,45
Si in %	5,7	7,3	6,5	5,9	20,0	15,7
Al in %	2,2	4,9	2,9	5,4	9,7	7,0
Ca in %	0,7	3,3	1,4	2,3	4,8	3,3
Mg in %	0,24	0,70	0,36	0,21	0,92	0,40
C in %	23,8	40,9	32,4	17,4	24,0	21,0
F in %	0,06	0,19	0,12	0,01	2,2	0,69
Cl in %	0,35	0,44	0,38	0,11	1,1	0,44
Br in %	0,7	2,4	1,2	1,2	2,8	2,0
Ag in ppm	558	1070	927	1660	600	1100
Au in ppm	38	66	53	193	138	169
Pd in ppm	12	34	26	30	88	64
Calorific value in j/g	9.800	16.800	13.300	7.400	10.900	9.417

Investigation for upscaling the process idea of an autothermal WEEE recycling

The main goal of this research is to establish a process to directly and autothermally treat WEEE in a sustainable way. Therefore, the trial series for the direct recycling of WEEE without thermal pretreatment are divided into a lab scale and a demonstrational part. The lab scale trials were conducted to set a process window for the demonstrator whereas the demonstrational part shows the feasibility of this process for industrial application.

Lab scale trials to define the process window

The basic setup of the trials is shown in figure 7. The empty crucible is heated up to a temperature of 900 °C and oxygen was blown into the crucible via an alumina lance. The material was charged at once into the hot crucible. Since it became clear during the experiments that not all material directly melted and reacted, remaining unreacted material was pushed manually into the reaction zone after approximately

half of the reaction time. At the end of every experiment, the oxygen was switched off and the crucible was removed out of the furnace.

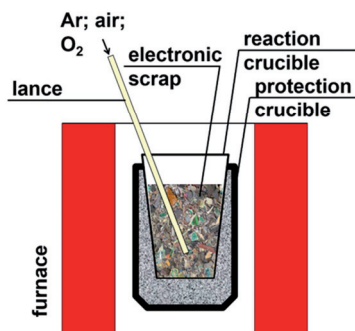


Figure 7: Principal experimental set up for the lab scale trials

The results of the lab scale trials are subsequently summarized. The lance material should be metal instead of ceramics due to higher resistivity against thermal shock and mechanical stress. This leads to the necessity of cooling the lance by the blowing oxygen in order to prevent the lance from oxidizing. During the lab scale experiments, the material inhomogeneity has caused a process instability due to the low material input. However, this will be compensated in the demonstration scale due to the higher mass throughput. Nevertheless the combustion of the fractions showed a very representative heat transfer although the material was very inhomogeneous. A fast off-gas cooling is necessary to prevent the formation of dioxins or furans due to de-novo-synthesis. Moreover, an incomplete combustion can create bromide salts which are volatile and increase the losses of valuable metals. The optimal oxygen input based on the lab scale trials should be at $18 \text{ l/kg}_{\text{WEEE}} \cdot \text{min}$. The lab scale trials point out that the WEEE recycling process needs to be done in furnace with good mixing conditions of the input material. Furthermore, the produced phases also need good mixing conditions in order to fully combust the input material and to closely reach phase equilibrium. As a flux iron oxide increases the selectivity of the slagging of the heavy metals. Basic additives decrease the slagging in total. But the viscosity is very low of the fluxless slag, which is created by the scrap itself. This makes it unnecessary to add any fluxes in the upscaling trials.

Demonstration trials for WEEE recycling in a TBRC

For the demonstrational trials, the top blown rotary converter TBRC, as part of the IME recycling research centers (IRRC) in Aachen, was used. This TBRC has a maximum operative melt volume of 600 l depending on the tilting angle. The furnace can be operated in any angle. The furnace vessel has a diameter of 1.8 m and an outer length of 1.3 m. The rotation speed can be varied from 1 to 10 rpm and the furnace is powered by a flexible 500 kW burner which can operated with pure air, enriched air

and pure oxygen. The burner can be adjusted from a reducing to an oxidizing flame. The furnace without the charging and off-gas system can be seen in figure 8.

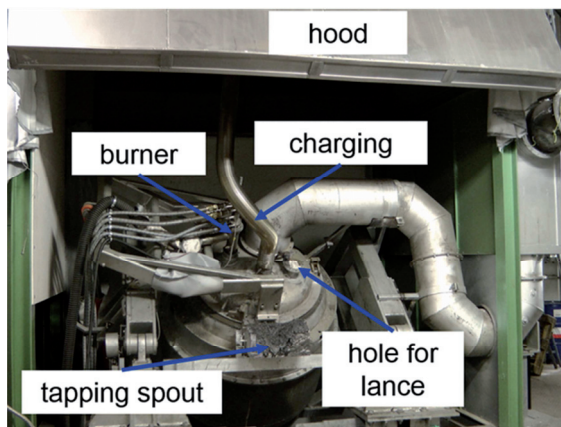


Figure 8: 0.5 MW TBRC at the IME Recycling Research Center

The Lid of the furnace has four openings; one for the burner and one for the off-gas. The third is for the oxygen lance, which is inserted in a way that it is adjustable at any time. The lance itself is 3 m long with half an inch diameter made out of steel 1.4878. The fourth opening is used for material feed. The feeding system consists of a vibrating conveyor which adjusts the material mass flow feed to the furnace continually. Through a flexible tube the material is fed into the furnace. Temperature measurements are installed in the off-gas system before and after an air quench. In the furnace chamber the only way of a temperature measurement is manually by using a glowing wire pyrometer. This temperature measurement and the tapping of the furnace are displayed in figure 9.



Figure 9: Temperature measurement with a glow wire pyrometer and the furnace tapping at the end of the trial

The off-gas cleaning consists of a two way system. The TBRC is located in a house in house system to collect all diffusive emissions. This hygienic off-gas is cleaned by a bag house filter is then used to quench the process gas before a scrubber. The process off-gas with a temperature of about 1400 °C is first air quenched to a temperature of 200 °C. At this point a first analysis for dioxin, furans, halides, CO, CO₂ and oxygen takes place also a flow profile is detected. The next step is an addition of a mixture of lime hydrate, mineral adsorbents and 5% of active coal to bind dust, dioxins or furans in the off-gas. A first dedusting step takes place in an electrostatic precipitator. Before a final cleaning step in a scrubber to remove remaining dust and gaseous impurities, the process gas is quenched with the hygienic off-gas. The scrubber solution is kept on a basic level (pH10) and a puffer volume of 5100 liters. The entire off-gas cleaning can be seen in figure 10.

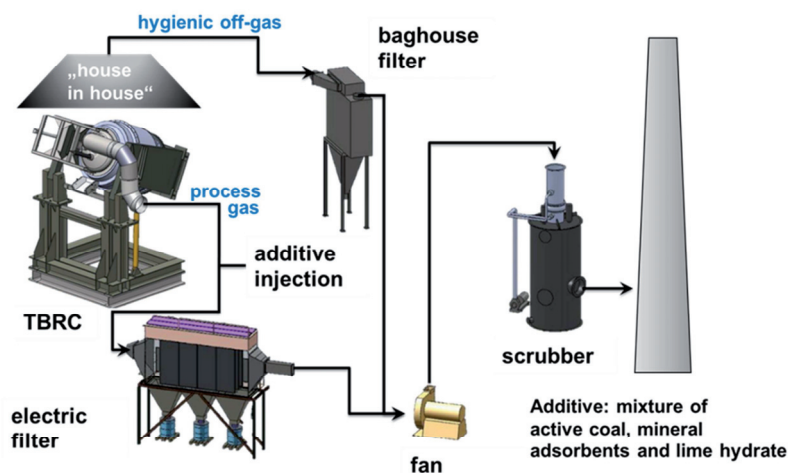


Figure 10: Off-gas cleaning system for the demonstration scale trials

When reaching a furnace temperature of 1250 °C, the experiment started with the feeding of the material while the burner was still powering. After 10 min the burner was switched off. The furnace angel was adjusted in a way that the material directly fell onto the melt. During the trial, samples of the slag and the scrubber were taken. The samples of the metal and flue dust from the electric filter were taken at the end of the process. A holding time at the end of the process could not be realized due to a massive heat loss out of the furnace, which lead to a cool down of the slag and thus in a strong increased slag viscosity. Direct tapping after stopping the material feed results non reacted particles as well as in a decreased settling behavior of the metal droplets and thus metal entrapment in the slag phase. Figure 11 presents a cross section of the slag phase and two more detailed pictures. The viscosity of the slag is low and the solidification boundary moves from the outside to the inside, that is why metal droplets appear mostly at the phase boundary and not within the slag body.

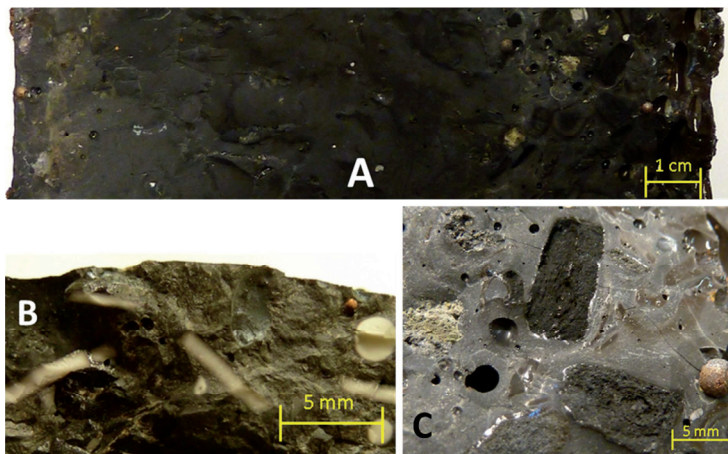


Figure 11: Cross section through the tapped slag phase (A); air slag surface to the right; two detailed pictures showing ceramic (light color in B) and high carbon containing inclusions (dark color in C)

For each fraction the optimal feeding speed was determined based on an energy input into the furnace that is high enough to keep the temperature inside the furnace in the range of 1350 °C to 1400 °C. For LPF the optimal feeding speed was 190 kg/h. With a feeding speed of 180kg/h the furnace temperature would decrease and with 200 kg/h increase. For CRF the feeding speed was lower whereas the off-gas amount for CRF was higher than for LPF. This resulted in the off-gas system working at its limit. Besides, a visible post combustion at the air quench took place. During the trials, the online CO measurement indicating concentrations of 0 to 10 ppm showed a complete combustion of the organic material. With a feeding speed of 160 kg/h CRF, the energy input was high enough to ensure a stable furnace temperature. The oxygen consumption during the demonstrational scale trials were lower than in the lab scale due to false air post combustion. In the LPF trials $6 \text{ l}_{\text{O}_2}/(\text{kg}_{\text{LPF}} \cdot \text{min})$ and in the CRF trials $7 \text{ l}_{\text{O}_2}/(\text{kg}_{\text{CRF}} \cdot \text{min})$ were used. These oxygen flows enabled a stable process and the false air consumption the organic combustion was not substoichiometric.

With all recorded data during the trials such as masses and elemental analysis of both scrap fractions, an element mapping (compared to [35]) can be done. This mapping is displayed in figure 12. A statement about calcium was not possible due to of the lime containing off-gas additive. As expected, the noble elements like gold, silver, copper, tin and antimony remain in the metal phase. The less noble elements like aluminum and silicon remain in the slag and the halides were separated into the off-gas. Iron, zinc and lead behaved differently depending on the used scrap fraction. Using LPF they were transferred into the slag and with CRF into the metal. This is also visible in the distribution coefficients. One huge difference between the two fractions is the reduction potential. CRF has higher reducing potential due to the higher carbon

content. The partition coefficient of the precious metals and the halides are independent of the feed materials. The liberation of bromine and chlorine takes place because of thermal decomposition and not because of an oxidizing reaction. The precious metal behavior is explained by the particle size. Precious metals are mostly used in surface technology and thus are usually applied very thin at huge surface areas which loosen during feeding as tinsel. Through the high turbulences inside the furnace, a small amount of the precious metal tinsel is carried out into the off-gas.

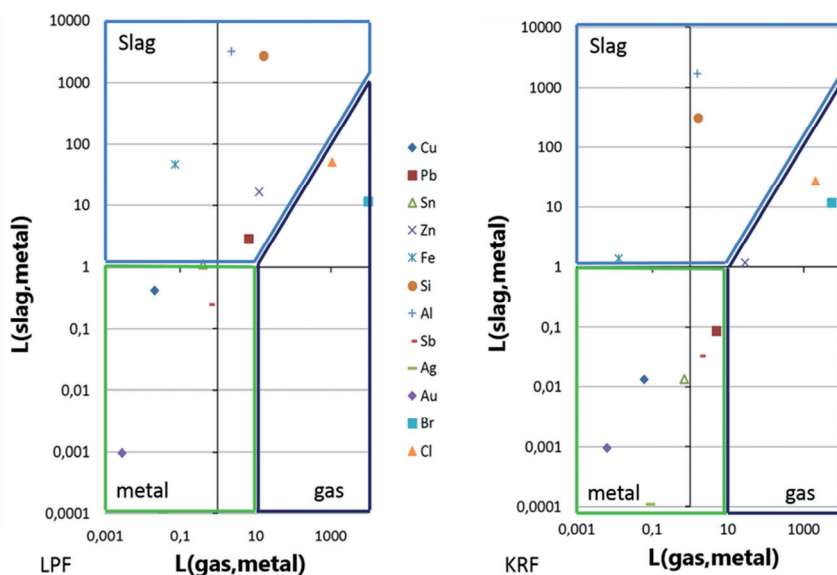


Figure 12: Element mapping of the three metallurgical phases in a TBRC during WEEE recycling

Off-gas losses of silicon, copper, silver and gold are based on occurring dust discharge. However, most of the losses, especially gold, are less than stated in literature, apart from the silver losses. Regarding silver, the occurred losses are higher than in literature data. Lead losses appear due to dust discharging and by forming volatile compositions with halides into the off-gas stream. A higher oxygen partial pressure in the furnace chamber lowers this losses through halide formations. Zinc, tin and the halides are transferred into the off-gas stream due to the reducing furnace conditions and their high vapor pressure. Zinc and tin are collected with the flue dust and the halides in the scrubber solution. The halides do not leave the furnace as acids first but as salts. This can be seen in high metal loss in the off-gas without any halide detection in the flue dust. In the off-gas post combustion these salts are decomposed and halide acids are formed.

The material is decomposed thermally in the furnace chamber. The oxygen, which is blown onto the melt, partly combusts the formed and flammable gases, adding the sucked in false air leads to a complete combustion. This fact can be used to cool down the furnace when using a higher throughput. In this case, the thermal decomposition, which is an endothermal process, and the energy needed to melt down more metal and slag is increasing whereas the energy input on the other hand is constant. The off-gas is energy rich and can be used for energy recovery. It is important that this energy leaves the furnace via the off-gas, otherwise the limit of the refractory lining would be reached quickly. The autothermy of the process is working excellent. The process even can be operated without a burner and therefore external energy addition. However, the thermal conditions inside the furnace are not in balance. The oxygen input into the furnace chamber has to be increased to reduce the losses of valuable metals. This, however, would increase the process temperature, which could be controlled by adding cooling scrap. During the presented work, adding cooling scrap was not possible. Nevertheless, cooling scrap addition has one big disadvantage, its addition dilutes strategic elements which WEEE bare but were not investigated in this work.

For this work the evaluation of the slag is very important. According to [130], a slag has to fulfill mechanical and water provision characteristics to be used uncritically in environmental surroundings. Mechanical characteristics are strongly influenced by cooling rates which cannot be influenced in this work. Therefore, the focus is on the water provision characteristics which is a leaching test. Its results are shown in table 2. The produced slags are uncritical because the limits for the conductivity of 700 $\mu\text{S}/\text{cm}$ and for metal content in the solution of 100 $\mu\text{g}/\text{l}$ are not reached and the pH-value is between 6 and 10.

Table 2: Analysis of the slag leaching of the four end slags of the trial campaign

	LPF 1	LPF 2	CRF 1	CRF 2
pH start value	6.1	6.0	6.0	6.0
pH end value	6.4	8.9	7.2	7.9
el. conductivity start in $\mu\text{S}/\text{cm}$	0.6	0.6	0.7	0.7
el. conductivity end in $\mu\text{S}/\text{cm}$	12	62	4.4	13
Cu in $\mu\text{g}/\text{l}$	30	<20	<20	40
Cr in $\mu\text{g}/\text{l}$	<20	<20	<20	<20
Ni in $\mu\text{g}/\text{l}$	<20	<20	<20	<20
Pb in $\mu\text{g}/\text{l}$	<20	<20	<20	<20
Zn in $\mu\text{g}/\text{l}$	<20	<20	<20	<20

A mass balance for WEEE recycling process in a TBRC based on this experiences, also considering optimized process parameter, is shown in figure 13. This developed named mass flow permits a further upscaling of the process. The maximum feeding speed of a reactor with 1 m³ furnace volume and an off-gas volume of 12,000m³/h is nearly 180kg/h. The carbon content and the content of metallic aluminum influence the feeding speed. By increasing the carbon content, the off-gas volume is increasing. The oxidizing of the metallic aluminum takes place in the furnace chamber, which leads to a temperature rise. Furthermore, the feeding velocity has to be adjusted to the energy release in order to prevent an overheating of the furnace.

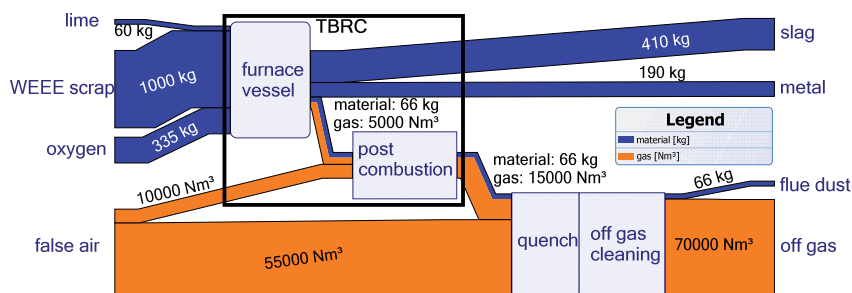


Figure 13: mass balance of the WEEE-recycling process in a TBRC at IME

Summary

The major result of the presented work is that the investigated mono process in a TBRC is suitable for the recycling of WEEE. The separation of the components such as containing fluxes, carbon and halides of such a complex input material into the metallurgical phases is possible in a good way. The separation of the valuable metals works but needs to be further improved, because for copper, silver, tin and lead the distribution is not as accurate as it should be. The carry-over of these valuable into the off-gas system is too high. This creates losses and the necessity of the flue dust treatment. Due to a high lime content, caused by the additive, the generated flue dust can be added in the TBRC process itself as a flux, but this was not investigated in this work.

The mono process creates different valuable elements carrying products which can be extracted in further processes. Beside the flue dust, these are the metal phase and the scrubber solution. The metal phase can be easily added into the converter of the primary copper route. The scrubber solution enriches with bromine which needs to be extracted out of this solution. The produced slag quality enables the slag to be used uncritically as a product. The chosen off-gas concept, consisting of an air quench, ESP and scrubber, is suitable for the WEEE recycling process since all governmental limits are fulfilled.

The thermal decomposition velocity is high enough to ensure a complete reaction, when the furnace temperature is above 1250 °C. Also some of the pyrolysis oils evaporate and prevent an agglutination of the scrap particles. The heat transfer is optimal when the scrap particles are fed directly onto the melt. Depending on the density of the particles, they either swim on the slag phase or reach the metal phase immediately. Plastic containing particles and aluminum swim on the slag phase and therefore can react with the oxygen in the furnace atmosphere. For example iron screws submerge directly under the slag surface but not into the metal phase due to their density and dilute slowly. The rotation induces a good mixing in the furnace and through that a good distribution of the scrap inside the furnace. In that way cold spots caused by endothermal decomposition of the scrap are eliminated which, in addition, leads to an increase in the reaction velocity.

Comparing the use of lance to a burner, less false air is sucked through the lid and the furnace body into the furnace chamber when using a lance. This amount is further reduced when the lance is submerged.

Concluding it can be said, that apart from minor adjustments, the TBRC as an aggregate can be used for a WEEE recycling mono process. This leads in general to a more sustainable WEEE recycling process where all generated phases are won as a product.