The 46th International October Conference on Mining and Metallurgy
01-04 October 2014, Bor Lake, Bor (Serbia)
www.ioc.tf.bor.ac.rs

SIMULTANEOUS RECOVERY OF VALUABLES FROM A DUMPED SLAG

Alois Unger[1], Stefan Steinlechner[1], Jürgen Antrekowitsch[1],
[1]Christian Doppler Laboratory/Chair of Nonferrous Metallurgy, University of Leoben, Austria

Abstract
In this thesis a pyrometallurgical recycling technique to recover valuable metals from a dumped residue, which was generated in the primary lead production is investigated. Within this process, the residue is charged on a lead bath and the containing valuables like zinc, lead and if present silver as well as some others are recovered. Beside the characterization of the lead blast furnace slag also the importance of the slag formation and of additives is described. According to this a process evaluation for technical scale trials, in a Top-Blown-Rotary-Converter (TBRC) and in a DC-Submerged-Arc-Furnace (SAF) are studied.

***Keywords**: simultaneous recovery, zinc and lead containing slag, lead bath recycling process*

1. INTRODUCTION

The investigated residue is a dumped slag generated in the lead production. Therefore the following part deals with the chemical analysis of the slag. Table 1 includes the chemical analysis of the lead blast furnace slag which was studied in this thesis. It can be seen, that the concentration of valuables like zinc, lead and also sliver is very high. On the other hand the ratio between CaO/SiO_2 with 0.29 is much lower compared to other smelters, where it is between 0.55-1.15.[1]

Table 1 - Chemical analysis of the studied residue

Element	Concentration [wt.-%]	Method	Element	Concentration [wt.-%]	Method
Pb	9.3	DIN EN ISO 11885	MnO	0.26	DIN EN ISO 11885
Zn	22.5	DIN EN ISO 11885	MgO	1.30	DIN EN ISO 11885
Ag	0.10	DIN EN ISO 11885	Fe 2+	3.0	AM_EG.26 (Tit.)
Cu	0.25	DIN EN ISO 11885	Fe 3+	0.6	Calculated
SiO_2	23.9	DIN EN ISO 11885	S	0.05	DIN EN ISO15350
CaO	7.00	DIN EN ISO 11885	Al_2O_3	4.2	DIN EN ISO 11885
Na	8.4	DIN EN ISO 11885			

A special characteristic of this slag is the high concentration of sodium with 8.4 % and the very low concentration of FeO with 3.9 %. A possible source for the concentration of Na can be the recycling of CRT glass (cathode ray tubes) or the addition of fluxes like Na_2CO_3[2].

The recycling of CRT glasses in the lead blast furnace brings the positive effect of decreasing the viscosity of the slag due to the input of fluxes like Na_2O (2-8.3 %) as well as the decreas of the melting point of the slag which is also influenced by the concentration of SiO_2 (45-66 %). CRT glass is a source for lead, whereby the concentration varies strongly between 0.0-34.0 % PbO, based on the type and the section (panel, funnel or neck) of the CRT. [3]

2. SLAG FORMATION AND ITS IMPACT ON THE RECOVERY OF VALUABLES

The three most important parameters in the formation of metallurgical slags which have a very high impact on economic and efficiency in pyrometallurgical winning processes are the liquidus temperature, viscosity and the solubility of the valuables in the slag. [1]

Impact based on the liquidus temperature of the slag [1,2]

It is selfevident that a low melting point saves energy. Therefore, mainly SiO_2 or alkaline fluxes like $NaCO_3$, Na_2O, K_2O or halide containing fluxes like CaF_2 are added. The use of these fluxes has also a positive effect on the viscosity but it has to be taken into account that the containing alkalis and halides influence the quality of the products (ZnO dust), harm the refractory lining of the furnace and are furthermore, dangerous for the environment.

Impact based on the viscosity of the slag [4,5,6]

The viscosity of liquid slags has a very high impact on material transportation between metal and slag. A low viscosity is essential for the convective transportation which increases the material transport and also the thermal conductivity. Furthermore, it enhances the coagulation and separation of metal droplets from the slag. On the other hand a low viscose slag increases the corrosive and erosive attack of the refractory material.[4,5]

Beside the addition of fluxes, as mentioned above, several oxides influence the viscosity. The ratio between oxides which increase the viscosity and oxides which decreases the viscosity of the slag is described by the Kz value “slag strength”. Equation 1 shows the formula for the calculation of Kz.[4,6]

$$Kz = \frac{\%FeO(FeO + ZnO + MnO + MgO) + \%CaO}{\%SiO_2 + \%Al_2O_3(Al_2O_3 + Fe_2O_3)}$$

Equation 1

Figure 1 illustrates the effect of the Kz value on the viscosity of a slag from the lead blast furnace and a slag form the copper industry. It can be seen that an increasing value of Kz leads to a decreasing viscosity of the slag. Due to that fact, oxides like CaO, MgO and ZnO, which have a strong impact to increase the melting point of the slag, have on the other hand a very positive effect on the decrease of the viscosity. The revers effect can be seen for SiO_2, which decreases the melting point but increases the viscosity.

The influence due to the viscosity is based on the crystal structure of the oxides in the slag as well as on the type of bonding. For example the tetrahedron structure of SiO_4^{4-} increases the viscosity. By adding CaO this structure is cracked, the size of the silicate anions decreases and therefore the viscosity decreases. This works till the orthosilicate structure $2CaO \cdot SiO_2$ is reached and from that point on adding more CaO increases the liquidus temperature and therefore increases the viscosity again. Furthermore, oxides with covalent bonding (P_2O_5, B_2O_3,…) have a much higher viscosity than oxides with ionic bonding (Al_2O_3, FeO,…). Halide components like CaF_2 have the lowest viscosity based on their omnidirectional electrostatic bonding and their little molecular structure.

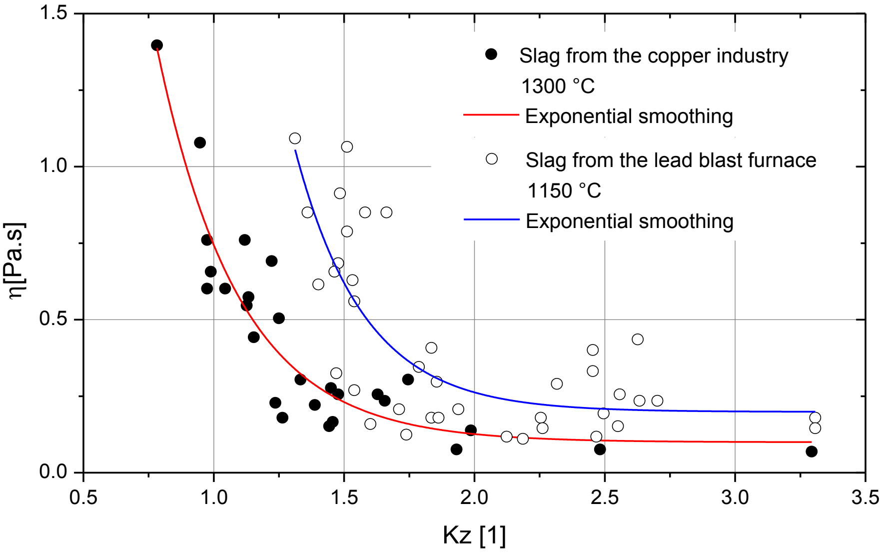

Figure 1 - Slag viscosity against the Kz value for slags form the copper industry and slags from the lead blast furnace [4]

Impact based on the solubility of the valuable metals [5,6,7]

This part deals with the solubility of zinc-oxide in the slag, described by the Law of Henry, which can be seen in Equation 2. The equation describes, that the activity of ZnO (a_{ZnO}) depends on the molar concentration of ZnO (x_{ZnO}) in the slag, influenced by the activity coefficient (γ_{ZnO}). The activity coefficient (γ_{ZnO}) is related to the concentration of additional slag components like CaO, Al_2O_3 and SiO_2. A $\gamma_{ZnO}{}^{H}$ value > 1 stands for separation of ZnO from the slag and therefore increases the recovery of zinc.

$$a_{ZnO}{}^{H} = \gamma_{ZnO}{}^{H} \cdot x_{ZnO}{}^{H} \qquad \text{Equation 2}$$

The right illustration of Figure 2 characterizes the dependence of the activity coefficient (γ_{ZnO}) according to the main slag components at a certain process temperature (1250 °C). The left illustration shows the limit of the zinc-oxide activity (a_{ZnO}) to avoid the iron reduction according to the process temperature.

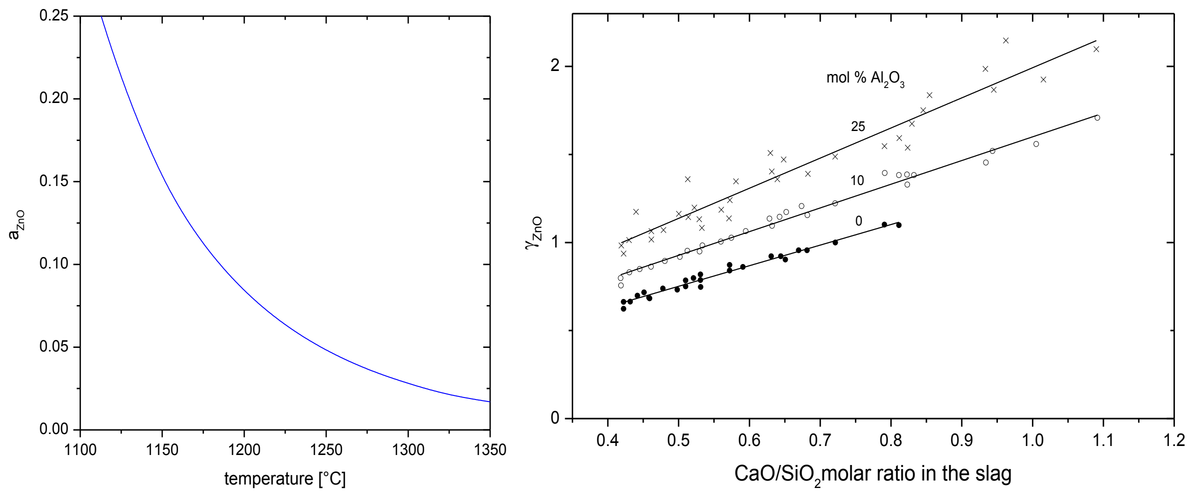

Figure 2 - Right: Influence of CaO, SiO_2 and Al_2O_3 to the activity coefficient at 1250 °C and a ZnO concentration in the slag (x_{ZnO} = 4–8 %) [6,8,9]
Left: Activity limit of ZnO in the slag to avoid the iron reduction [7,8,9]

3. PROCESS EVALUATION AT THE TBRC AND DC-SAF [8,9]

This chapter gives an overview on a series of tests at the Top-Blown-Rotary-Converter (TBRC) and at the DC-Submerged-Arc-Furnace (SAF).

3.1 Top-Blown-Rotary-Converter (TBRC)

The right illustration in Figure 3 shows a photo of the TBRC located at the Chair of Nonferrous Metallurgy at the University of Leoben. The aggregate consists of three main parts, which are the burning vessel, the closure head with the methane-oxygen burner and the off-gas system. The atmosphere in the vessel can be adjusted by the burner to be reducing or oxidizing. The rotating speed of the burning vessel can be adjusted between 0 and 10 R/min. It is possible to tilt the vessel between the vertical position (90° against horizontal) and the pouring position (-35° against horizontal).

The tilting angel and also the rotating speed of the vessel are depending on the process. A flat tilting angel and a high rotating speed generate a large surface of the charged material which increases the reaction rate. These adjustments are perfect for recycling or for roasting processes. The reverse adjustment is ideal for phase separation via settling.

3.2 DC-Submerged-Arc-Furnace (SAF)

The left illustration in Figure 3 shows the technical drawing of the DC-SAF. The heating up of the material is done by electricity, based on resistance heating of the liquid slag. In the illustrated setup the current flows from the rod-electrode through the slag and the metal bath to the ground-electrode. The electrodes are made out of graphite and contacted with a DC-transformer. It has to be taken into account that the maximum current and therefore the maximum energy input depends on the cross-section area of the electrodes. The feed material is charged from the top into the vessel and generates a burden column which melts down slowly.

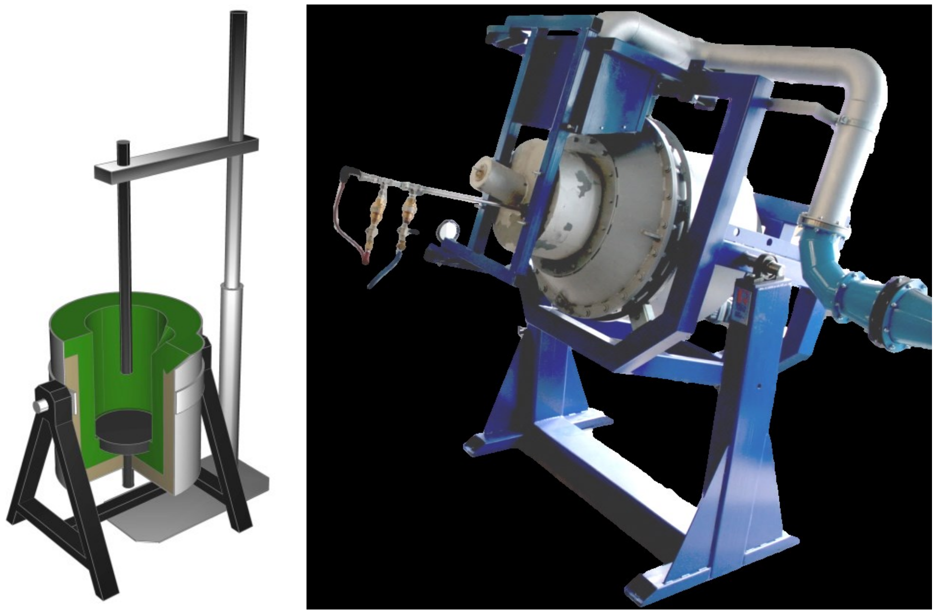

Figure 3 - Left: Image of the DC-Submerged-Arc-Furnace (DC-SAF) [8,9]
Right: Photo of the Top-Blown-Rotary-Converter (TBRC) [8,9]

4. CONCLUSION TO THE FIRST TRIAL IN THE DC-SAF

Figure 4 shows the first results of the technical scale trials in the DC-SAF where the valuables are recovered by the lead bath recycling process. The two illustrations include the analysis of zinc and lead in the treated slag and also their recovery yields during the process.

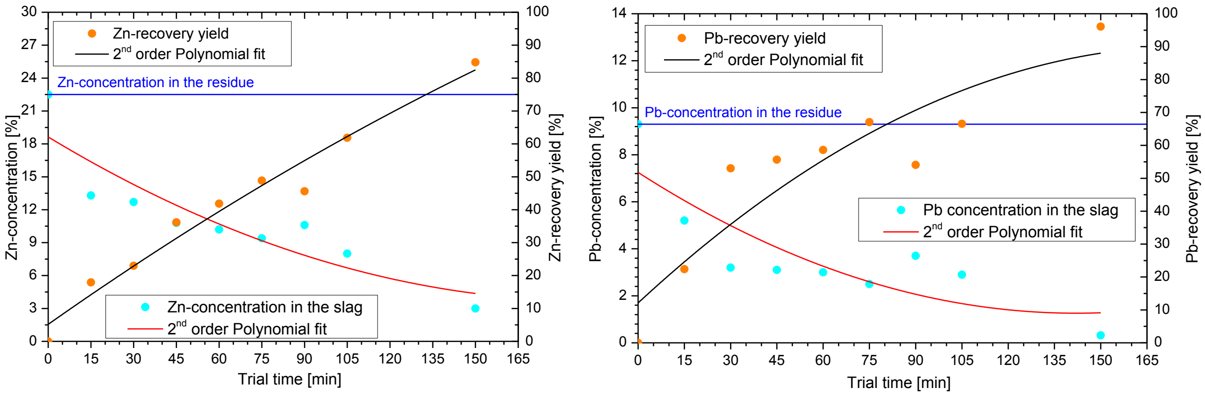

Figure 4 - Left: Results for the Zn recovery and remaining Zn concentration in the slag
Right: Results for the Pb recovery and remaining Pb concentration in the slag

After 105 min trial time, lime was added to raise the B2 (CaO/SiO_2) from 0.29 up to 0.75. The positive effect can especially be seen on the Pb concentration in the treated slag. From 30 min till 105 min trial time the Pb concentration seems to be constant at 3.0 % but at 150 min the concentration decreases to 0.32 % which brings a recovery yield for Pb of 96.1 %. This effect is for the Zn concentration and the recovery yield not as pronounced as for Pb. The remaining Zn concentration is 3.0 % which results in a recovery yield of 84.8 %. Due to that there is still some potential for improvement in the slag formation.

ACKNOWLEDGEMENTS

The authors would thank the sponsors of this research; these are Railly&Hill Metal Recovery Inc. and Befesa R&D.

REFERENCES

[1] A. Longval, T. Shannon, Q. Jiao and B. Davis., Operational improvements at Brunswick´s lead blast furnace, 47th Annual Conference of Metallurgists of CIM, August 24-27, Winnipeg, Manitoba, Canada,2008, p.29-39.
[2] M. Kenezevic, M. Korac, Z. Kamberovic and M. Ristic., Possibility of secondary lead slag stabilization in concrete with presence of selected additives, MJoM Vol 16(3) 2010, p.195-204.
[3] F. Andreola, L. Barbieri, A. Corradi and I. Lancellotti, CRT glass state of the art A case study: Recycling in ceramic glasses, Journal of the European Ceramic Society 27, 2007, p.1623-1629.
[4] D. Janke., Schlacken in der Metallurgie (K. Koch and D. Janke), Verlag Stahleisen mbH, Düsseldorf 1984, p.31-60.
[5] W. Krajewski, J. Krüger., Schlacken in der Metallurgie (K. Koch and D. Janke), Verlag Stahleisen mbH, Düsseldorf 1984, p.105-120.
[6] W. Krajewski, J. Krüger., Schlacken in der Metallurgie (K. Koch and D. Janke), Verlag Stahleisen mbH, Düsseldorf 1984, p.147-160.
[7] W. A. Richards: Practical implications of the physical chemistry of zinc-lead blast furnace slags, Canadian Metallurgical Quarterly, 20, 2, 1981, p.145-151.
[8] A. Unger, J. Antrekowitsch and S. Steinlechner, Recovery of valuable metals like Zn, Pb and Ag from a hazardous residue generated in the pyrometallurgical lead-, zinc- production, 2nd International Wastes conference, September 11-13, Braga, Portugal, 2013.
[9] A. Unger, J. Antrekowitsch and S. Steinlechner, A sustainable recycling process for simulataneous recovery of Zn, Pb and Ag from a dumped slag, Shechtman International Symposium 2014, 29 June - 04 July, Cancun, Mexico, 2014.