

CARBOTHERMIC REDUCTION OF ELECTRIC ARC FURNACE DUST AND CALCINATION OF WAEZL OXIDE BY SEMI-PILOT SCALE ROTARY FURNACE

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Abstract

The paper gives a common outline about the known recycling techniques from electric arc furnace dusts and describes an investigation of a pyrometallurgical process for the recovery of zinc and iron from electric arc furnace dusts (EAFD). In the waelz process, the reduction of zinc and iron from the waste oxides using solid carbon (lignite coal) was studied. In the reduction experiments; temperature, time and charge type (powder and pellet) were investigated in detail. It was demonstrated that zinc and iron recovery (%) increases with increasing temperature as well as time. Pelletizing was found to be a better method than using the powder as received for the zinc recovery and iron conversion ($Fe^{3+} \rightarrow Fe^0$). In the calcination (roasting) process, crude zinc oxide, which evaporated from non-ferric metals were collected as condensed product (crude waelz oxide), was heated in air atmosphere. Lead, cadmium as well as chlorine and other impurities were successfully removed from crude waelz oxide by this method. In the calcination experiments; temperature and time are investigated in detail. It was demonstrated that zinc purification (%) increases with increasing temperature. The highest zinc refining (%) was obtained at 1200°C for 120 minutes. A kinetic study was also undertaken to determine the activation energy of the process. Activation energies were 242.77 kJ/mol for the zinc recovery with powder forms, 261.99 kJ/mol for the zinc recovery with pellet forms respectively. It was found that, initially, the reaction was chemically controlled.

Keywords: Zinc; Zinc oxide; Iron oxide; Waste mixed oxides; Pyrometallurgy.

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1. Introduction

Zinc is one of the most important base metals next to aluminum and copper. It is widely used in many industrial applications all around the world such as metallurgy, chemistry, agriculture, paint, and rubber industries etc [1-3]. World's zinc supply comes from recycled zinc which is recovered from secondary sources such as zinc ash, brass smelting, automobile shredder scrap, zinc dross, die casting scraps, dusts of electric arc furnace, leach residues, etc [3-5].

When the steel at the end of its use is re-melted in an electric arc furnace (EAF) dust is generated, which is referred to as electric arc furnace dust (EAFD). About 15–20 kg of dust, which is of economical value, is generated per ton of steel [6-8]. The dust components close the material loop between the steel and the zinc industry. This dust contains predominantly zinc oxide, iron oxide and zinc ferrite, and also oxides of various other metals introduced into the electric arc furnace from the scrap charge.

In the past, all these steelworks dusts were discarded. Nowadays, steelworks increasingly

process dust in order to recycle the valuable metals in it. The higher the zinc content, the more attractive is the possibility of treating EAFD. Therefore, electric furnace steelworks attempt to raise the concentration of zinc in EAFD by various technical means. These include increasing the amount of zinc-bearing scrap charged to the EAF and recycling dust until its zinc content reaches 18 to 35%, which makes it an attractive raw material for zinc production [9-11]. Zinc producers, who wish to diversify their sources of raw material for zinc production, regard electric arc furnace dust as a valuable alternative source. However, the zinc industry normally uses raw materials which have a higher zinc concentration. As a result, EAFD undergo a further process before the zinc can be recovered from them. Many processes in various stages of commercial development are used worldwide to manage some techniques for the recovery of metal from EAFD including pyrometallurgical processes [12-16] and hydrometallurgical processes [16-20]. There are many methods for industrially treating EAFD from carbon steel scrap melting which are summarized in Table 1.

Table 1. Commercial processes for EAFD treatment [12-20].

Process	Type	Zn bearing product	Fe-bearing product	Other Product
Waelz Kiln (Stage 1)	Pyro	ZnO	Fe ^o /Fe _x O _y	-
Waelz Kiln (Stage 2)	Pyro	ZnO	-	PbCl ₂ /CdCl ₂
Rotary Heart	Pyro	ZnO	Fe ^o /Fe _x O _y	-
Shaft Furnace	Pyro	ZnO	Fe ^o /Fe _x O _y	-
Plasma Furnace	Pyro	ZnO	Fe ^o /Fe _x O _y	-
Electro Thermal	Pyro	Zn ^o	Slag/residue	-
Ezinex (with electrolysis)	Hydro	Zn ^o	Slag/residue	-
Leaching NH ₄ Cl	Hydro	ZnO	Slag/residue	-
Leaching in H ₂ SO ₄ (with electrolysis)	Hydro	Zn ^o	Slag/residue	-
Leaching in NaOH (with electrolysis)	Hydro	Zn ^o	Slag/residue	-
Leaching in (NH ₄) ₂ CO ₃ (with Calcination)	Hydro	ZnO	Slag/residue	-

The most frequently applied pyrometallurgical processes such as Waelz Kiln, Rotary Hearth or Shaft Furnace are for the recycling of dusty steel mill residues world-wide, especially for EAF dust.

Waelz process carried out in the rotary kiln is the most used technology of recovery of zinc oxide which is presented in EAFD. It is a pyrometallurgical process characterized by the volatilization of non-ferrous metals like zinc, lead and cadmium out of an oxidized solid mixture by means of reduction by coal in a rotary kiln without generating a liquid slag. The target of the recycling process is to make the metals, which are containing in the residues, available for further re-use. This raises the zinc content to 55 - 65%, at which point the product can be used as a raw material for primary zinc plants. However, this production (waelz oxide or crude waelz oxide) method requires a following refinement process because of the high concentration of lead and chlorine [13-15]. Calcination or roasting process ensures the removal of hazardous chlorides and lead from the off-gases [14].

Other processes are emerging too and mostly depend on dissolving the dust and recovering zinc metal from solution, are also under development. Some of these have been developed to the pilot plant or small commercial plant scale. Hydrometallurgical techniques result in effective but generally they do not recover zinc completely and generally a further treatment is necessary.

Finally; Waelz process has some advantages from the other pyrometallurgical processes.

The reasons for the major application of the Waelz process are:

- Established technology
- Reliable and robust
- Simple installation, well known metallurgical process
- Economic
- Saleable (The product Waelz oxide is welcome to all zinc smelters)
- The by-product waelz slag can be used for road construction flexible
- Sponge iron can be recycled to the arc furnace.
- Extended range of treatable feed material by process modifications
- Low consumption of energy
- Most modern development < 200 kg of coke per 1 ton EAFD feed

Normally, a waelz process is characterized by the volatilization of non-ferrous metals like zinc, lead and cadmium out of an oxidized solid mixture by means of reduction by coke or coal. In parallel ferrous oxides are also reduced if they are present.

Under normal operation (Industrial applications) conditions, the waelz process does not require additional heating since the reduction reaction is exothermic. The hot air enters the kiln; the solid charge is first dried, and then heated up until the reaction starts. The maximum temperature of the solid reaches about 1200 °C.

In the industrial Waelz process, crude zinc oxide is obtained as a product. But in our study, we produced zinc oxide as well as sponge iron. In industrial process, the reaction occurs below 1000°C for longer durations. However, experimental conditions are different to industrial conditions in terms of temperature and time. We carried out the reaction at 1200°C for 90 min. Thus, increasing temperature gives rise to the

increment of recovery percentage and resulted in shorter reaction time.

The objective of the present study was to outline an effective waelz process using the solid carbon as a reducer for the high-efficiency recovery of zinc oxide from EAFD and effective calcination (roasting) process using the rotary kiln furnace for the high grade zinc oxide product from crude zinc oxide. The optimum conditions and parameters for these processes were also described.

2. Experimental Study

The EAFD used in this study was provided from Colakoglu Metalurji Co., Istanbul, Turkey. The chemical composition and X-ray diffraction patterns of the dust are shown in Table 2 and Figure 1, respectively. As can be seen, EAF dust is composed of mainly zinc ferrite ($ZnFe_2O_4$, franklinite), zinc oxide, silica as well as minor phases, such as $Pb(OH)Cl$, Mn_3O_4 , $NaCl$ etc. It is worth mentioning that $Pb(OH)Cl$ is a hydroxide formation that easily dissociates to PbO , $PbCl_2$ and H_2O at $100.35\text{ }^\circ\text{C}$ [9]. The lignite coal obtained from Tuncbilek region, Turkey was used as a reducing agent and has a particle size between $-9.00 + 2.36\text{ mm}$. The chemical composition of the coal used in the experiment is summarized in Table 3.

The flowchart for the pyrometallurgical treatment of EAFD is shown in Figure 2.

In first step, waelz kiln process was

carried out in a Ruhstrat rotary drum furnace (1400°C max.) having an open end stainless steel tube with a length of 520 mm and diameter of 160 mm of reaction zone. The rotation speed of the furnace was selected as 1 rpm. The temperature of the reaction zone was measured with two PtRh10/Pt thermocouples and the heating cycle was controlled by a programmable controller to keep the temperature stable ($\pm 5\text{ }^\circ\text{C}$) at a predetermined temperature. A dust collector having an air delivery rate of $1140\text{ m}^3\text{h}^{-1}$ was placed 100 mm away from the open end of the reactor tube to collect waelz oxide.

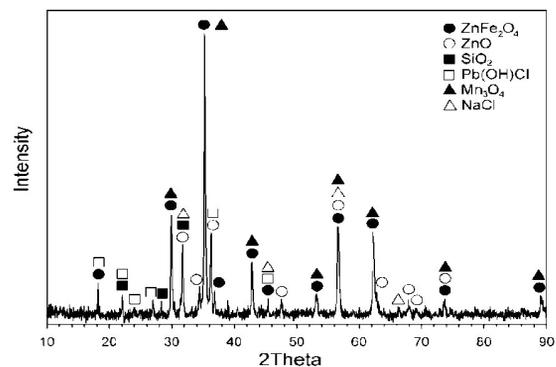


Figure 1. XRD pattern of the EAF flue Dust.

Table 3. Composition of the lignite coal.

Wt. %				
Fixed Carbon	Volatile Matter	Ash	Sulphur	Moisture
39.24	43.47	16.24	1.03	7.26

Table 2. Composition of the EAFD used in the present study.

Wt. %														
Zn	Fe	SiO ₂	C	Pb	Mn	Na	Mg	K	Al	Ca	S	Cl	Cd	Moisture
29.19	26.89	6.1	3.23	3.16	2.72	2.5	1.34	1.19	0.65	0.92	0.72	0.65	0.04	3.06

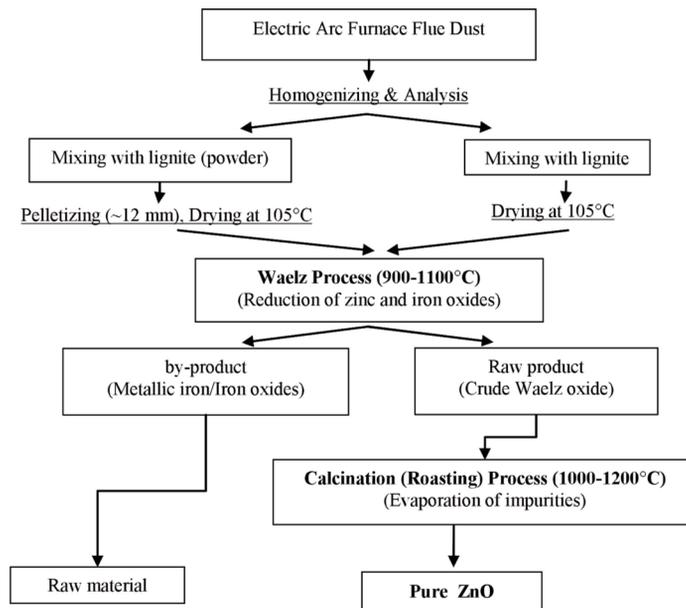


Figure 2. The flowchart for the pyrometallurgical treatment of EAFD.

The experimental set-up is illustrated schematically in Fig. 3. After reaching the predetermined temperatures (900, 1000, 1050 and 1100 °C), 1000 g of initial mixture (EAFD and lignite) were charged into the reaction zone in either powder or pellet form. The lignite, as a carbon source, were 36 wt % of the initial mixture to reduce the oxides of zinc, iron, and lead. Pellets with diameters

around 12 mm were prepared in a pellet machine using only fine EAFD and water following drying at 110 °C for 120 min. Inserting the sample into the hot zone after attaining the desired temperature eliminated the possibilities of any reaction taking place at lower temperatures. Reaction times from 0 to 90 min were examined and samples of about 20 g each were withdrawn from the hot

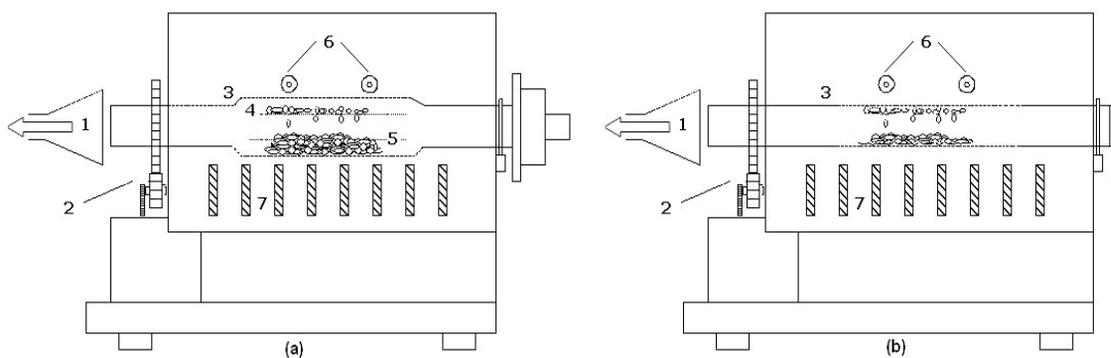
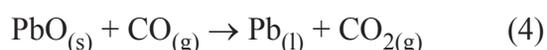
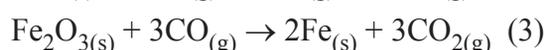
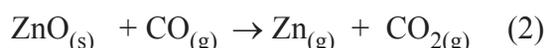


Figure 3. Schematic of the laboratory-scale furnace for the a) Waelz kiln process; b) Calcination process. (1-Dust Collector, 2-Rotary Wheel, 3-Stainless Steel (a) Ceramic Tube (b), 4-5-Stirring Blades, 6-PtRh10/Pt Thermocouples)

zone at different intervals.

The possible reactions during the reduction process are mainly as the following:



Normally, direct reduction of zinc oxide with carbon occurs for longer durations or does not take place at all. So oxygen reacts with carbon forming CO(g) and this formed CO(g) is used for the reduction. This is called indirect reduction.

In the second step, the calcination process of the obtained crude waelz oxide was carried out to eliminate the volatile matters such as lead, cadmium, chlorides, carbon by using same rotary furnace but with a both end open alumina tube (Figure 3b). After reaching the predetermined temperatures (100, 1100, 1150 and 1200 °C), 1000 g of waelz oxide was charged into the reaction zone as collected form from filter bag. Reaction times from 0 to 120 min were examined and samples of about 20 g each were withdrawn from the hot zone at different intervals.

After weighing and ring milling, the samples obtained from the both processes were characterized by using X-ray diffractometer (XRD, PANalytical PW3040/60 with a Cu K α radiation) and atomic absorption spectrometer (AAS, Perkin-Elmer Analyst 800).

The degrees of zinc removal (*volatilization fraction*) during waelz process

and zinc yield during calcination process were calculated by using Eq.5.

$$\alpha = [(W_o * \%Zn_o) - (W_t * \%Zn_t) / (W_o * \%Zn_o)] * 100 \quad (5)$$

Where W_o : initial weight of sample, W_t : final weight of sample at time t , $\%Zn_o$: wt. % of zinc in initial sample, $\%Zn_t$: wt. % of zinc in final sample at time t . In order to determine the reduction percentage during waelz process, metallization degrees of each samples were calculated by using Eq.6.

$$\text{Metallization Degree (\%)} = [\text{Metallic Iron (wt.\%)} / \text{Total Iron (wt.\%)}] * 100 \quad (6)$$

3. Results and Discussion

3.1 Waelz Process

As it is evident from Figure 4 that rate of zinc removal increases with time and temperature. At high temperatures and beyond 60 min, no significant difference in zinc removal was found in the residues that were initially charged as powder or pellet form. The highest zinc recovery was obtained as 98.6 % at 1100 °C for 90 min. The advantage of pelleted mixture over the powder one can be seen easily from the Figure 5. The pellet formation allowed fast reduction and high metallization rates due to high and uniform porosity. Highest metallization degree was found as 96.2 % at 1000 °C and 60 min. beyond 1000 °C, the metallization degree decreased to some level which can be described as re-oxidation of iron to reduce zinc oxide at high temperatur

Chemical composition of waelz oxide obtained at 1100 °C and 90 min is given in Table 4. In addition of high amount of zinc, lead and chlorine, as well as other volatile

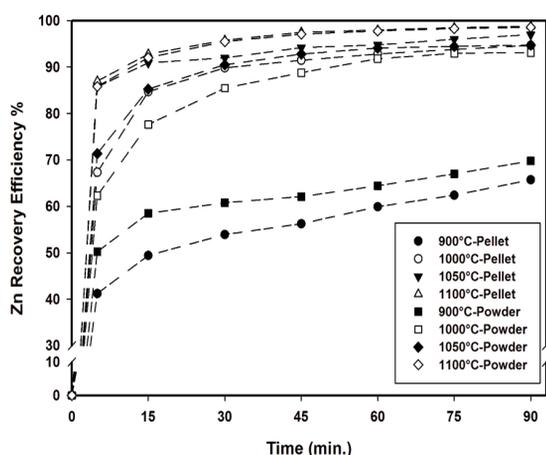


Figure 4. Zinc recovery percentage as function of time and temperature.

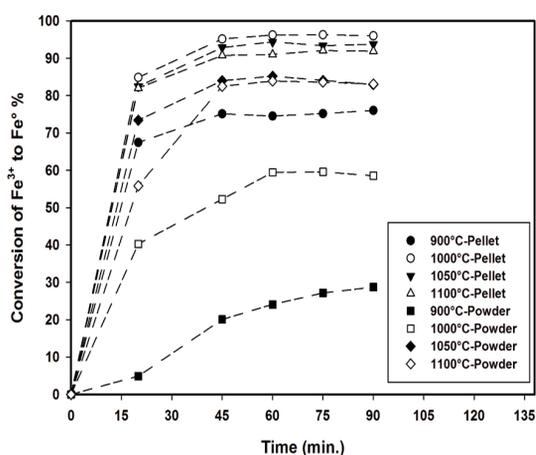


Figure 5. Conversion as a function of time and temperature of reducing process.

impurities were found in the product. Figure 6 is shown the XRD result revealed that in addition to ZnO, a zinc complex, hydrous zinc- and sodium-rich hydroxy-chlorosulfate ($Zn_4Na(OH)_6(SO_4)Cl \cdot 6H_2O$, Gordaite) formed during condensation process. Lead was found in the waelz oxide as $PbCl_2$, $Pb_4O_2Cl_4$, and PbO_2 .

Chemical composition of sponge iron obtained at 1100 °C and 90 min is given in Table 5. Figure 7, the XRD peak is shown in the diagram confirm that present Fe^{3+} in the dust were reduced to metallic iron.

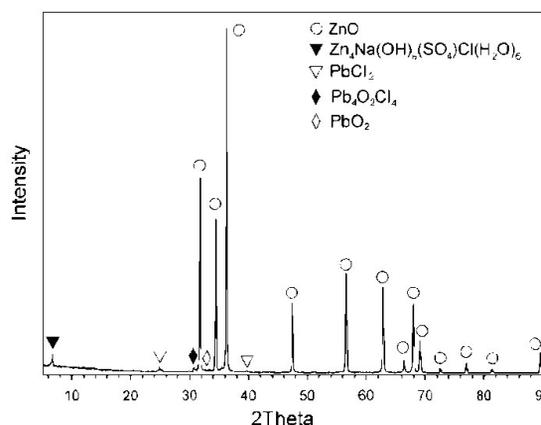


Figure 6. The XRD pattern of the waelz oxide (1100 °C and 90 min).

Table 4. Composition of the waelz oxide (1100 °C and 90 min).

Wt. %								
Zn _(Total)	Fe _(Total)	C	Pb	Na	K	S	Cl	Cd
66.24	0.18	0.9	5.55	2.88	2.06	0.18	4.99	0.0859

Table 5. Composition of the sponge iron (1000 °C and 90 min).

Wt. %						
Fe _(Metallic)	Fe _(Total)	C	Si	S	Cl	Cd
66.24	0.18	0.9	13.54	0.28	0.047	0.0859

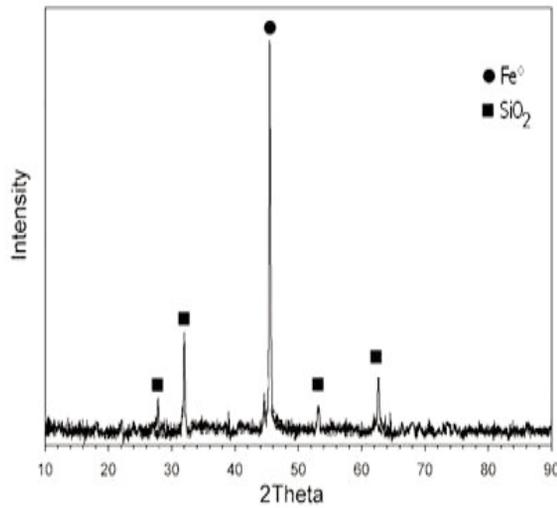


Figure 7. The XRD result of the metallic iron (sponge iron) (1000 °C and 90 min).

3.2 Kinetics study of zinc recovery

The kinetics of zinc recovery in EAFD was investigated. Different mathematical model equations are proposed to represent different rate controlling steps, which are given in Table 6.

The results of the zinc recovery from EAFD for different time, temperature and recovery percentages are shown in Figure 4. In order to ascertain the appropriate kinetic equation, these results were checked against recovery versus time plot. This plot of experimental data is then superimposed on them in order to determine which theoretical

plot fits the experimental data (plot not shown here). It is found second order that the following model would change linearly with time.

To determine the rate constant (k) of the waelz process in the temperature range of 1173 to 1373 K, second order (Eq.7) was plotted over time and as shown in Figure 8.

$$kt = - [1 - (1 - \alpha)^{-1}] \quad (7)$$

Where; k is the rate constant; t , time(min.); α , zinc recovery (%).

This model shows that the reduction process was a chemical control. Figure 9 shows the Arrhenius plot.

Slope of the graph gives the value of activation energy which was calculated from Arrhenius Eq. 8:

$$K = A * e^{-Ea/RT} \text{ or}$$

$$\ln k = \ln A - Ea/RT \quad (8)$$

Where; k is the rate constant, Ea is activation energy, R is the gas constant, and T is temperature (K).

Figure 9. displays the Arrhenius plot of $\ln k$ vs. $10^4/T$ for zinc recovery (%). The activation energies for zinc recovery by powder and pellet forms were calculated to be 242.77 and 261.99 kJ/mol, respectively. This value shows that initially the reaction was under chemical control with a strong dependence on temperature [21].

Table 6. Solid-state rate equations.

Reaction-order models	Differential form $f(\alpha) = (1/k) d\alpha/dt$	Integral form $g(\alpha) = kt$
Zero-order	1	α
First-order	$(1 - \alpha)$	$-\ln(1 - \alpha)$
Second-order	$(1 - \alpha)^2$	$- [1 - (1 - \alpha)^{-1}]$
Third-order	$(1 - \alpha)^3$	$-0.5 [1 - (1 - \alpha)^{-2}]$

The activation energy of the pellet form was greater than that of the powder form, which was also confirmed by the experimental series that investigated the temperature effect, which was more profound for pellet form than the powder form (Figure 5).

This reaction energy is lower than the value reported for pure zinc oxide as 356 kJ/mol by Rao and Jalan [22]. This can be explained by the fact that the total process was accelerated by exothermic carbothermal

reduction of the iron and lead oxides (Gibbs free energy is negative at 900°C) in the EAFD.

3.3 Calcination (Roasting) Process

The concentration of lead in the calcined waelz oxide as a function of time and temperature is shown in Figure 10. As can be seen from the figure, the influence of temperature is more profound, particularly within the temperature range 1050-1100°C.

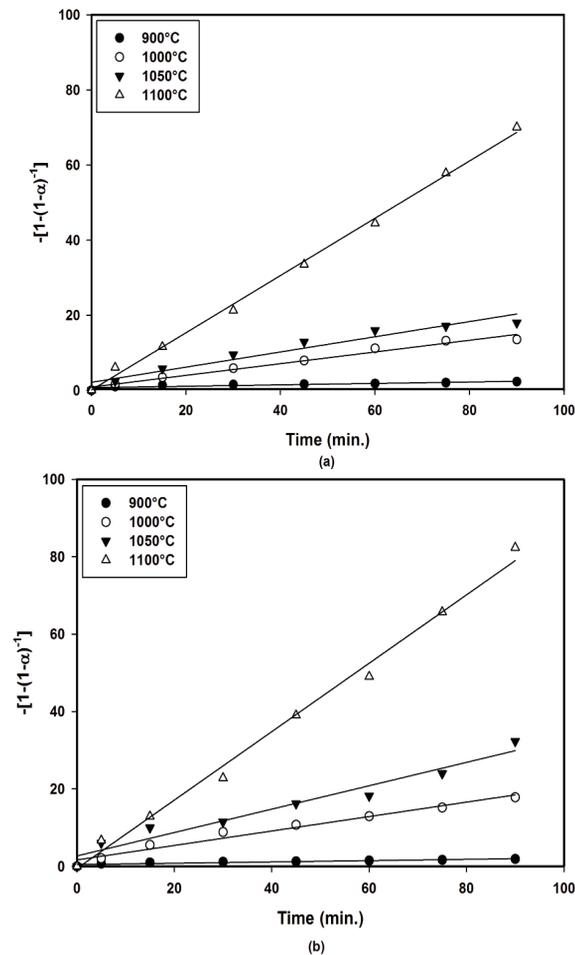


Figure 8. The plot of $kt = -[1 - (1 - \alpha)^{-1}]$ vs. time for the zinc recovery; a) Powder form, b) Pellet form

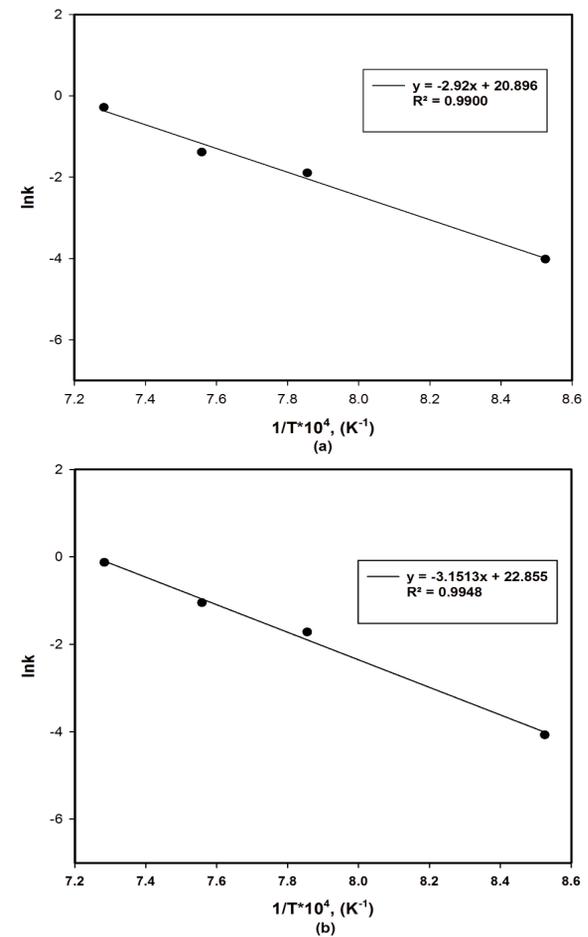


Figure 9. The Arrhenius plot of $\ln(k)$ vs. $104/T$ zinc recovery a) Powder form; b) Pellet form.

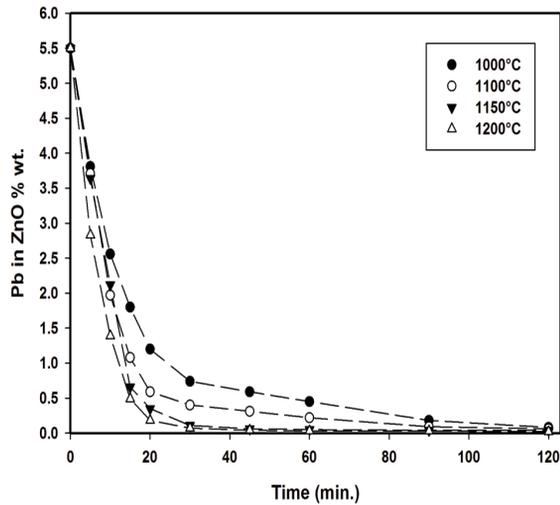


Figure 10. Lead concentration in ZnO as function of time and temperature of purification process.

For example, lead concentration decreased from 0.45 to 0.22, 0.05, and 0.03 wt. % after 60 min and from 0.08 to 0.06, 0.04, and 0.02 wt. % after 120 min at temperatures of 1000, 1100, 1150 and 1200°C, respectively. Figure 11 shows that the concentration of zinc in the condensed phase increased with an increase in time and temperature. For example, the zinc oxide yield was found to be 91.1 % at 1000°C and 99.1 % at 1200°C for 120 min.

Chemical composition of calcined zinc oxide employed at 1100 °C and 90 min is given in Table 7.

The XRD pattern of zinc oxide is displayed in Figure 12.

Table 7. Composition of the calcined zinc oxide (1200 °C and 120 min).

Wt. %								
Zn _(Total)	Fe _(Total)	C	Pb	Na	K	S	Cl	Cd
79.58	0.26	0.055	0.02	0.12	0.09	0.011	0.3	0.0087

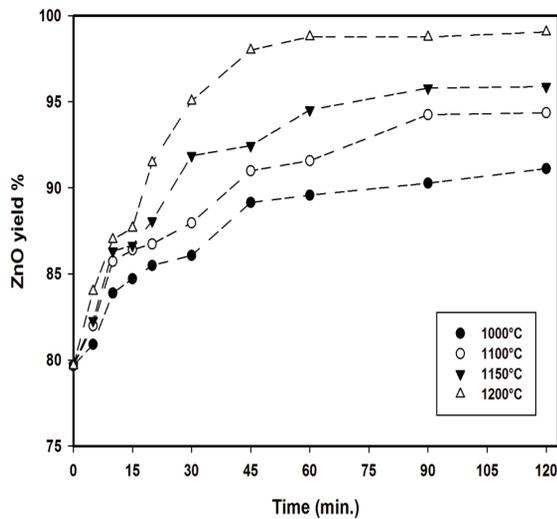


Figure 11. Zinc oxide yield as a function of time and temperature of purification process.

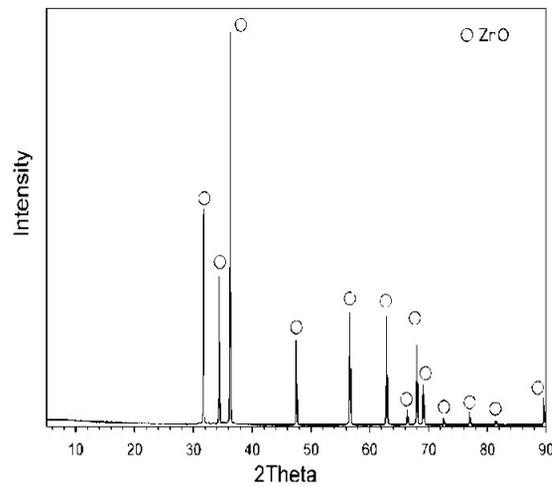


Figure 12. The XRD pattern of the calcined zinc oxide (1200 °C and 120 min).

4. CONCLUSION

A pilot-scale work has proven the technical feasibility of the waelz kiln process for the recovery of zinc and iron from EAFD. Use of EAFD in powder form presents difficulties during recycling.

Carry-over of the dust along with the product

Low bulk density.

The volume of the furnace required to process dust will be large due both of these problems.

Produced good pellets, and did not require any additional binders. Addition of water to the dust removal of zinc and iron from the dust samples depended on temperature and time. Pilot-scale experiments conducted rotary furnace. Possible to complete the reduction of zinc oxide in 90 minutes at 1100°C. However, the advantage of pellets allowed fast reduction and high metallization rates due to high and uniform porosity. Highest metallization degree was found to be 96.2 % at 1000 °C and 60 min. Sponge iron obtained from the waelz process experiments was low in manganese and cadmium content, and can be recycled to the arc furnace. Zinc oxide formed by humidification of the product vapors contained 66.24% by weight zinc.

The activation energy of the pellet form was greater than that of the powder form, which was also confirmed by the experimental series that investigated the

temperature effect. The activation energies for zinc recovery by powder and pellet forms were calculated to be 242.77 and 261.99 kJ/mol, respectively.

The calcination process of the obtained crude waelz oxide was carried out to eliminate the volatile impurities such as lead, cadmium, chlorides, carbon by using same rotary furnace but with a both end open alumina tube. The highest zinc refining efficiency was obtained at 1200°C and 120 min. for 79.58 % by weight zinc.

The proposed process avoids environmental problems and allows for the non-hazardous pyrometallurgical recovery of zinc and iron from EAFD.

The explained process can successfully be applied for baghouse dusts obtained from both electric arc furnaces and cupolas.

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