Slag Design for Electronic Waste Recycling in TBRC Reactors

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Abstract

Since the enactment of the WEEE-directive (**W**aste **E**lectronic and **E**lectric **E**quipment) 2002/96/EC from 27.01.2003, which ensures a separate collection from other wastes, the recycle flow of used electric and electronic devices is rapidly increasing in Western Europe. With an average content of 30 % on used devices, WEEE arising is more than 200,000 t/a, even today. WEEE contains metals like copper, silver, gold, selenium, tellurium, indium, nickel, tin and lead, which build up in total to a value between 1,000 and 4,000 €/t_{scrap} depending on the commodity price. Despite economical and ecological advantages only 40 % of WEEE is recycled in Europe. And besides the high content of valuable metals WEEE contains plastics, ceramics and glass, which contain hazardous elements like bromine, chlorine and fluorine causing special attention. At the Institute for Process Metallurgy and Metal Recycling IME a new process based on a top blown rotary converter (TBRC) is developed to recycle electronic scrap autothermically.

For the new process a specifically adapted slag has to be designed. This designed slag will be of high solubility. The task of this slag is a high solubility for impurities contained in electronic scrap and at the same time a low solubility for the valuable metals. During all smelting steps viscosity and melting temperature have to be in manageable range. Furthermore the slag has to be built-up by a small quantity of additives. The final process slag must allow the use as a product e.g. in road construction. In this presentation the methodology for the slag design will be discussed based on thermochemical modelling and equilibrium trials.

Keywords: Electronic Scrap, Recycling, thermo chemical calculation, autothermal

1 Introduction

The WEEE directive 2002/96/EG from 27.01.2003 of the European Union defines “**E**lectric and **E**lectronic **E**quipment (EEE)” as a device, which is dependent on electric currents or electromagnetic fields in order to work properly or which is an equipment for the generation, transfer and measurement of such currents and fields up to a dimensioning of an AC-voltage of 1000 V and a DC-voltage of 1500 V.

An estimate of the current WEEE arising across the EU27 is between 8.3 and 9.1 million tonnes per year for 2005. This amount makes up about 4 % of the municipal waste stream. A number of forecasting assumptions were applied which predict that the total WEEE arising will grow annually between 2.5 % and 2.7 % reaching about 12.3 million tonnes in 2020. [1]

Electronic scrap is a very complex mixture of different materials. It consists of about 15 to 30 % plastics, 40 to 50 % ceramics and 20 to 30 % metals like copper, aluminium, iron etc. Figure 1 presents more details about the average composition of a common WEEE mixture. The composition however depends on the age, origin and manufacturer of the EEE. [3][2]

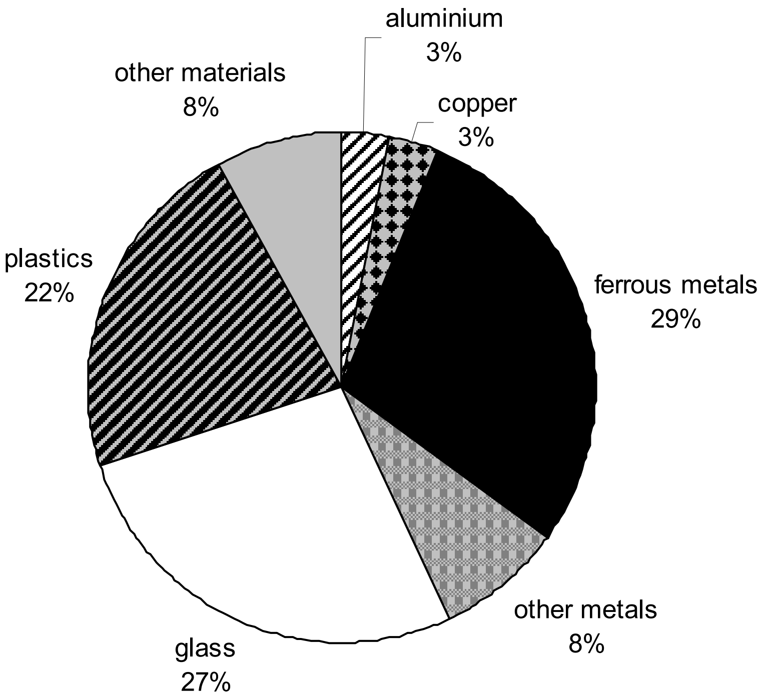

Figure 1: Average composition of WEEE [4]

A non-ferrous metal fraction is produced by dismantling, crushing, iron and metal separation, grinding, milling and sorting. In the non-ferrous metal fraction a large amount of carry over can be found due to an imperfect liberation and separation of the highly complex composites. Table 1 compares a typical copper ore with the composition of different kinds of WEEE.

Table 1: Analysis of four e-scrap streams compared to typical copper ore [5]

	Keyboard	Personal Computer	Printed Circuit Board	Car Electronic	Typical Copper Ore
High Value Extractable Metals					
Ag / ppm	500	90	3000	1200	3.4
Au / ppm	50	10	80	70	0.1
Cu / wt.%	13	7	25	20	0.8
Zn / wt.%	3	1.2	1.5	1	0.12
Pd / ppm	2	4	-	-	400
Al / wt.%	18	11	3	-	-
Medium – Low Value Extractable Metals					
Ni / wt.%	0.6	0.2	0.5	0.3	-
Pb / wt.%	0.3	1.5	-	1	-
Bi / wt.%	<0.0003	<0.0004	0.17	0.01	-
Fe / wt.%	3	<0.1	5	5	-
Sb / wt.%	0.3	0.5	0.06	0.08	-

The composition of WEEE will change in the future due to the following facts:

- The content of Aluminium, Magnesium und Phosphate will increase because compounds with these elements will replace the present bromide containing flame retardants [6].

- The amount of valuable material will decrease due to the cost cutting strategy in new electronic equipment.

- Due to technical improvements in the separation process connected with a better sorting efficiency the content of copper will increase and the content of plastics will decrease.

Why is the recycling of WEEE so important? There are four strong driving forces that lead to the recycling of WEEE. One of them is environmental protection: A lot of hazardous material is contained in WEEE. In the case of landfill deposition, these hazardous components are solubilised out of the WEEE by rainwater and pollute the environment. Another driver is of economical nature: High valuable materials such as silver, gold, platinum and palladium are contained in WEEE. The commercial relevance ranges between 1,000 and 4,000 €/t_{scrap} depending on the commodity price. To landfill WEEE means to dump this whole value. The high value metals together with Cobalt, Indium, Antimony, Tantalum, Selenium and Tellurium are considered strategic metals in the EU because they are necessary to keep high technological standards and have reserves for future developments [7]. To keep these materials inside the borders of the EU is a social driver. Finally the implementation of the WEEE directive 2002/96/EG from 27.01.2003 in the EU member states can be regarded as a fourth driving force on a legal level. Up to the year 2016 a recycling quote of 65 % has to be ensured.

The IME and Europes largest copper producer Aurubis are jointly developing a new process for the recycling of WEEE. The aim of this project is to create a continuous and autothermal process in a rotary converter exclusively for WEEE with both a maximised recycling efficiency and avoiding new waste. For copper and noble elements the aspired recovery rate is higher than 97 % and for nickel, lead and tin it is 80 %. The generated mineral phase should have low contents of valuable or hazardous materials.

First of all metallurgical fundamentals are investigated and parameters for 1-t-scale trials are defined. The acquired results enable a forecast for scale up to a 100,000 t/a furnace. One of the first development steps is the design of a slag which is specialised for this application.

2 Methodology and Materials

In designing a slag for a certain process the first necessary step is to know and understand the material feedstock. After characterisation of this feedstock strict design goals can be established.

In this work WEEE is characterised and analysed in the first place. With that composition thermochemical calculations are done in order to obtain perfect combustion conditions. This will result in determination of a slag composition and metal phase which is created by the combustion of electronic scrap. By adding fluxes to the slag a new slag is created, which in a third step get in contact with the metal phase to reach the equilibrium state. The results of these equilibrium calculations are proven in trials.

2.1 Characterisation of WEEE

For the investigations two different kinds of WEEE, printed circuit boards and cable scrap, were used. Four different samples were taken in two different sampling processes for each variant of scrap. Together with analyses of samples from another electronic scrap mix the average content of the electronic scrap as a random mixture was calculated. Average compositions are shown in Table 2. and it becomes obvious that the analytical results are very heterogeneous. Even for one type of electronic scrap the composition is spread in a wide range.

Table 2: Average composition of investigated WEEE

Element	C	Cu	Si	Al	Fe	Pb	Sn	Sb
Content in wt.%	21.8	17.2	13.3	5.3	4.4	1.6	1.6	0.43
Deviation	7.6	4.6	5.3	2.6	1.8	0.9	0.6	0.20

Element	Ca	Br	F	Cl	Ag	Au	Pd	Pt
Content in wt.%	2.55	1.4	0.51	0.29	0.1	135 ppm	58 ppm	1.7 ppm
Deviation	1.48	0.8	0.84	0.10	0.05	66 ppm	35 ppm	0.4 ppm

2.2 Slag design

The characterisation of WEEE leads to the aim to extract Cu, Ni, Pb and PGM in a metal phase, Fe, Sn, Al and Si in the slag and Zn and halides in the flue dust. Next step is the design of a slag which has a high solubility for these slag components and a high immiscibility for the components aimed for flue dust and metal phase.

Firstly ideal combustion was calculated to obtain the composition of an ideal metal and slag phase. In the second step the formation of metal and slag phase was simulated, in which fluxes and additions to the slag are included. After that the equilibrium between the metal and slag phase was identified. In the fourth step these calculations were validated in equilibrium trials. And finally the slagging of this slag was investigated.

2.2.1 Thermo chemical calculations

Thermochemical calculations were done with the FactSage™ program. For the combustion and the metal slag interaction calculations the databases Fact53, FToxid and FScopp were used. For calculation of the melting point of the slags the same databases except FScopp were chosen.

2.2.2 Validation of the calculations by equilibrium trials

A vacuum induction furnace, which is pictured in Figure 2, was used for equilibrium trials. The equipment has a maximum power output of 4 kW and the furnace chamber has a volume of 124.1 l which is connected to a vacuum system. An induction coil made of water cooled copper tube with eleven windings (height: 170 mm, diameter: 142 mm) hosts the crucible.

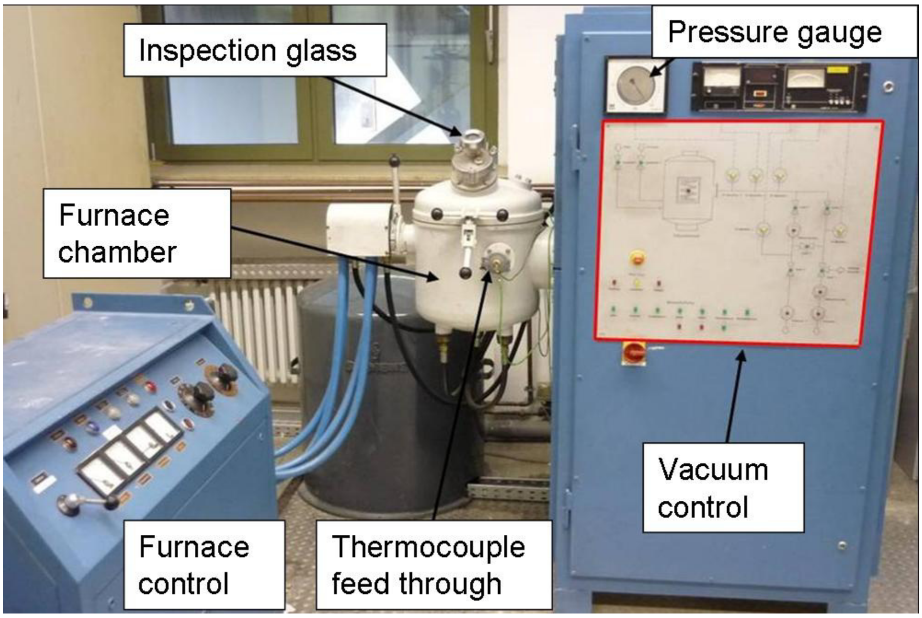

Figure 2: The IME induction furnace which was used for equilibrium trials

In every trial 40 g of copper and additionally 80 g of slag were fed to an alumina crucible. To achieve a better coupling of the electromagnetic field and hence a better heat distribution the alumina crucible was embedded into a graphite crucible. A cover with graphite felt was used to minimise further heat losses by radiation.

All considered slags, 24 different compositions in total, were synthesised from components with a purity grade not less than 99 %. The slags were premelted in order to homogenise composition and to achieve the right level of FeO.

In the beginning of each trial a vacuum was generated and the chamber was flooded with argon. In the next step vacuum restored and 15 mbar of CO as well as a quantity of argon up to a total pressure 600 mbar were injected. CO was inserted in order to lower the oxygen partial pressure to 10^{-10} bar. The crucible was then heated up to a temperature of 1250 °C with a heating rate of 1500 °C/h. The holding time was one hour.

3 Results

The combustion calculations, which are given in figure 3, reveal that the complete combustion of carbon takes place at a mass ratio of oxygen to WEEE of 0.38. There is an ideal combustion point at a mass ratio of 0.35. The composition of the metal phase can be calculated with the metal yield of each metal. This expected composition is displayed in Table 3. The slag composition in table 4 is calculated from the FactSage™ data.

Table 3: Composition of the metal phase determined by combustion calculation

Element	Cu	Fe	Sn	Pb	Ni	Sb	Zn	Ag	Au
Content in wt.%	75.3	10.1	7.1	3.4	1.9	1.4	0.3	0.5	0.05

Table 4: Composition of the slag phase determined by combustion calculation

Element	SiO_2	Al_2O_3	CaO	FeO	MgO	PbO	Cu_2O
Content in wt.%	62.8	19.9	8.4	7.0	1.6	0.2	0.03

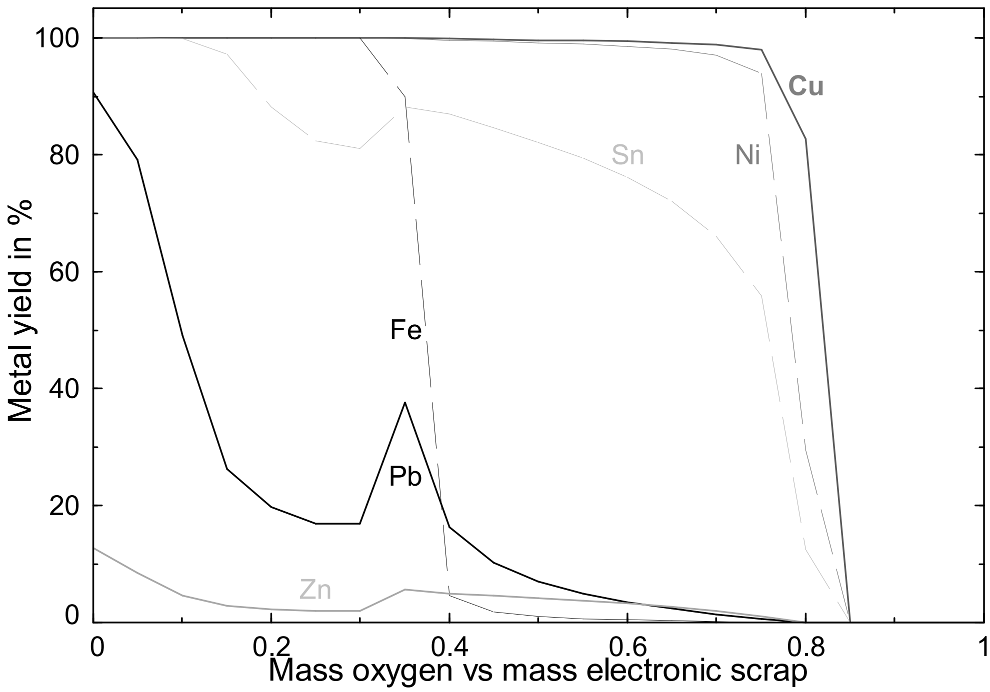

Figure 3: Results of the calculation of the WEEE combustion

Calculations of a seven dimensional system are very complicated. To simplify this system the slag of Table 4 is cut down to only four components despite the fact that this type of slag has a very high viscosity. Therefore the composition is directed towards lower viscosity without changing the metal slag interaction of the slag. The new slag consists of 50 % SiO_2, 25 % FeO, 15 % Al_2O_3 and 10 % CaO.

To choose the capable slag systems two different types of calculations for the different fluxes and additions are done. In the first step the equilibrium of the slag systems with the metal phase is calculated. The next step is the calculation of the melting point of the slag systems.

Figure 4 depicts an example of an equilibrium calculation between the metal phase and a slag with a variable amount of titania. The sum of these two components is fixed at 10 %. It is to be seen, that the metal yield of lead is decreasing with increasing content of titania. On the contrary the yield of nickel and tin is increasing with increasing soda amount. In this case the metal yield of copper is not influenced significantly by the chemical composition of the slag.

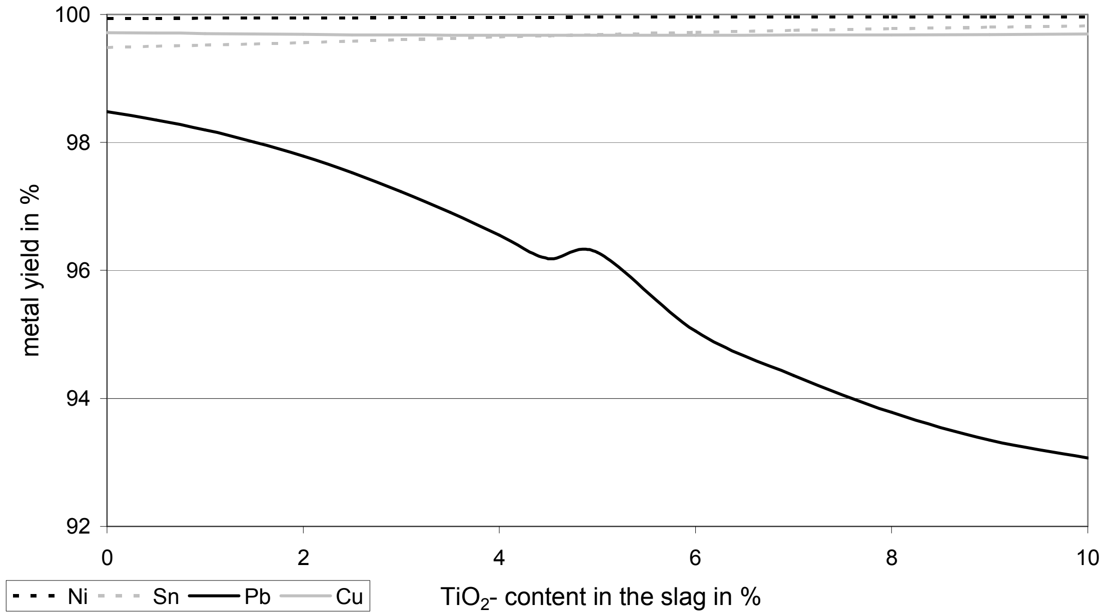

Figure 4: Example of an equilibrium calculation with the addition of TiO_2

Figure 5 shows the results of an investigation of the same slag melting points, which is displayed in Figure 4. The melting point is defined as the temperature where no solid phase is present. With an increase of the TiO_2 content the melting point rises. Up to a titania content of about 5 % the slag can be used for the process.

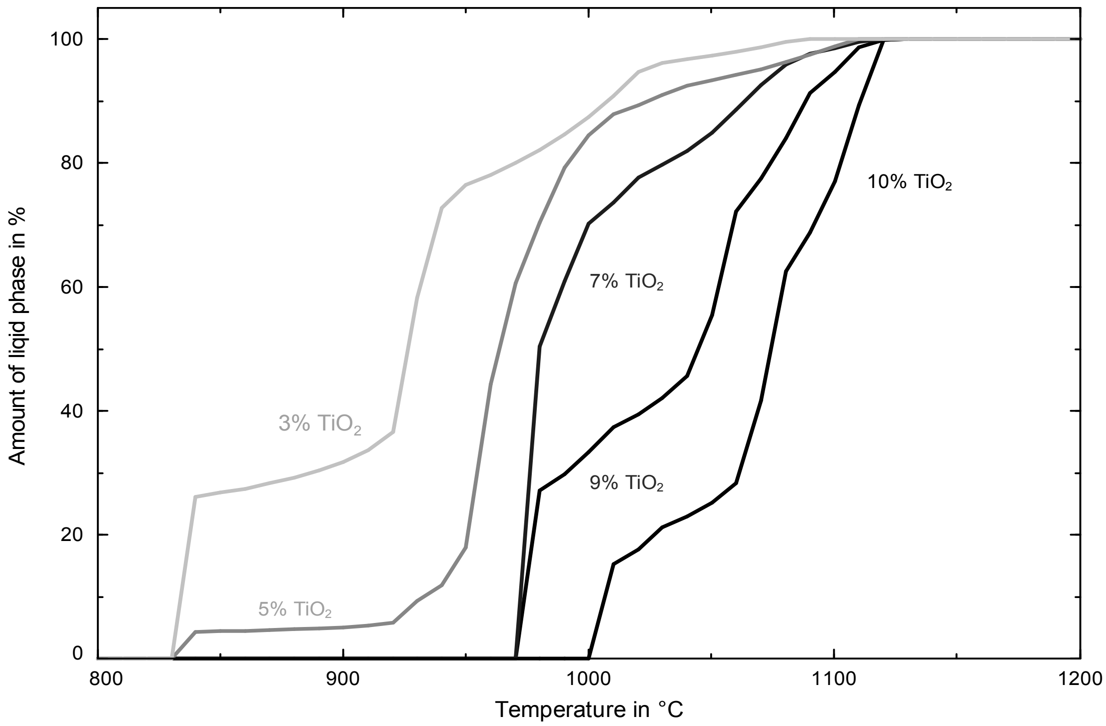

Figure 5: Example of a melting point calculation by different TiO_2 additions

Out of the calculations, 24 slag systems are chosen to be verified in equilibrium trials. Soda, titania, magnesia, calcia, boron oxide and lithium oxide are the additives used for the slag. The chosen slag systems are shown in Table 5.

Table 5: Used slag additions for the trials

No.	1	2	3	4	5	6	7	8
Add.[1)]	none	WEEE	Mg 3	Mg 5	Mg 7	Mg, Ti1	Mg, Ti3	Mg, Ti5
No.	**10**	**11**	**12**	**13**	**14**	**15**	**16**	**17**
Add.[1)]	Ti5	Ti, Na 1	Ti, Na 3	Ti, Na 5	Na 3	Na 5	Borax[2)] 7	Borax[2)] 11
No.	**18**	**19**	**20**	**21**	**22**	**23**	**24**	
Add.[1)]	Borax[3)] 10	Borax[3)] 15	Li 5	Ca 14	Ca 20	WEEE CaO 5	WEEE CaO 15	

[1)]: Addition to the slag in % of the oxide of the named metal; [2)]: Borax as $Na_2B_4O_7$; [3)]: Borax with a ratio of Na_2O to B_2O_3 of 0.864

In the equilibrium trials no copper or tin are slagged. For iron no grade of slagging can be concluded, because the metal yield of iron is higher than 100 %. A reason is that during composition of the premelted slag metallic iron was added on purpose to ensure for the necessary FeO content by oxidation. Residues if this metallic iron is dissolved in the copper phase and raise the metal yield to values higher than 100 %. The slag systems 23 and 24 can not be analysed, because these slags are not melted. The metal yield of copper, nickel, lead and zinc is pictured in Figure 6.

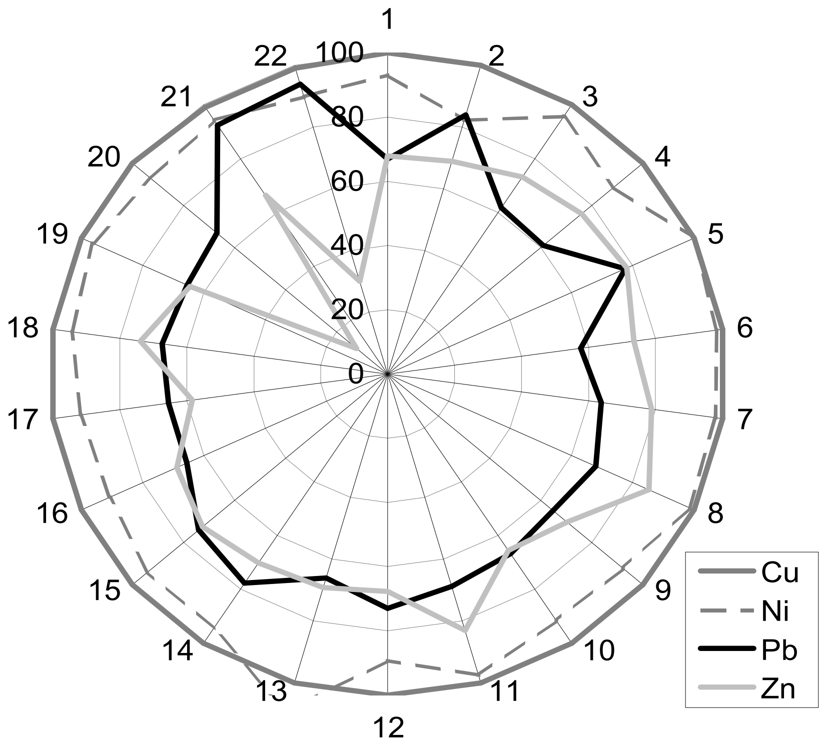

Figure 6: Results of the equilibrium trials (net arms: No. of trial /-; net rings: metal yield / %)

Figure 6 shows that magnesia, sodium oxide, lithium oxide, Borax 0.864, calcia and a mixture of titania and magnesia are effective additions. Lithium oxide as a slag component (trial No. 20) results in the same metal yields as the standard slag and low yields on zinc. Calcia causes minor reduction copper yield but results in a higher yield of nickel and lead. Magnesia and especially in combination with titania produces better metal yields of copper, lead, nickel and zinc. A small addition of sodium oxide also raises the metal yield. Another effect is that borax with a higher amount of soda (with a ratio Na_2O/B_2O_3 of 0.864 instead of 0.527) has a better effect on the metal yield, as observed by Tandon et al. [8]

4 Summary and Outlook

A common composition of used WEEE mixture, which is created of two types of e-scrap, was investigated by four samples of each type and two of the mixture.

In a next step the combustion of this scrap was simulated by thermochemical calculations. The results of these calculations, which are the expected equilibrium compositions of the generated metal and slag phase, were then used for further calculations to create an improved slag composition, which can be used for WEEE recycling. The metal-slag-interaction-calculations and melting point calculations were established as criteria for the selection of 24 slag systems for a trial validation.

These equilibrium trials took place in a vacuum induction furnace under inert gas atmosphere in 100 ml scale. After the trials the metal yield was determined by analysing the metal composition. The most capable slag additions were observed around 7 % MgO, 5 % CaO and Na_2O in combination with B_2O_3 as Borax 0.864.

In the future further series of trials are necessary to examine the slagging of these slag systems. Additionally the influence of additives on the viscosity of slag will be investigated to determine the smallest necessary amount of additives. Trials in a small scale for WEEE recycling with preconditioned material will take place before first melts in a TBRC, with a melt capacity of 0.6 m³ will be conducted. These trials will take place in the new RRC (recycling research centre) currently under finalisation at IME.

5 Acknowledegement

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