

Lead and Zinc Recovery from Metallurgical Slags

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Abstract

In the course of the pyrometallurgical production of lead and zinc it is unavoidable that the slags which are produced as a by-product contain significant amounts of lead and zinc. These contents of lead and zinc in the slags lead to a decreased yield and economy of the production and present a latent danger to the environment. Therefore, the treatment of these slags in an electric arc furnace aiming at the recovery of zinc and lead and production of a useable slag is investigated at the IME Process Metallurgy and Metal Recycling in a project which is financed by the German Federal Ministry of Education and Research. The conducted investigations include inter alia chemical analysis, thermodynamical modelling and experimental test work in laboratory scale submerged arc furnace and pilot scale submerged arc furnace. The aim of the project is to produce slags which can be utilised in further applications instead of having to be dumped and at the same time increasing the efficiency of the lead and zinc operation by recovering lead and zinc from the slags.

Keywords: lead, zinc, slag treatment, environment

1 Introduction

The world wide production of lead in 2006 amounted to 7.89 million tons of which roughly 50 % was produced from secondary raw materials [1]. A by-product of the pyrometallurgical production of lead and zinc is the slag phase that contains the gangue and the less noble metals as well as remaining valuable lead and zinc. The presence of lead and zinc in the slag is unavoidable due to thermochemical and kinetic effects. Typical contents and spans of the main constituents of slags from lead and zinc production can be seen in Table 1.

Table 1: Typical composition and span of lead slags [2]

	Pb	ZnO	SiO ₂	Fe ₂ O ₃	CaO	Al ₂ O ₃	MgO
Typical [%]	3	12.5	20	30	20	3	3
Span [%]	2–6	8,5–16	15–25	20–45	8–25	2–5	2–4

It can be roughly estimated that the weight ratio of metal to slag in the overall production of lead is approximately three to one, which leads to a total slag production of approximately 2.6 million tons in 2006. For each individual slag the question has to be answered if a downstream treatment of the slag is necessary and sensible. The motivation for such a downstream treatment can be argued along the following requirements:

- the fulfillment of external obligations (authorities, customers, other stakeholders)
- increase of metal yield and production of a marketable slag product and thereby improvement of profitability
- protection of the environment by decreased heavy metal emissions

The operation of any additional process leads to higher cost and effort, so that the addition of a downstream treatment for a slag is situated in an area of conflict between benefits and drawbacks. This is shown exemplarily in Figure 1 for six important criteria. The net diagram is set up in such a way that any optimisation results in a minimisation of the area of the net. Due to the fact that some criteria oppose each other, a change of the process chain will usually rather lead to a shifting of the net than to a reduction of all values.

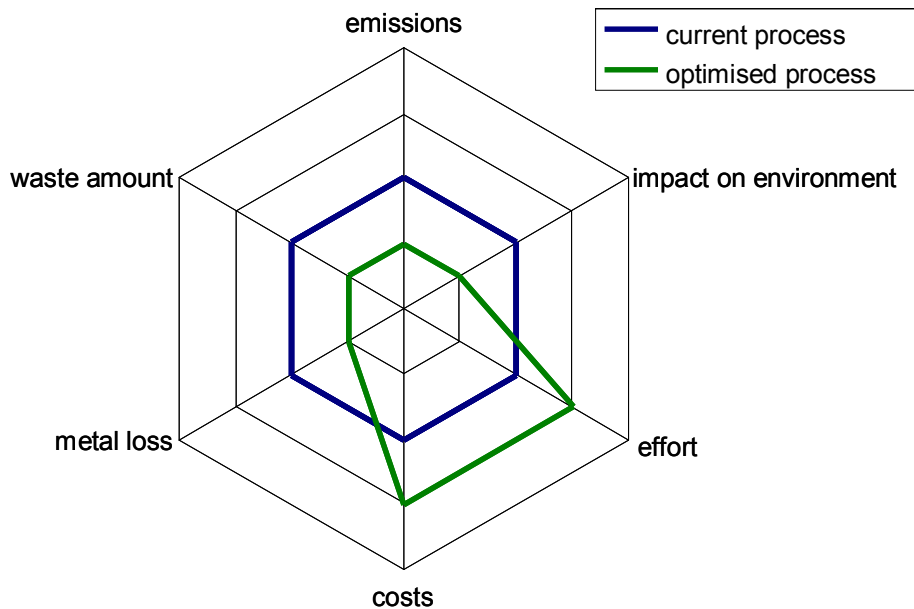


Figure 1: Possible benefits and drawbacks of a downstream slag treatment

Especially in the case of lead it can be said that in the last years because of its classification as environmentally hazardous the consideration if a downstream treatment for a slag should be adopted or not needs to be revised regularly. In order to meet future standards and requirements old processes have to be improved and new processes have to be developed. The presented work focuses on investigating the possibility of treating a lead/zinc-slag in an electric arc furnace (EAF). Subsequent to chemical analyses and thermo-chemical modelling, test runs with different industrial lead and zinc slags have been conducted in a pilot scale EAF aiming on the recovery of the contained lead and zinc and production of a valuable slag product.

2 Theoretical Considerations

The recovery of lead and zinc from slags depends mainly on three mechanisms. These are the reduction of oxides, the settling of metal droplets and the evaporation of metals from the melt. For the reduction of oxides it can be concluded from the Richardson-Ellingham-plot (see e. g. [3]) that under ideal conditions lead oxide can be reduced easily whereas for the reduction of zinc oxide elevated temperatures are needed. If the reductant is solid carbon temperatures must be above 950 °C, if instead of solid carbon, carbon monoxide serves as reductant, at least 1350 °C are required. Alternatively solid iron may act as reductant for zinc oxide; in this case the temperature has to be above 1200 °C for the reaction to take place.

As these considerations are only valid for ideal conditions, thermo chemical modelling with the FactSage-software has been done for some of the treated slags. The

aim was to verify or to correct the theoretical basis for the slag treatment, so that a process window could be set up for the experimental test work. For average lead and zinc bearing slags several states of equilibrium have been calculated using different sets of process parameters such as temperature, gas atmosphere and reductant addition. The results refine the above mentioned considerations to the recommendation that at temperatures over 1400 °C and with strong reducing conditions a recovery of lead (as metallic bullion or in the gas phase) and zinc (in the gas phase) up to almost 100 % is possible. Although such a high temperature leads to a high energy demand it ensures a low viscosity of the slag which is needed for any pyrometallurgical process. The modelling also shows that sulphur may act as reducing agent for zinc and thus decreases the demand for an external reducing agent (such as coke).

Whereas from a thermochemical point of view the reduction by solid carbon is preferred, it is not favourable from a kinetic perspective. This is due to the fact that when zinc oxide reacts with solid carbon three phases need to be in contact (slag containing zinc oxide, carbon, and the gas phase containing carbon monoxide and gaseous zinc), whereas during the reaction of zinc oxide with carbon monoxide only two phases need to be in contact (slag containing zinc oxide and the gas phase containing gaseous zinc, carbon monoxide and carbon dioxide).

At the necessary process temperature any metallic zinc will immediately be vaporised and be transferred into the gas phase. The continuous exchange of the furnace atmosphere supports the reduction of zinc oxide as well as the use of some inert gas for hollow electrode or pneumatic injection. Contrary to zinc, reduced lead will only be vaporised to a small extent. Here the settling of metallic droplets into a metal bullion is relevant. The settling of lead from the slag is very much dependent on the slag viscosity and on the flow regime in the furnace. According to Stoke's law and Newton's law the settling takes place much slower under laminar conditions than under turbulent conditions as Table 2 shows. This is due to the fact that viscosity (i.e. the inner friction of the slag) does not influence the settling anymore. But of course turbulent conditions may lead to increased splashing of the melt and unwanted reoxidation of the lead.

Table 2: Settling time for lead

d_p / mm	laminar conditions			turbulent conditions		
	u / (m/s)	$t_{0,5}$		u / (m/s)	$t_{0,5}$	
		/ s	/ h		/ s	/ h
0,001	$4.07 \cdot 10^{-9}$	$1.23 \cdot 10^{-8}$	$3.42 \cdot 10^{-4}$	0.223	2.25	$6.24 \cdot 10^{-4}$
0,01	$4.07 \cdot 10^{-7}$	$1.23 \cdot 10^{-6}$	342	0.704	0.710	$1.97 \cdot 10^{-4}$
0,1	$4.07 \cdot 10^{-5}$	$1.23 \cdot 10^{-4}$	3.42	2.22	0.225	$6.24 \cdot 10^{-5}$
1	$4.07 \cdot 10^{-3}$	123	0.034	7.04	0.071	$1.97 \cdot 10^{-5}$
10	0.407	1.23	$3.42 \cdot 10^{-4}$	22.3	0.023	$6.24 \cdot 10^{-6}$

d_p : particle size; u : settling speed; $t_{0,5}$: settling time for 0,5 m distance to settle; 0.5 m; density of slag: 3.5 g/cm^3 ; viscosity of slag: 0.79 Ns/m^2 ; density of lead: 9.394 g/cm^3 ;

3 Experimental Test Work

In the course of the experimental test work slags of different industrial pyrometallurgical lead and zinc production processes have been treated in a laboratory scale and in a pilot scale EAF respectively. The procedure and the results of the laboratory scale test work have been reported elsewhere [4] and will not be repeated here. Results confirmed the theoretical considerations that under suitable conditions and sufficiently high temperatures final slags with a minimum lead content of 0.03 wt.% and a minimum zinc content of 0.08 wt.% could be produced. It could further be shown that lignite coke is a suitable reducing agent and that the addition of it should start early because the share of the process that takes place under reducing conditions has a major impact on the success of the reduction. The only exceptions are slags with higher sulphur content. These slags need some time under neutral or even oxidising conditions so that sulphur can act as reducing agent for the zinc. The laboratory scale test work served as basis for the following pilot scale experiments. In pilot scale test runs have been carried out with six different starting slags that were selected with the aim to ensure the treatment of the wide range of possible industrial lead/zinc slags.

Table 3 shows the concentration of the main components of these starting slags. It can be seen that slags III and IV have very high initial lead concentrations, and that slag II exceeds the other slags in sulphur content. All together 31 test runs have been conducted in which more than 8 tons of slag were treated. All slags that have been treated in the EAF had been provided in water granulated form, with a particle size of about 0.5–5 mm.

Table 3: Compositions of starting slags in wt.%

slag	Pb	Zn	Fe	S	SiO ₂	CaO	MgO	Al ₂ O ₃
I	8.9	11.7	28.2	0.1	25.1	9.8	1.3	2.3
II	1.1	5.1	25.5	2.2	24.6	16.4	4.4	7.9
III	55.3	5.9	10.3	0.1	7.1	3.4	0.4	0.7
IV	54.4	7.7	9.5	0.4	7.4	3.1	--	1.0
V	6.8	12.4	23.4	0.3	23.5	9.9	2.2	2.4
VI	5.8	11.4	24.5	0.4	23.0	10.8	1.5	2.8

3.1 Pilot scale test work

Test runs in a 500 kW pilot scale EAF followed the initial test work in the laboratory EAF. The furnace is lined with refractory bricks inside a water cooled shell and provides a total volume of 250 litres for melting. It is equipped with a water-cooled copper bottom electrode and a graphite top-electrode, which is 150 mm in diameter and can be either a solid or a hollow electrode with a free inner diameter of 65 mm for the charging of fine materials directly into the electric arc zone. It is possible to tap melt from two separate tap holes, one on bottom level of the furnace and a second one 500 mm above. The whole furnace is enclosed in order to collect the entire off gas which is gathered at 5000 m³/h, cleaned in a bag filter for collection of flue dust for weighing and sampling, and subsequently routed through a gas scrubbing unit. A

PC-based data logging device automatically saves important measures such as several temperatures from the furnace lining, cooling water and off gas system and electrical parameters for later analysis. Other parameters like the temperature of the melt have to be measured manually and thus discontinuously. Figure 2 shows an overview of the pilot scale EAF at IME. For the injection of coke into the melt a pneumatic injection unit is being used. Coke is continuously conveyed with pressurized air as carrier gas out of a 45 litre storage bin with an accuracy of 0.1 kg. A steel tube with a fixed SiC immersion piece serves for submerged injection of the coke into the melt.

Treatment of the slags has been carried out batch-wise in DC mode with the copper bottom electrode poled as the anode. In each test run approximately 250–400 kg of water granulated slag have been molten and treated, the tap-to-tap time was usually 2–2.5 hours. The test runs have been conducted in series of three or four in order to gain comparable and reproducible results. Before each first run of the day the furnace was pre-heated by smelting 150 kg of steel scrap for 2 hours, with the intention of preheating the refractory lining. Charging of the feed material takes roughly 1 hour of the total time and is done with a power input to the slag of up to 350 kW. After or already during the charging of slag, lignite coke (particle size: 1–5 mm) can be added to the melt through the hollow electrode using a small amount of nitrogen as carrier gas. Alternatively coke can be injected with pressurised air through a submerged lance by the pneumatic injection system. The amount of added coke is calculated on the basis of the lead and zinc contents of the slags with a 20 % stoichiometric coke-excess. A temperature of 1500 °C is aimed at, especially in preparation of tapping. Temperatures of the melt are measured discontinuously by a lance. Table 4 shows an overview of some parameters of the test runs.



Figure 2: Pilot scale EAF and pneumatic injection unit

Table 4: Overview of parameters of the pilot-scale test runs

slag	test runs	total slag amount [kg]	Coke addition [kg]	method of coke addition	reduction time [min]	weighed temperature [°C]
I	9	2160	6–8	h. e.	40–168	1341–1559
II	10	2520	5.4–8	h. e.	81–192	1318–1542
III	3	750	8.5–13	h. e.	146–152	1356–1509
IV	2	800	24.5	premixed	184–205	1453–1622
V	5	1246	6.1–8.4	injection	27–132	1472–1531
VI	2	500	10.7–11.1	injection	72–77	1552–1575

“h. e.”: hollow electrode

Several samples of the liquid slag are taken during every test run, either by inserting a cold iron bar into the melt or by using a scoop for extracting a larger portion of the melt. After a holding time of about half an hour the treated slag is tapped into ladles and the next test run starts. During tapping of the slag a small portion of slag is granulated in a water bath. The produced slag, the collected flue dust and where possible, the produced metal are weighted with the intention to establish mass balances. Moreover, samples are taken from the water granulated final slag, the flue dust and if possible the metal and analysed by ICP and X-ray fluorescence analysis.

3.2 Results and discussion

In most of the test runs (with exception of those that had to be aborted due to technical reasons) the lead and zinc contents of the starting slags could be significantly reduced. Table 5 shows for the achieved minimal lead and zinc contents each investigated slag type. It can be seen that lead and zinc contents of under 1 % have been reached repeatedly, down to a final slag with less than 0.1 % lead and zinc respectively. In general the lead content of the final slags is lower than the zinc content. This is due to the fact that lead is nobler than zinc.

Table 5: Minimal Pb and Zn contents in final slags after EAF- treatment

Slag	Pb [wt.%]	Zn [wt.%]
I	0.08	0.10
II	< 0.1	< 0.1
III	0.29	0.16
IV	3.30	1.36
V	0.38	2.98
VI	0.32	2.49

Figure 3 shows the decline of lead and zinc in the course of two test runs where slag I and slag II were treated. It can be seen that lead is removed noticeably from the slag right from the beginning. This can be seen as a proof for the presence of metal-

lic lead in the slag which does not need to be reduced but only has to melt settled out of the slag phase into a molten lead phase. Contrary to the behaviour of lead the removal of zinc from the slags starts delayed at the beginning but accelerates after some time. This can be ascribed to the fact that zinc is completely bonded as oxide or sulphide in the slags and has to be reduced and evaporated for removal. This requires higher temperatures in the melt than the melting of lead, temperatures which are difficult to achieve as long as cold material is charged. Whereas the reduction of zinc is inhibited during the charging of the feed slag, it increases and results in quickly decreasing zinc contents when homogenous conditions and higher temperatures in the melt are achieved.

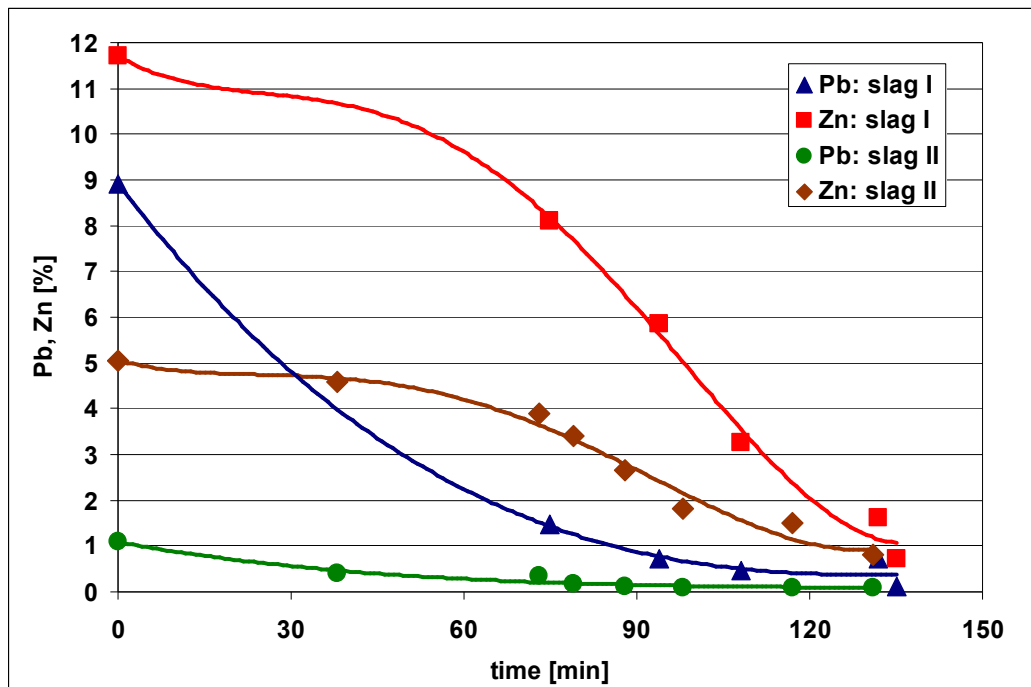


Figure 3: Decrease of lead and zinc in two test runs

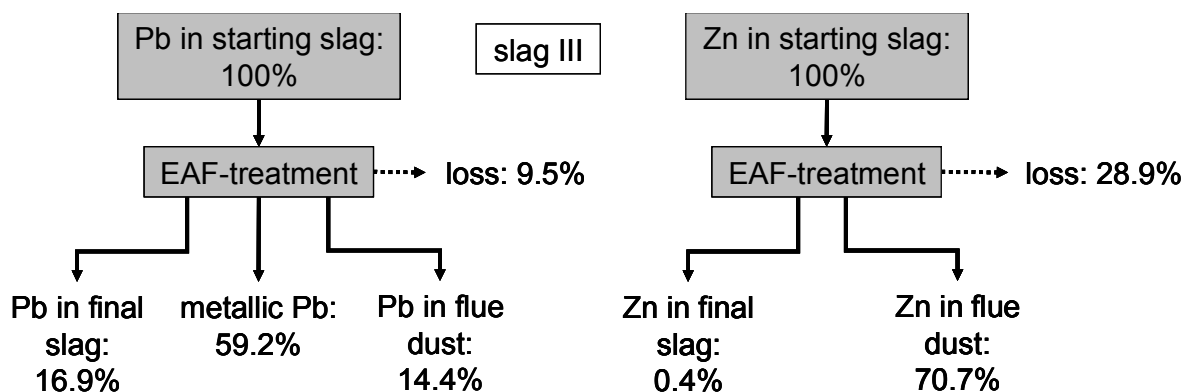


Figure 4: Distribution of Pb and Zn between the products of a test run for slag III

Figure 4 shows the distribution of lead and zinc between final slag, a metallic lead phase and the flue dust for a test run with slag III. It shows that 59.2 % of the lead content of the initial slag is collected in the metal phase and 16.9 % of the lead remains in the treated slag phase. From optical inspection it can be assumed that lead

in the final slag phase is still partly present as metallic droplets that did not settle into the metal. Another 14.4 % of the lead content can be found in the flue dust, and 9.5 % must be considered as loss. A main part of this loss is assumed to be caused by infiltration of the refractory lining. For zinc the distribution is quite different. Here 70.7 % of the zinc content of the feed slag is collected in the flue dust and only 0.4 % of the initial zinc content remains in the slag phase. As zinc is not included in the metallic phase, this leads to a mass balance loss of 28.9 %. The loss is mainly caused by diffuse emissions of zinc oxide from the off gas.

4 Summary

Slags from pyrometallurgical zinc and lead winning processes contain significant contents of lead and zinc, so that a process-integrated treatment should be applied for economical, legislative and ecological reasons. The EAF-technique is very utilizable for such a treatment process due to high flexibility regarding feed material, operation mode and process conditions. Therefore the treatment of lead and zinc bearing slags in an EAF has been investigated by slag characterisation, thermodynamic modelling and by test work in laboratory and semi-pilot scale EAF at IME. The use of the EAF-technique provides very good results up to pilot scale under previously defined suitable process parameters. It is possible to produce slags that contain very low amounts of lead and zinc, so that these final slags can be used for a wider range of applications than the starting slags. Lead and zinc can be recovered as metal bullion or as oxidic flue dust. This ensures a future market for these slags and increases lead and zinc yield of the overall processes of lead and zinc smelting.

5 References

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