Substituting Coal by PCB for primary Lead Slag Treatment – A Proof of Principle

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Abstract

The volume of WEEE scrap fractions is increasing in the era of further digitalisation. The recycling of WEEE in pyrometallurgical copper production is primarily aimed at the extraction of copper and precious metals. Lead reduction furnaces, in which lead is extracted from oxides, offer a further recycling option. The advantage of using lead is its excellent collection properties for valuable (copper, silver, gold) and technology metals (antimony, bismuth, tin). Industrial lead refining also enables the selective separation and recovery of by-metals. Furthermore, when used in a reduction furnace, the carbon contained in WEEE scrap is recycled and fossil raw materials are conserved.

In this article, the theoretical and thermodynamic processes involved in the addition of PCBs in lead slags are described with FactSageTM and based on this, laboratory tests are carried out on a 750 g scale. For this purpose, PCB are added into a rotary drum furnace and reduction efficiency is evaluated. Chemical analyses are carried out to investigate the final contents in the metal and slag phase and to determine distribution equilibria. The oxides contained in PCB are partially acting as fluxing agents. The investigation will be rated in case of feasibility and resulting potentials or problems for lead industry.

1 Introduction

The European Union sets an ambitious target with the planned CO_2 neutrality “Green Deal” [1] by 2050. This must be met not only by steel industry but also by non-ferrous industry, which emits significant amounts of fossil CO_2. In primary lead extraction, the lead(II)oxide-rich slag is reduced with coal after sulphur separation and lead is produced. This is done both in two-part and direct reduction processes. Replacing fossil carbon with recycling carriers could help justify the emission.

With the trend of digitalization waste of electric and electronic equipment (WEEE) demand is rising. Per year a global average of 7.6 in 2013 and 8.1 kg/(capita·year) in 2016 [2] showing increasing recycling potential. Only 20 % of produced WEEE were recycled in 2016, leaving around 80 % untreated [2]. Regarding E-Waste-Monitor the volume will increase to 9.0 kg/(year·capita) in 2030 [3]. One influencing factor is incorrect disposal in poor, but also highly developed countries. In view of the legally increasing recycling rates in the European Union (EU), not only the collection but also the processing companies must treat more WEEE in the future. After reaching a collection rate of 45 % in Germany in 2017 [4], this rate must increase to over 65 % in 2019 [4]. This corresponds to an additional WEEE-mass of 400 mt in Germany [4]. In addition to the use of electronic scrap, the EU’s ambition to achieve a 55 % recycling rate on packaging plastic by 2030 [5] shows further potential for the metallurgy sector. According to the EU, one third of the plastic consumed was landfilled in 2014 [5]. In terms of 2015 generation, this translates to 106 million tons of unused plastic [2]. Another point is that from one third of the plastic “only the energy was recovered” [5]. The inclusion of plastics in the metallurgy industry thus offers further variants to replace fossil reduction carriers.

Electronic scrap is mostly used in the production of copper according to the current state of the art [6, 7]. Due to the high copper content in WEEE, this use is evident, but partly rare technology metals are neglected. The addition of WEEE in the copper route is industrially performed in primary converter or secondary reduction and oxidation step [7]. Due to low value oxide contents in slag, only little reducing agent is required in these processes. A large part of plastics burn and are energetically utilized. Additionally, less noble base elements are oxidized into the slag [8] or collected in the flue dust. These phases are reprocessed either in the construction sector or by external preprocessors. Other promising research approaches of autothermal Printed Circuit Boards (PCB) combustion for copper route according to TRENTMANN [6] and BOROWSKI [7] have not yet become established on an industrial scale.

Introduction of WEEE and plastics in lead metallurgy would take place in slag reduction process. As a main benefit in lead metallurgy, it provides a metallic lead phase with high capacity for collection of technology metals. Also, the reductive atmosphere tends to favor, if thermochemical possible, the metallic state of metals [9]. In addition to element recovery, this is an opportunity for chemical utilization of the carbon to reduce PbO and other oxides present in the slag. The lower reduction energy released, in contrast to combustion, also lowers the problem of energy imbalance in the furnace. The selective separation of Pb and Cu, Sn, Sb or Bi is state of the art in subsequent lead refining. Other benefits are listed below.

- Tolerance of impurities in incoming material streams
- Flexibility for metal contents in lead phase in lead refining plants
- Existing requirements for health protection
- Existing requirements for environmental protection
- Off gas system designed for high temperature caused by Zn-fuming

Some of the advantages mentioned are already being applied at industrial scale. For example, UMICORE [10] and AURUBIS [11] already treat WEEE in a combination of copper and lead metallurgy and achieve high yields for valuable and technology metals. Such a process requires copper treatment furnaces, as well as lead reduction furnaces in the company. On the other hand, the use of non-WEEE plastics in a zinc volatilization furnace has already been investigated by BOLIDEN [12], with the result that the use results with similar reduction rates, as well as higher steam production. In primary steel process GUDENAU [13] successfully tried to add pure plastics in blast furnace process. Post-combustion in the exhaust gas plays a greater role compared to coal with plastic carriers.

The present study aims to reveal limitations of the lead reduction process with the highly metal and ceramic containing WEEE stream of printed circuit boards. It is especially laid on the change of slag metallurgy and the trend of chemical carbon utilization. First of all PCB additions are simulated using FactSage^{TM} 8.0 [14] with same carbon acticity like coal. In the experimental part, both the coke reference and mixtures with PCB were carried out with same net carbon content. From the results, opportunities for the use of WEEE and high plastic containing streams, as well as limits, for primary lead facilities are to be identified.

2 Feed material

Figure 1 shows the main feedstocks used for the experimental part and the compositions from Table 1, which are used for the thermochemical simulations. The lead slag used comes from a primary plant and was water granulated after conversion. It contains over 70 % PbO and only small amounts of valuable metals (Cu, Sn, Ag, Au). A further 5.68 % ZnO content is included. PCBs with approx. 20 % metallic Cu and high proportions of SiO_2 and Al_2O_3 are used as WEEE feedstock. The plastic content is usually around 25 %. The precious metal content of silver and gold is less than 0.3 %. Metallurgical coke containing over 87.5 % carbon and 9 % ash (Rheinbraun Brennstoff GmbH) with an average grain size of under 1 mm is used as the comparative reducing agent.

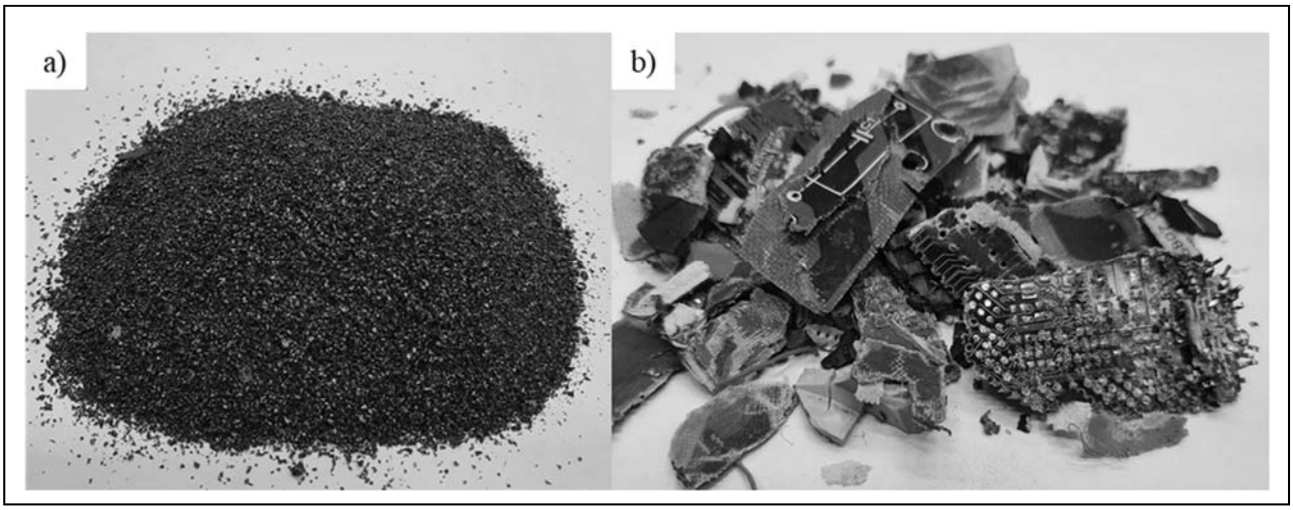

Figure 1: Picture of primary lead slag (a) and printed circuit boards (b)

Table 1: XRF-Analysis of used primary lead slag and PCB from literature

Primary lead slag

wt.-%	PbO	ZnO	CuO	Fe_2O_3	SiO_2	CaO	MgO	Al_2O_3	SnO_2
slag	72.30	5.68	0.61	9.90	5.13	2.68	0.51	0.62	0.23

PCB [15, 16]

wt.-%	Cu	Fe	Al	Sn	Pb	Ni	Zn	Ag	Al
Min.	15		2.0	1.0	0	0.5	0	0.1	2.0
Max.	30	8.0	5.0	4.0	2.0	2.0	1.5	0.3	5.0

wt.-%	SiO_2	CaO	Al_2O_3	TiO_2	MgO	Plastics
Min.	15.0	0.0	6.0	0.0	0.0	20.0
Max.	40.0	9.9	7.0	3.0	0.5	30.0

Conversion of those PCBs are described by DIAZ [16]. Thermolysis begins when the PCBs are immersed in the melt, or when the plastic is heated abruptly above 600 °C. According to him, gasification begins in the temperature range above 500 °C, so that hydrogen, carbon dioxide / monoxide and methane are formed preferentially. These can react directly with metal oxides when contacting within the slag. Compounends that have not reacted burn off after oxygen contact in gas phase. Also a better kinetic behaviour in comparison to metallurgical coal is reported for pyro / thermolyzed carbon residue [17].

3 Thermochemical simulation of PCB injection

Figure 2 plots the slag composition calculations for 1100 and 1200 °C. The reduction of lead is not temperature dependent. The varying contents of PbO are obtained due to the deviating zinc contents caused by evaporation. Zinc is reduced starting with a PCB addition of 7 % and drops sharply from a PbO content of less than 5 wt.-%. From an addition of 7 % PCBs, the activity of ZnO (0.08) exceeds that of PbO (0.07). The complete reduction of the zinc content cannot be achieved with 15 % PCB addition. A further decrease is found at Cu_2O and SnO_2 contents with 7 % PCB addition. After an increase of the Cu_2O concentration to a maximum of 1.14 wt.-%, it drops to below 0.10 wt.% at 11 % addition. Similarly, the SnO_2 content drops from a maximum of 0.35 to below 0.10 wt.% at 10 % addition. Thus, an addition of 11 % of the slag mass is sufficient for valuable metal recovery. The final slag composition after 11 % addition is 4.78 wt.-% Al_2O_3, 25.13 wt.-% SiO_2, 10.30 wt.-% CaO, 30.70 wt.-% FeO and 15.78 wt.-% ZnO. Additional PCB addition will decrease zinc concentration linearly by around 1 wt.-% Zn per 1 % PCB, thus showing a temperature dependence by increased vapour pressure. Reduction with carbon without companion elements shows similar behaviour. The carbon reduction proceeds slightly slower than with the addition of PCBs, caused by dilution ceramic elements from PCB. Also ZnO and FeO is diluted by 7 and 6 wt.-%, while SiO_2 and Al_2O_3 were increased with PCB addition.

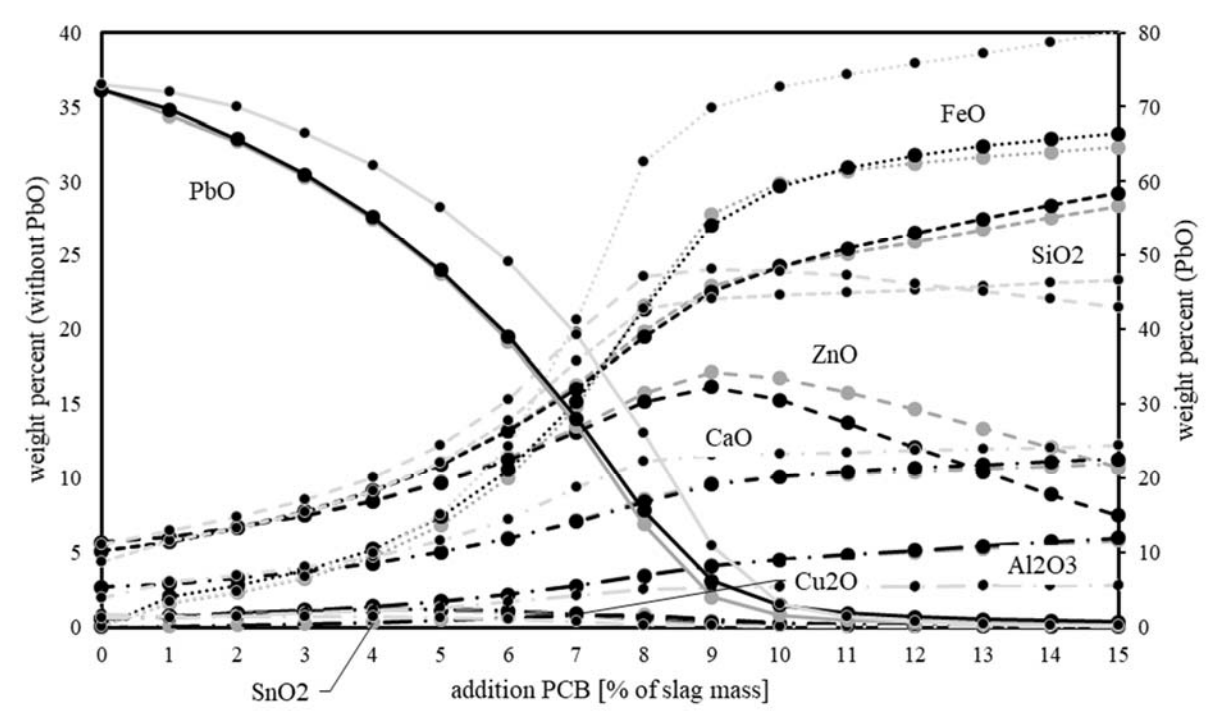

Figure 2: Composition of lead slag with simulated PCB addition (1100 °C – grey, 1200 °C – black, 1200 °C pure Carbon grey line with black points) [14]

A second important process parameter is slag viscosity. In Fig. 3, it is plotted under the assumption that the slag remains liquid. The influence of the concentrations of lead oxide can be observed. The reduction of lead oxide poses only minor problems with respect to the process due to low viscosities below 0.5 Pa·s. In the further course of the reduction, the ZnO content in the slag decreases and thus the concentrations of the ceramic oxides SiO_2, CaO, Al_2O_3 and MgO rise. The viscosity continues to climb up to 0.7 Pa·s with 12 % PCB addition. Increasing the temperature reduces the viscosity on average by approximately 42 % (1200 °C) and 64 % (1300 °C). The simulated viscosities should not cause serious disadvantages in terms of process control.

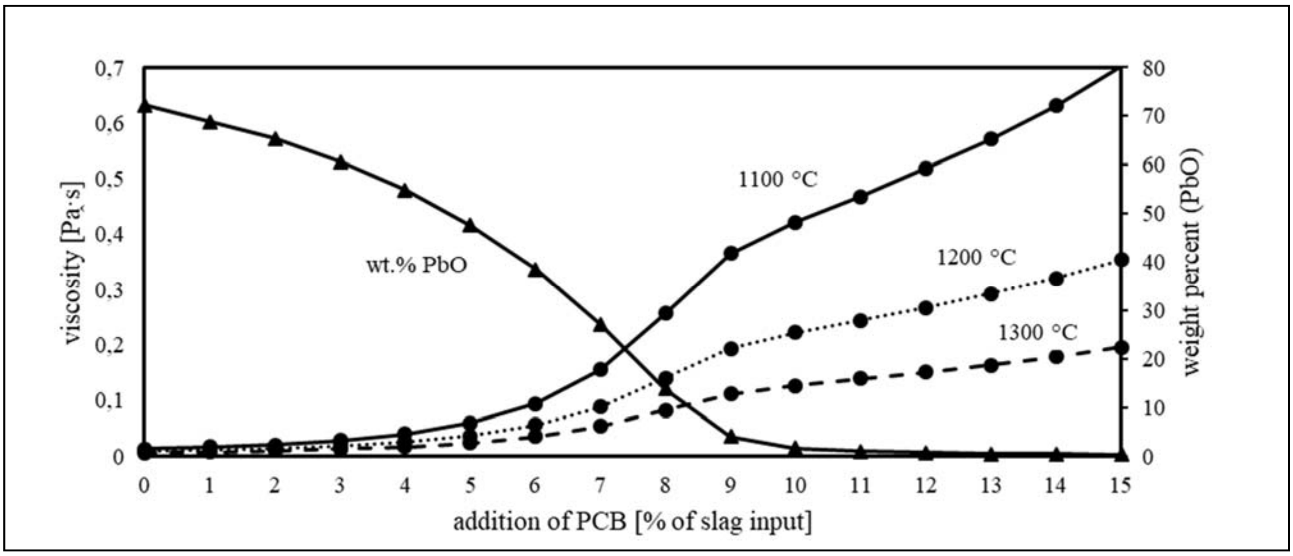

Figure 3: Viscosity of liquid slag at 1100, 1200 and 1300 C [14]

4 Process behaviour of PCB in lead slags

The experimental set up is taking place in a laboratory rotary drum furnace at IME, which is shown in figure 4. It is resistant heated and insulated with ceramic wool. The inner crucible has an inner diameter of 53 and a height of 420 mm. It is made from $Al_2O_3 \cdot MgO$ and placed inside a graphite crucible for mechanical stability. The rotation axis is fixed on the bottom of the graphite crucible and could be adjusted in speed. Temperature regulation is adapted via thermocouple 2 and occasionally controlled with thermocouple 1 inside the melt. On top of the furnace a flue dust collector is used to condensate zinc- and lead-dust and products of PCB-thermolysis.

The furnace is heated to the experimental temperature at a rate of 300 °C/h and then held. From 600 °C, an inert gas supply of 10 l/min argon is applied in the inner crucible to reduce oxidation. For these experiments, a speed of 18 rotations/min (3 m/min) and an angle of 40° is used. Suction is decreased to a minimum during the experiments. After reaching the holding temperature, the reducing agents are added in steps of 25 g (2 – 3 % of slag mass) on top of the bath and the holding time of 15 or 30 min is kept in each case until the next addition. Afterwards the crucible cooled down slowly inside the furnace.

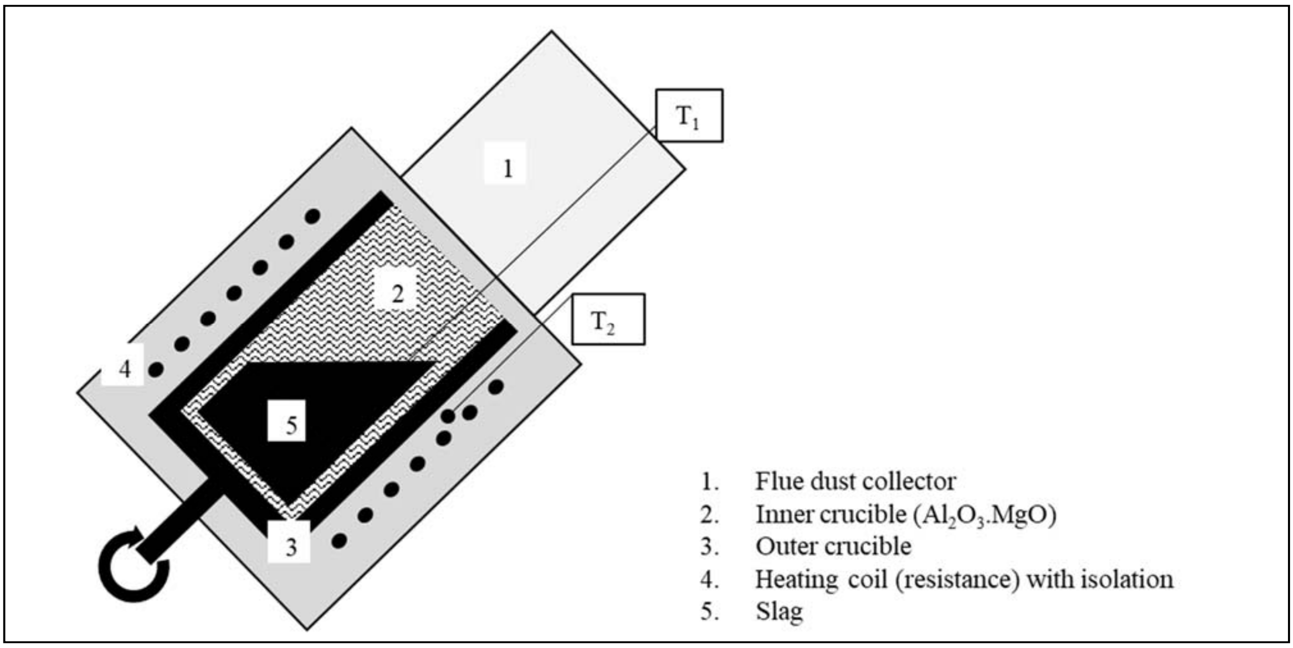

Figure 4: Tiltable rotary drum furnace at IME

The test parameters include variation of reducing agent addition, temperature and holding time. In sum, 8 experiments were carried out. Thus, the efficiency of the reductant conversion is to be determined with decreasing PbO content. Trials with sub-stoichiometry of 0.6 to 0.9 will prevent unreacted carbon and low PbO activity. In those trials, the reduction of other oxides should be prevented as much as possible to detect carbon yield by PbO decrease. Also the effects of the dissolution of the containing ceramic amount on the process and the slag shall be shown and evaluated. In the experiments 4 and 5, the carbon content is increased to stoichiometries of 1.0 and 1.8 to start the reduction of oxides besides PbO. The reducing agent mix is varied between 50 and 100 % PCB to counteract any viscosity limitations that may occur and to simulate the addition of lower ceramic content feedstocks. All slags were analysed by wavelength dispersive x-ray fluorescence (XRF) spectroscopy. The holding time between reduction agent addition was set to 15 minutes shown for full PCB-reduction / dissolution in pre-test.

Table 2: Table of parameters and trials

No.	Temperature	Holding time	C-Stoichiometry	PCB addition[1]
1	1100 °C	15 min	0.7	0 %
2			0.7	50 %
3			0.9	100 %
4			1.0	100[2] %
5			1.8	100 %
6		30 min	0.7	50 %
7	1200 °C	15 min	0.7	50 %
8			0.9	100 %

[1] % of total molar carbon input, [2] pyrolyzed PCBs

The experiments demonstrate that PCBs have a significantly shorter reaction time than metallurgical coke. The coke remained after 15 min holding time, while PCBs reacted directly at additions below 13 % of slag mass and ceramic ingredients were dissolved in the slag. At additions above 15 % PCB, the ceramic absorption capacity is reduced and parts of the fibre structure remain on the molten bath. The addition of PCB above 15 % slag mass also shows increased viscosity. Direct ignition of the PCB is observed when charging (see dust in Figure 5), as well as strong carbon deposition in the flue dust collector. Pretreatment by pyrolysis prevents direct ignition of the material and ensures significantly smoother process behaviour and lower carbon deposition in the flue dust.

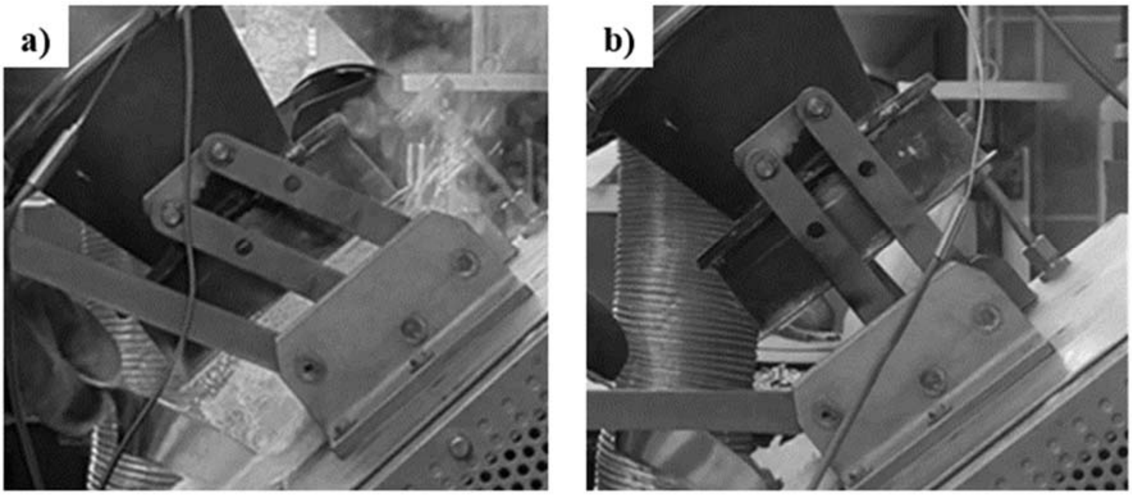

Figure 5: Spontaneous inflammation directly after charging of unpyrolysed PCB (a) and pyrolyzed PCB (b)

The reaction process is analysed in the over-stoichiometric tests 4 and 5. By taking samples directly before the addition of reducing agent, the direct influence can be determined. Figure 6 shows the development of the 10 most important compounds in the slag. In test 5 the lead content decreases linearly, while the other oxide contents increase strongly. The particularly increasing proportion of SiO_2 should be considered, which rises from 5 to over 15 wt.-%. Similarly, FeO / Fe_2O_3, ZnO and CaO increase particularly sharply, while MgO remains below 1.5 wt.-% and hardly increases at all. A linear relationship can also be seen for most of the oxides. The outliers in the contents can be justified by the inhomogeneous composition of PCB shredder at addition quantities of 25 g. In comparison to test 5, the pyrolyzed PCB in trial 4 results in greater decrease of PbO and hence higher oxide contents of Fe_2O_3, SiO_2, ZnO and others. Cu accumulates in the slag up to a content of 2 wt.-% and is reduced to 1.50 wt.-% in experiment 4, 1.35 wt.-% in experiment 5 and starts to decrease with a PbO content of less than 50 wt.-% in the slag.

The pretreatment of pyrolysis shows a significantly higher efficiency in the reduction of lead oxide. With the addition of 150 g pyrolyzed PCB, the lead content can be reduced to 24 wt.-% although a 10 % decrease in hydrocarbons mass is reached during pyrolysis. In comparison with 150 g untreated PCBs, this is a 48 % higher PbO reduction in the slag phase. The other contents increase comparably to those of the unpyrolyzed PCB addition.

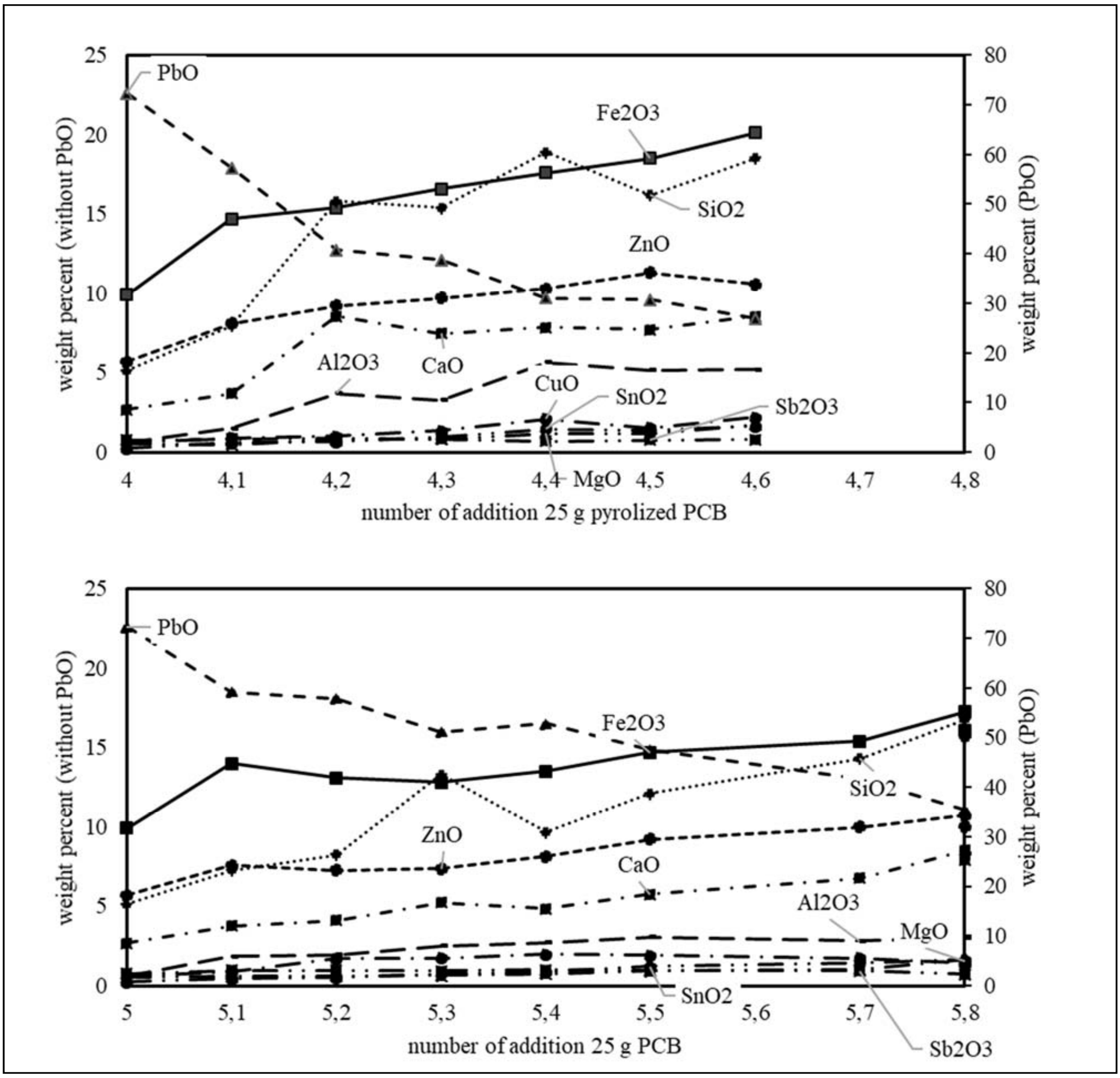

Figure 6: Slag composition of trial 4 (1100 °C, C-Sto. 1.0, 100 % pyr. PCB) and 5 (1100 °C, C-Sto. 1.8, 100 % PCB) with additions of PCB

The comparison of the reducing agent mixture in table 3 demonstrates that the efficiency varies greatly. The carbon contained in untreated PCBs is converted to between 35 and 38 % for reduction. The pretreatment of pyrolysis in experiment 4 results in a carbon conversion of 63 % for reduction and thus a considerably increased value. The addition of coke and PCB as a combination shows an efficiency of 48 – 54 %, which is little smaller than pyrolyzed PCB addition. A influence in temperature can not be detected, caused by higher yield with 100 % PCB addition at 1200 °C but lower with 50 % PCB addition. The low yield of metallurgical coal is caused by slow kinetics. A longer reaction time of 30 minutes regarding to over 50 % yield, with still unreacted coke on the bath surface. The increase in yield by extension the time cannot be confirmed for PCBs.

Table 3: Carbon yield of lead reduction in separate trials and as average for reduction medium

No.	Temperature [°C]	C-Stichometry	PCB addition [% of C]	PbO content [wt.-%]	Mol. C-yield [%]
1 (Ref.)	1100	0.7	0	64.2	35.17
2		0.7	50	50.2	54.12
3		0.9	100	58.7	37.46
4		1.0	100 (pyrolyzed)	24.0	62.86
5		1.8	100	32.9	32.70
6		0.7	50	55.1	47.53
7	1200	0.7	50	58.0	52.58
8		0.9	100	57.9	35.16

The comparison of the strongly influenced slag components Al_2O_3, CaO, SiO_2, and PbO in test 5 with 100 % PCB addition with the simulation shows that the PCBs used here have a higher concentration of ceramic components. It can also be seen that the lead reduction performs significantly worse than predicted by the simulation. Therefore, the oxides were solved, while the lead content is not decreased.

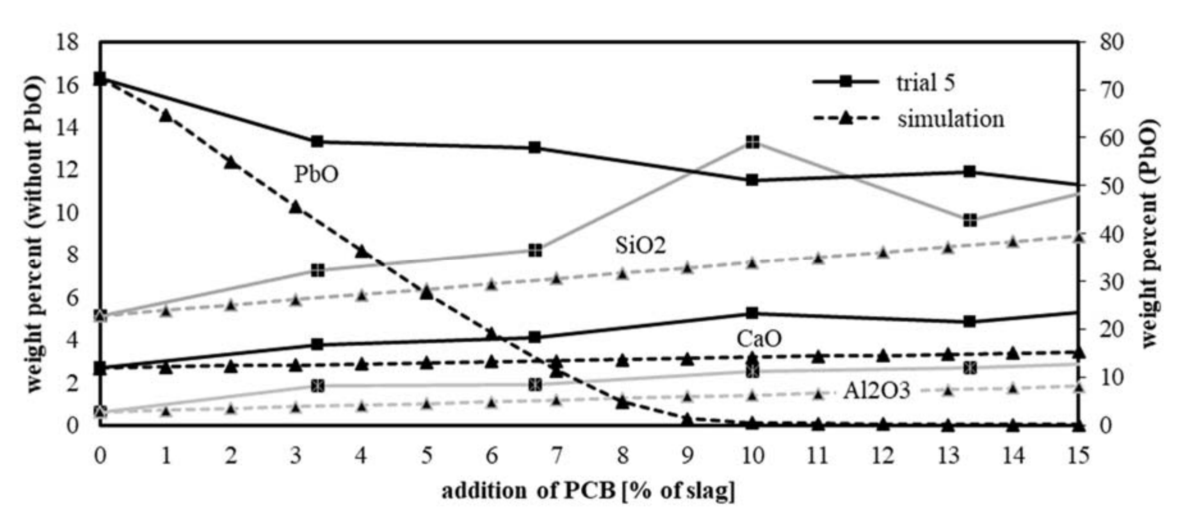

Figure 7: Comparison between simulation and trial 5 with main verified slag components

The analyses of the metal phase were carried out with Spectro MAXx spark spectrometry analyzer. Diagram 9 shows the metal values as a function of the tests and PCB addition as a percentage of slag feed. It can be seen that the copper content increases up to 14 wt.-% with increasing PCB addition. The copper content obtained in the reference test is 0.24 wt.-%. It is interesting to observe that despite high PbO content in the slag, up to 0.35 wt.% antimony can be found in the metal. The content of tin also increases by a factor of 2 to 10 in relation to the reference test. The content of lead is over 97 wt.-% in 5 tests, and over 85 wt.-% with a high PCB addition. Precious metals such as silver and gold can only be detected in the metal phase and are up to 0.11 and 0.006 wt.-%, respectively. The yield of those two metals is above 70 % regarding the input analysis from literature.

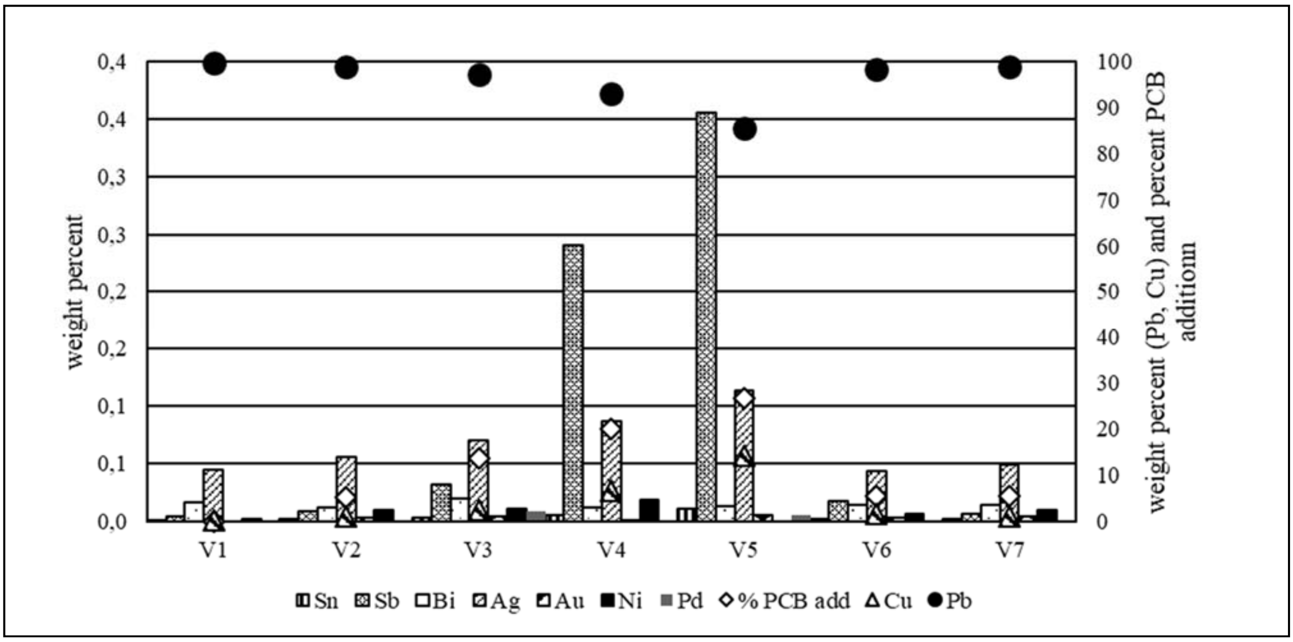

Figure 8: Metal contents in dependence of PCB addition

5 Summary / Conclusions

The addition of WEEE to lead slags indicats that addition of plastic-containing residual streams is possible and can help meet legal recovery rates, also for plastics. The addition of those materials should be done under bath in industrial scale to be able to use the decomposition gases of the thermolysis and increase mixing behaviour. An upstream pyrolysis lowers the resulting off-gas flow, as well as the level of post-combustion. Also resulting in an improved process handling and yield of reacted carbon. Pyrolysis gases can be used as a reducing agent or as a substitute fuel in holding burners, like it is done in aluminium industry.

The yield of valuable metals cannot be determined in the experiments exactly, although they are above 70 % (Ag, Au). High concentrations above 10 wt.-% copper were measured in the metal phase, resulting in a high liquidus temperatures and good conditions for segregation. Thus, in an industrial process, large parts of the copper could be easily separated. In the slag phase, an increase in viscosity was observed, which also reduced the absorption capacity of the slag for ceramic components above 15 % PCB addition. Precious metals are found in metal phase, also their activity in slag were low due to high PbO contents in the system. It was not possible to reduce the content below 24 wt.% in the rotary drum furnace while charging PCBs. Best yields are shown with pyrolyzed PCBs, containing reactive pyrolysis char.

A reduction process using only high ceramic content residual materials is not recommended, due to higher viscosity of the slag and also high copper contents in the metal phase. Small amounts of technology elements could be found in metal phase. Otherwise injection of plastics and additions of PCBs show potential for meeting legal regulations and improve circular economy.

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