

A TWO-STAGE METAL VALORISATION PROCESS FROM ELECTRIC ARC FURNACE DUST (EAFD)

Received – Primljeno: 2015-03-18

Accepted – Prihvaćeno: 2015-10-10

Original Scientific Paper – Izvorni znanstveni rad

This paper demonstrates possibility of separate zinc and lead recovery from coal composite pellets, composed of EAFD with other synergetic iron-bearing wastes and by-products (mill scale, pyrite-cinder, magnetite concentrate), through a two-stage process. The results show that in the first, low temperature stage performed in electro-resistant furnace, removal of lead is enabled due to presence of chlorides in the system. In the second stage, performed at higher temperatures in Direct Current (DC) plasma furnace, valorisation of zinc is conducted. Using this process, several final products were obtained, including a higher purity zinc oxide, which, by its properties, corresponds washed Waelz oxide.

Key words: electric arc furnace, dust, separation, valorisation, zinc, lead

INTRODUCTION

Production of steel in electric arc furnaces is considered the best available technique for secondary steel industry [1]. An inevitable by-product of secondary steel production is dust, EAFD, formed in a de-dusting system in the amount of 15 - 20kg per ton of liquid steel [2]. It is estimated that about 3,7 million tons of EAFD is produced every year worldwide [3].

EAFD is characterised as hazardous waste (characteristics H11/H12/H13) [4], with the assigned number 10 02 07*. Disposal of this type of waste is not considered a favourable option, not only due to negative economic and environmental effects, but also due to the increased content of valuable metals. Although EAFD re-utilisation as a valuable raw material was intensively investigated in the last decades, still there is no simple, economical, technical, and environmentally accepted solution for EAFD processing [5].

According to [1], one third of the world EAFD production is disposed, one third is treated by the Waelz process for zinc recovery and one third is treated by means of other processes. A typical Waelz plant consists of several units; a raw material preparation unit, a Waelz unit and a washing plant. Although crude Waelz oxides contain ~ 60 % zinc in the oxide form, they are still contaminated as a result of relatively high levels of halogens and lead compounds. The washing plant is installed in order to remove halogens, and increase grade of crude zinc oxide; by washing, attained content of halogens could be $Cl < 0,1 \%$ and $F < 0,15 \%$ [6]. Although the Waelz process proved to be the best availa-

ble technique [1], there are some disadvantages to this process, such as intensive energy consumption, no iron recovery, financial infeasibility if capacity is less than 50 000 t/year or the average zinc content in EAFD is $< 15 \%$ [7], and it requires further improvements [8].

By removing lead and halogens prior to the performance of the Waelz process, it is possible to produce a high purity zinc oxide, without installing a washing plant.

Separation of zinc and lead is based on a higher affinity of lead towards chlorine than zinc, so the free energy and possibility of volatilisation of lead as $PbCl_2$ is significantly higher than that of Zn and Fe chlorides. Several research groups investigated the possibility of separation of lead and zinc by lead volatilisation in presence of chlorides contained in dust [9, 10] with minimising zinc loss from EAFD. According to the results by Yoo et. al. [9] obtained on small samples, about 98 % of lead and chlorine was volatilised at 950 °C in 90 min, with only 1 % of zinc loss.

Steinlechner et. al. [11] investigated the influence of various halides compounds on decreasing the lead content in a mixture of similar characteristic to EAFD. The best results were obtained by using KCl and NaCl, which decrease the necessary retention time of the material by increasing the lead oxide yield (due to formation of lead chloride). In order to increase a lead oxide yield, the optimum temperature and retention time should be 1 100-1 200 °C and 20 min, respectively.

EXPERIMENTAL RESULTS

The subject of this paper is to investigate separate zinc and lead recovery from coal composite pellets, composed of EAFD with other synergetic iron-bearing wastes and by-products (mill scale, pyrite cinder, mag-

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netite concentrate), through a two-stage process. The first, low temperature stage should enable removal of lead as a result of the presence of chlorides in the system, and in the second stage at higher temperature, zinc should be valorised. Using HSC chemistry 6.12, a model of two-stage process was developed. Model was verified in semi-industrial conditions.

The presented process is highly suitable for locally available zinc rich and iron-bearing wastes and by-products and production of lead-chloride, zinc-oxide, pig-iron and slag, all as commercial grade products.

All materials used in this research, EAFD, Pyrite cinder, mill scale and magnetite, were obtained from the local steelworks production lines.

EAFD is hazardous waste generated at steel plants in Serbia, quantity 4 800 tpa.

Pyrite cinder is technogenic waste, generated in the process of sulfuric acid production; this material is used as an iron source in defined mixture.

Mill scale is formed during steel hot rolling process in the amount of 1 000 tpa.

Magnetite concentrate was obtained from a newly opened mine in western Serbia; due to its chemical composition, this concentrate is not suitable for usage in blast furnaces, and it was used in defined mixture as an iron source.

Coke as a reducing agent and lime as flux and binder were of a commercial grade.

The characterisation of the utilised raw materials is presented in the previously published research works of the authors [12, 13].

The definition of feed mixture was guided with maximal annual amounts of EAFD and mill scale generated per year, iron content in mixture of 45 % and a mixture basicity of 0,75. The basicity (B) was calculated using formula:

$$B = \frac{(\text{CaO} + \text{MgO})}{\text{SiO}_2} \quad (1)$$

Using the Excel Solver Programme that includes functional equations for the running of the process, the composition of the target mixture was optimised.

According to the Solver results, the mixture composition was as follows:

EAFD	20 %
Mill scale	4 %
Pyrite cinder	42 %
Magnetite	23 %
Coke	10 %
Lime	1 % (as 10 % lime milk)

RESULTS

Process modelling

For the process modelling in HSC software, chemical compositions of charge components derived from Solver functions were used. The results of modelling are pre-

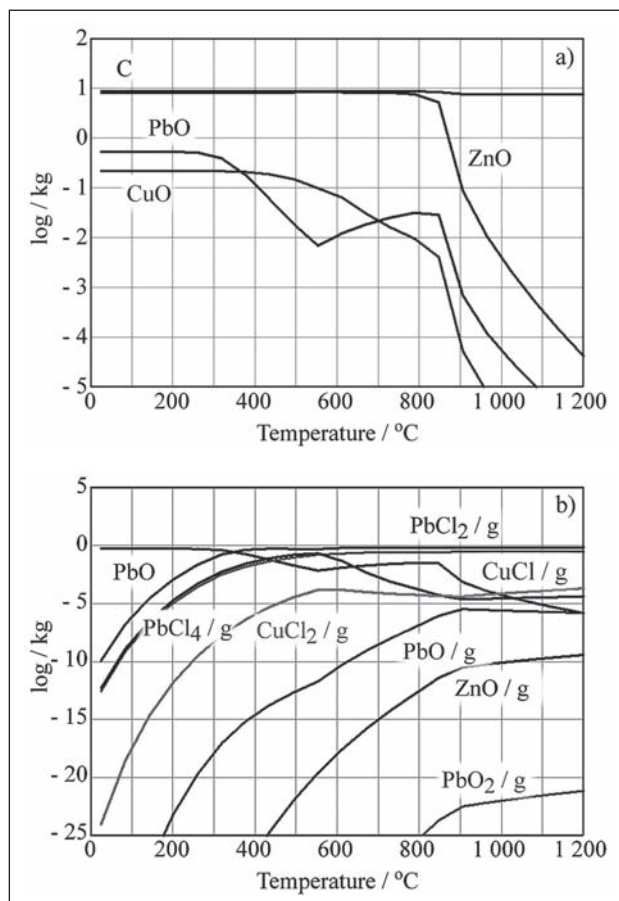


Figure 1 HSC modelling for mixture heat treatment a) solid phase and b) gaseous phase

sented in Figure 1 as a logarithmic function of the equilibrium amount contingent upon the temperature.

It could be seen from Figure 1 that zinc and lead could be separated during a two-step heating regime, as anticipated. In the first step, lead is vaporised in chloride form, while in the second step, zinc is valorised as oxide.

By utilisation of this method, the produced zinc-oxide would be of a higher grade and the washing stage could be omitted. At the same time, the produced lead-chloride could be sent to lead smelters.

Semi-industrial investigations of zinc and lead separation

All used materials were dried for 24 h at 105 °C, and weighed in dry room condition. The mixture quantity was 50 kg.

Industrial pelletizing disc (Ø 100 × 22 cm) was used for materials agglomeration. The pelletizing disc was placed at an angle of 45 ° at the speed of 15min⁻¹. All raw materials and additives were mixed and dried for 10 minutes before the start of lime milk suspension spraying. The produced pellets were cured at the room temperature for 2 days before further treatment. An electro resistant furnace (ERF), upgraded with the condenser system, was used for pellets pre-treatment and lead volatilisation. For the purpose of zinc valorisation, ERF

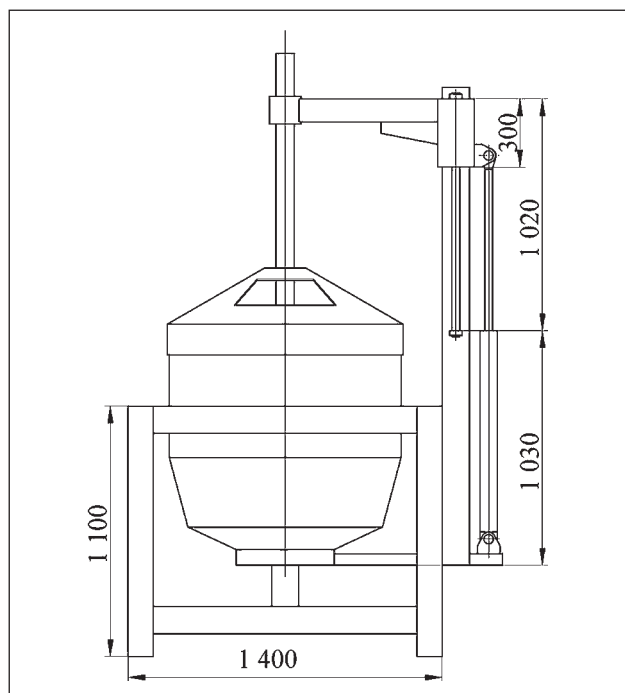


Figure 2 Technical drawing of DC plasma furnace

was connected with semi-industrial DC plasma furnace, of 50 kg capacity, equipped with a gas cooling system and a bag filter.

The annealing tests for lead valorisation were performed in the temperature range of 850-1 200 °C for 30, 60 and 90 min. The retention time was varied in order to optimise process parameters, necessary for design of industrial plant.

The process conditions during the ERF experiments were maintained constant. Samples from every experimental mixture were fed from the furnace bottom. After the expiration of selected process time at the designed temperature, the samples were left in the furnace to cool gradually for 24 hours.

The efficiency of zinc and lead separation during these experiments was established by measuring variations of metal content retained in the pellets.

The charge materials for DC plasma (Figure 2) tests were start slag and pre-treated pellets. The materials were added in portions, and smelting campaign lasted for 6 h at 1 490 °C. The start slag originated from previous smelting of similar material.

After smelting, materials were cast into a casting crucible, and left for metal and slag separation. Condensed gases were collected from the bag filter and analysed. No additional reducing agent was added, since pellets contained 10 % of coke.

Lead and halogens valorisation during pellets mild reactive vaporization

The percentage of retained Zn and Pb in pre-treated pellets for different experimental temperatures and times for the investigated mixture are presented in Figure 3.

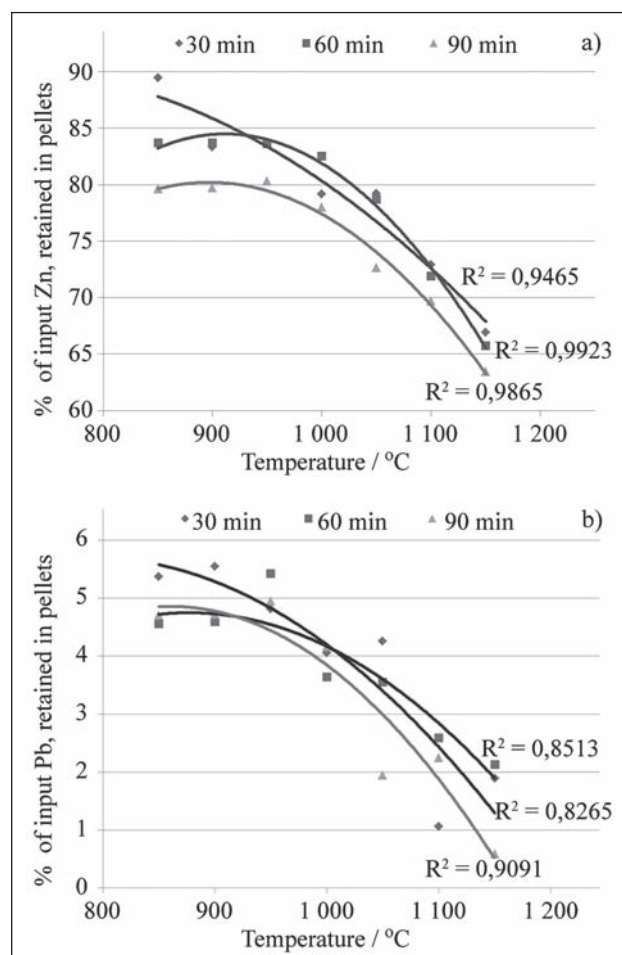


Figure 3 Efficiency of a) zinc and b) lead removal from pellets, presented as percentage of input materials retained in pellets

The results presented in Figure 3 represent the mean values of three experiments, and indicate that selectivity of zinc and lead volatilisation is possible. In the temperature range 850 – 950 °C most of lead is removed from pellets (~ 95 %), while 80 – 87 % of zinc remained in pellets.

With respect to the retention time, it can be noted that with a prolonged time, the levels of volatilised zinc and lead increase. For a design of industrial plant, 1h time would be suitable for achieving desired levels of lead removal from mixture. Furthermore, on an industrial scale, the process would be conducted in a dynamic system, e.g. rotary furnace, so this time / temperature regime would be appropriate.

For further experiments, the pellets pre-treated at 950 °C for 60 min were chosen.

Zinc valorisation during DC smelting of pre-treated pellets

For the second stage of the process, 40 kg of pre-treated pellets were charged in a DC plasma furnace in a molten start slag bath.

After finishing the smelting campaigns, the metal and the slag were cast.

The dust from off-gasses was collected in a bag filter. The obtained metal and slag were analysed. The main components of start slag were FeO, SiO₂, Al₂O₃, CaO, MgO, with small amounts of Zn, Pb, Cu, Ni and Mn. The characterisation of semi-industrial test products is presented in Table 1, representing the mean values of three campaigns.

Table 1 **Characterisation of semi-industrial test products / wt. %**

Comp	Metal	Comp	Slag	Dust
Fe	98,07	FeO	28,00	7,20
Zn	0,02	ZnO	0,32	78,20
Pb	0,10	PbO	0,02	0,37
S	0,00	S	6,38	
Cu	0,45	CuO	0,10	
Ni	0,62	C		1,30
C	0,21	Cl		0,03
P	0,05	SiO ₂	31,81	0,92
Si	0,15	Al ₂ O ₃	5,80	0,01
Mn	0,01	MgO	6,20	0,01
		CaO	19,80	0,65
		MnO	0,81	

The obtained results show that the filter dust contains 78 % of ZnO, i.e. 62 % of Zn, which is slightly lower than the level of industrially applied processes for sole EAFD treatment. However, a mixture of iron-bearing materials was used in the presented tests, so the first result of Zn recovery around 95 % shows the possibility of industrial application for joint treatment of different materials. The quality of produced metal is suitable for EAF charging, as a partial replacement of steel scrap. The obtained slag, according to its composition, is adequate for application in the construction industry.

CONCLUSION

The obtained results presented in this paper demonstrate the presence of synergy of input materials in respect of maximum metal yield, which enables a production of commercial grade products, while respecting principles of cleaner production and energy efficient processes. The presented research of EAFD treatment by a two-stage process demonstrates its potential for production of variety of final products: pig iron, slag, lead-chloride and higher purity zinc oxide.

The investigated process has a great potential for scale-up to an industrial level, and should be considered as a potential replacement of the Waelz process.

In the future, the chlorinating components of charge could be replaced by alternative fuels, such as waste plastics that contain heavy metals. The simple treatment of gaseous phase provides additional benefits to the proposed process.

Acknowledgements

Financial support for presented research was provided by Ministry of Education, Science and Technological Development, the Republic of Serbia, project TR34033.

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Note: The person responsible for the translation of the paper into the English language is Dejan Arsenovski, Certified Translator, Belgrade, Serbia