PYROMETALLURGICAL PROCESSING OF ZINC ASH AND FLUE DUST

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PYROMETALUTGICKÉ SPRACOVANIE POPOLČEKA A ÚLETU OBSAHUJÚCEHO ZINOK

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Abstrakt

Počas galvanizačných procesov sa na povrchu roztavenej zinkovej lázne a v komíne akumuluje veľké množstvo popolčeka a úletu obsahujúceho viac ako 80% zinku. V práci bol študovaný pyrometalurgický proces na jeho získanie zinku. Popolček bol presitovaný na priemyselnom zariadení s otvormi 0.9 mm. Nadsitná frakcia bola pretavená za normálnych podmienok pri teplote 550°C. Získaný ingot sa podrobil analýza a troska bola podrvená a spracovaná ako hrubozrný popolček alebo pridaná k popolčeku. Do úletu bolo pridané vhodné tavidlo a bol pretavený pri 600°C. Získaný ingot bol podrobený analýze a troska bola zmiešaná s jemným popolčekom a spracovaná hydrometalurgicky za účelom prípravy zinkových solí.

Boli študované parametre ovplyvňujúce proces ako sú doba, teplota a množstvo tavidla. Získané výsledky dokumentujú, že účinnosť prevodu zinku do ingotov bola ≥85%. Produkt spĺňa priemyselné požiadavky na čistotu pri relatívne nízkych nákladoch na jeho získanie. Takisto, využitie týchto odpadov napomáha udržiavať životné prostredie čisté.

Abstract

Large amounts of zinc ash and flue dust, containing more than 80 % zinc, are accumulated during galvanization processes at the surface of molten zinc bath and in the chimney, respectively. Pyrometallurgical recovery of zinc from both the ash and dust samples has been carried out. The ash was sieved with the help of an industrial sieve shaker provided with mesh sieve having a pore size 0.9 mm. The oversize fraction cut (+ 0.9 mm) was melted at 550 °C under ambient conditions. The produced ingot (1) was analyzed whereas the coarse fraction of the produced slag (+ 0.9 mm) was treated as the coarse ash or added to it. The dust was enriched with suitable fluxing salt prior to heat treatment at 600 °C for 1 h. The produced ingot (2) was analyzed whereas the resulting slag was mixed with the fines of the ash and treated by hydrometallurgical processing to prepare zinc salts.

Parameters affecting recovery processes such as time, temperature and flux percentage were studied. Results obtained revealed that the two prepared ingots (1&2) were successfully recovered with THE recovery efficiency amounting to ≥ 85 %. The obtained samples meet the standard specifications with relatively low price. Also reuse of these wastes helps in keeping the environment clean.

Key words: Zinc ash, Zinc flue dust, Pyrometallurgy, Hyrometallurgy, Waste treatment

Introduction

This study deals with the recovery of zinc metal from secondary resources namely zinc ash and flue dust, obtained during the galvanization process. Zinc ash is formed on the surface of that part of the galvanizing bath, which is not well covered with flux and is usually skimmed manually. It is usually of variable composition of metallic zinc and zinc oxide and may contain from 70 – 96 % of zinc (total). Zinc is also collected in the flue dusts that arise in both oxygen and electric furnace steel-making operations, especially from the treatment of galvanized steel scrap. Land zinc dross or slag generated during the melting of zinc cathode at the top of the molten bath is also considered as an important secondary zinc resource.

Zinc ash floating on the top of the galvanizing bath was treated by several authors to liberate it from metallic zinc. Mukerjee, et al. [1] were able to recover about 15 % of the recoverable zinc content by stirring the ash in the bath. The addition of 14% sawdust with stirring increased the recovery to 55 %. Zinc ash could be also thermally treated using a slopping hearth muffle or a reverberatory furnace at 700 °C, and the overall recovery was about 50 % of the metallic zinc. Fagg and Rutherford [2] developed a method called the cylinder method for treatment of zinc ash in a galvanizing bath. In this method the ash was transferred to a steel cylinder open at both ends, supported on one corner of the bath. When sufficient ash was transferred, the cylinder was stirred below the surface of the molten zinc. Recovery efficiency was 80 % of the metallic zinc of the ash. Rabah and Elsayed as well as Koros, et al [3,4] studied the factors affecting the performance and efficiency of the pyrometallurgical processes of zinc ash by using ammonium chloride flux. The recovery efficiency amounts to 89 % and 63 % for zinc ash having particle size diameter of + 1.25 mm and - 0.4 + 0.315 mm, respectively with 10 % flux at 600°C. Different methods were mentioned for zinc recovery from the hard zinc (dross). Ratherford [5] studied a process called decantation filtration process. A filter plate was attached on the top of the melting crucible. This gave a yield of 75 % of the recoverable zinc at 600 °C with a settling time of 37 minutes, the remained iron was 0.78 %. Hogan and Gibson [6] described an other method in which the dross furnace was located with its front wall overhanging the coating pot. The furnace front wall had top holes or a slit to permit the passage of molten zinc alloy while retaining slag. The furnace was maintained at 460 – 850 °C for 2h, the reclaimed alloy was of 50 – 70 % yield. Haartmann [7] mentioned a method called pressure filtration in which the dross was heated to the semi-molten state and transferred to a preheated filter through which it was forced under air pressure of about 360 kPa. The dross could also be treated by heating it within the temperature range from 470°C to 600°C on an inclined hearth and a high yield was obtained [8].

Different methods were investigated to recover zinc from zinc bearing dusts generated from ironmaking and steelmaking plants. The processes comprised pelletizing the dust, preheating the pellets in a shaft type furnace. Melting was followed by reducing zinc, iron, and lead oxides contained in the pellets with solid reductant [9, 10]. Sakamoto et al [11] developed a method in which dusts were mixed with cement and fine coke, and agglomerated as pellets or briquettes. Vacuum Heating Reduction (VHR) process was used for recycling of zinc from electric arc furnace (EAF) dust. The process involved separation of metallic zinc and recycling its ferrous residue briquette reductant (Fe, FeO) (under the vacuum-heating atmosphere) and converted to a metallic form [12-14]. Beckmann et al. and Siebenhofer et al. [15, 16] mixed the dusts with inert additives and briquette with a soft caking coal as a binder. The hot briquettes were heated > 700 °C for the reduction of lead, zinc oxides with associated recovery of zinc whereby the volatile zinc vapor was condensed.

The aim of this work was to make use of zinc ash and flue dust from galvanization processes applying a simple pyrometallurgical technique with high efficiency of zinc recovery. Parameters affecting recovery processes such as time, temperature and flux percentage were studied.

Experimental

Raw Materials

A - Zinc Ash:

Zinc ash is generated as dross at the surface of molten zinc bath during galvanization processes of steel pipes and sheets. The weight percentage of it amounts to 12-15 % of the total amount of the used zinc. It is skimmed manually from the surface of the galvanizing bath and kept in iron tanks. At El-Nasr Company for Steel Pipes and Fitting, Ain Helwan, Cairo, Egypt, about 60 tons of the ash are accumulated monthly. About one ton of such ash was supplied from the company.

b- Zinc Dust

During the same processes of galvanization, flue dust of fine particles is accumulated in the chimney. In El-Nasr Steel Company, about 10 tons are accumulated monthly, they are collected weakly and stored in separate tanks. About 100kg of dust sample was supplied from the Company.

Physico – Chemical Properties

X-ray fluorescence as well as atomic absorption analysis was used to determine the chemical composition of the raw materials and products. X-ray diffraction analysis was used to determine the phases of zinc ash and dust.

Recovery efficiency of zinc recovery (R.E.) can be calculated as follows;

R.E. = (zinc content in the produced zinc ingot/ zinc content in the ash or dust)*100

Process Flow Chart for Pyrometallurgical Recovery of Zinc

The experiments were carried out on scale of 6 kg of zinc ash and 1kg of zinc dust. This scale is identical to their accumulation rate. The ash was firstly classified with the help of a mechanical sieving shaker to two fractions; coarse (F1 + F2) with grain size of +0.9 mm, and fine (F3) with grain size of –0.9 mm. Figure 1 shows the process flow chart for the pyrometallurgical recovery of zinc from the ash and dust. Thermal experiments were carried out separately for the coarse ash and dust without and with addition of ammonium chloride flux. All the thermal experiments were carried out in silicon-carbide crucibles (type salimendar), in an electric muffle (Model – Naberthern, Germany). The temperature was gradually elevated up to 600°C (in about 30 minute) and maintained for 15 minutes at the required maximum temperature level. The molten metal was allowed to cool down to about 550°C then cast in moulds after skimming of the formed slag [(3)]. The recovered zinc ingots were weighed and analyzed, while the residual slag was also collected and its zinc content was determined.

Slag formed from the coarse ash was then classified into two fractions as the original ash (+0.9 & -0.9 mm). The coarse slag was mixed with the coarse ash for re-melting. The fine slag was mixed with dust slag (slag 2) and fine ash (F3) to form one blend of fines for acid leaching.

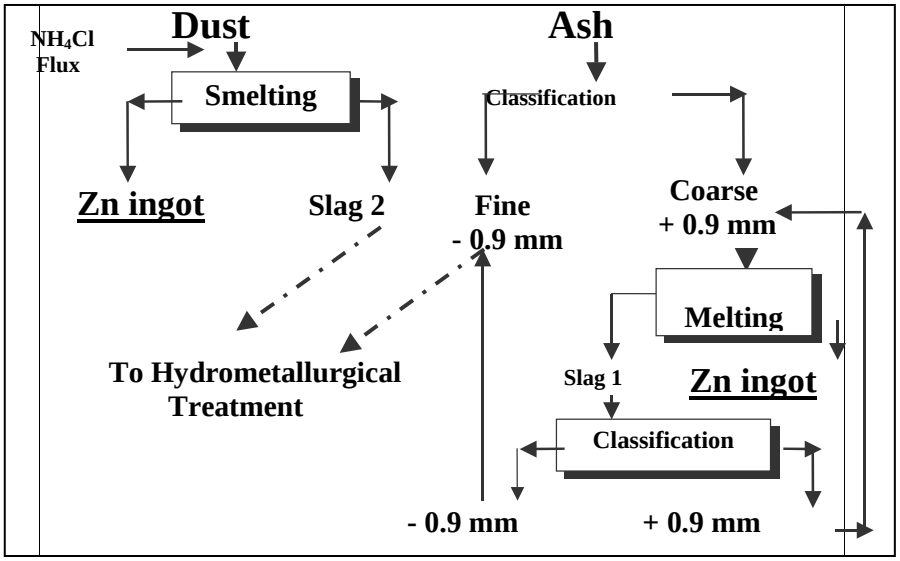

Fig.1 Process Flow Chart for Pyrometallurgical Recovery of Zinc From Both of Ash and Dust

Results and discusion

Particle Size Distribution

The whole sample of zinc ash ($\simeq$ 950 kg) was firstly homogenized by a large mixer and then classified into three fractions (Coarse F1, Medium F2 & fine F3). Representative samples of the medium and fine fractions (F2, F3) of about 50 kg each were then subdivided into sub-fractions with the help of a laboratory mechanical sieving. The particles of zinc dust are mainly of fine sizes, so the whole sample of the dust (100 kg) was mixed well and then a representative sample of it (5kg) was collected and classified by a shaker with sieves of $\leq$ 0.63 mm size.

Table (I) shows the designation and constitution of the blended samples of zinc ash. From the table, it can be seen that coarse, medium and fine fractions of zinc ash are designated as F1, F2 and F3 with particle sizes of (+8 mm), (-8 + 0.9 mm) and (-0.9 mm), respectively. Also the fractions F1 and F2 could be combined to one coarse blend which is designated as (F1 + F2), its weight represents 65 % of the total ash while the fine one F3 represents 35 %.

Physico – Chemical Properties

Table (II) shows the chemical composition of the coarse and fine fractions of the ash (+ 0.9 & - 0.9 mm) besides zinc dust. It can be seen that zinc is the major constituent of each of them, however its value in the coarse ash (0.9mm) is higher than that of the fine one (- 0.9 mm). For the free zinc metal content, the same behavior is observed. This can be attributed to the fact that zinc particles in the coarse fraction are nearer to each other, so they can agglomerate more easily. Dust is also rich in both total and free zinc metal contents. This is due to that fast collection of the dust particles in the chimney protects them from strong atmospheric oxidation. X-ray diffraction data of both zinc ash and dust are given in tables (III & IV). These data confirm that metallic zinc as well as crude zinc oxide are the main components of the ash and dust. However, other constituents such as silica, iron, and lead oxides are present. Some chloride ions are also present which originate from the fluxes used during galvanization processes.

Table I Particle Size Designation and Constitution of the Blended Samples of Zinc Ash

Grain Size, mm	Designation	Weight %	Designation	Weight %
+8.00	F1	37.5		
-8.00 + 4.69	F2-a			
-4.69 + 2.50	F2-b		F1 + F2	65
-2.50 + 1.168	F2-c	27.5		
-1.168 + 0.90	F2-d			
-0.90 + 0.63	F3-a			
-0.63 + 0.50	F3-b	35.0	F3	35
-0.50	F3-c			

Table II Chemical Composition of Coarse and Fine Fractions of Zinc Ash (+0.9 & -0.9) and Zinc Dust (XRF Analysis)

Constituent	Percentage		
	Zinc ash (+0.9 mm)	Zinc ash (-0.9 mm)	Zinc dust
Zn (total)	94.4	78.5	92.28
Zn (metal)	75.7	64.50	74.14
Pb	1.49	3.41	3.95
Cl	0.45	0.36	0.20
Fe	0.50	0.79	0.30
Al	0.10	0.24	0.17
Ni	0.02	0.02	0.01
Ca	0.20	0.15	0.10
Silica + Insoluble	5.60	2.10	0.90

Table IV X –Ray Diffraction Data of Zinc Dust

Identified Minerals	$I\backslash I_0$	d(A^0)	2 θ
ZnO	5	2.85	31.0
Zn	5	2.62	34.2
Zn-ZnO	90	2.49	36.0
Zn	60	2.33	38.6
Zn	100	2.11	42.8
Zn-ZnO	30	1.62	54.2
Zn-ZnO	25	1.34	69.8
Zn	25	1.33	70.4

Table V Chemical Composition of the Recovered Ingots of Zinc from Zinc Ash, Dust and Slag

Constituent	Percentage		
	From ash	From slag1	From dust
Zn	99.2 - 99.6	99.02 - 99.30	99.2 - 99.6
Fe	0.03 - 0.06	0.04 - 0.08	0.03 - 0.08
Pb	0.40 - 0.70	0.60 - 0.80	0.70 - 1.00
Al	0.20 - 0.40	0.20- 0.40	0.10 - 0.20

Table III X –Ray Diffraction Data of Zinc Ash

Identified Minerals	I\I$_0$	d(A^0)	2θ
$Zn_5(OH)_8Cl_2$	30	7.83	11.3
$Zn_5(OH)_8Cl_2$	3	5.34	16.6
$Zn_5(OH)_8Cl_{2\theta}$	3	4.67	19.0
$Zn_5(OH)_8Cl_2$	3	4.39	22.2
$Zn_5(OH)_8Cl_2$	3	3.57	24.9
$Zn_5(OH)_8Cl_2$	4	3.16	28.1
$Zn_5(OH)_8Cl_2$	5	2.94	30.5
ZnO	7	2.86	31.2
ZnO	85	2.81	31.8
$Zn_5(OH)_8Cl_2$	7	2.73	32.9
$Zn_5(OH)_8Cl_2$	8	2.65	33.8
ZnO	90	2.60	34.5
ZnO-Zn	100	2.46	36.3
$Zn_5(OH)_8Cl_2$	7	2.36	38.0
Zn	2	2.30	39.2
Zn	7	2.08	43.3
$Zn_5(OH)_8Cl_2$	7	2.02	44.8
ZnO	78	1.91	47.5
Zn	2	1.68	54.4
ZnO	80	1.62	65.6
$Zn_5(OH)_8Cl_2$	7	1.58	58.3
ZnO	83	1.47	62.8
ZnO	5	1.40	66.3
ZnO	35	1.38	68.0
ZnO	25	1.36	69.1
ZnO-Zn	6	1.34	70.2

Recovery of Zinc From Ash

Zinc ash was classified after sieving into three cuts; coarse fraction (F1), medium fractions (F2-a – F2-d) and fine fractions (F3-a – F3-c).

Figure 2 shows the recovery efficiency of zinc from each of these fractions without flux addition and with adding 15 % ammonium chloride flux. The thermal treatments were carried out at 600°C for 15 minute. The recovered zinc was cast at 550°C. From the figure it can be seen that the maximum zinc recovery was achieved from the coarse fraction (F1) with values of 87.2 and 87.5 % without and with flux respectively. This means that the flux has no effect on the zinc recovery using this fraction. For the other fractions, zinc recovery decreases with the decrease of the particle diameter of the ash fractions. This is explained through the fact that coarse fractions contain a higher ratio of free zinc metal : zinc oxide, while the opposite is verified in the fine fractions. The flux addition has a little improve in the recovery, however the

extent of recovery from the fine fractions is small, (The maximum recovery values from this cut were 27 and 38 % using F3-a without and with flux, respectively).

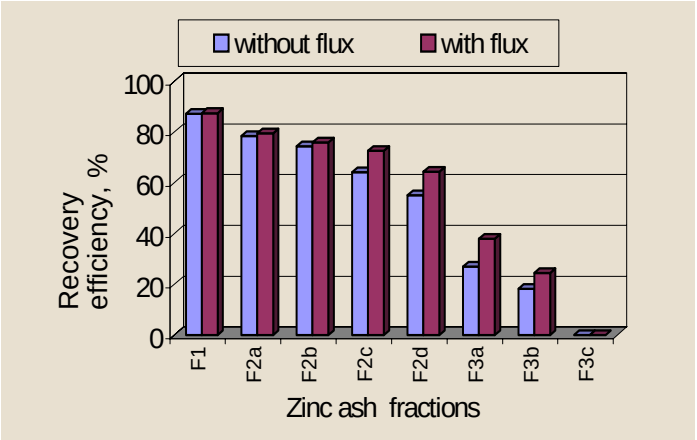

Fig.2 Recovery of Zinc from the Ash Fractions without and with 15 % Ammonium Chloride Flux for 15minute at 600°C

Figures 3 shows the effect of temperature on zinc recovery from each of the cuts F1 and F2 and their mixture (F1 + F2) without flux for 15 minute.

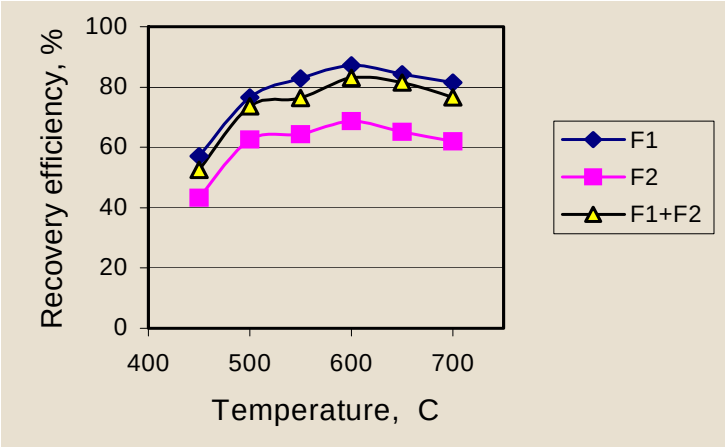

Fig.3 Effect of Temperature on Zinc Recovery from Blended Fractions of the Ash without Flux, for 15 minute (Gradually Heating)

As the melting point of zinc is ~ 420°C, any thermal treatment of the materials under this temperature is of no value. So the experimental temperatures lie in the range of 450-700 °C. In both figures, it can be seen that the maximum value of recovery is attained at 600 °C. Further increase in temperature results in a corresponding decrease in the recovery values. This can be attributed to the fact that heating at 600 °C before casting allowed the least amount of zinc metal

to be lost through vaporization. From the figures, it can be seen that the recovery values from the mix (F1 + F2) lie between F1 and F2 at any temperature. The maximum values were 89, 69.1 and 83 % for F1, F2 and (F1+F2) respectively.

The effect of time on the recovery values is illustrated in Figure 4. It is clear that the maximum recovery value is attained after 15 minute at 600 °C (gradual heating or direct insertion).

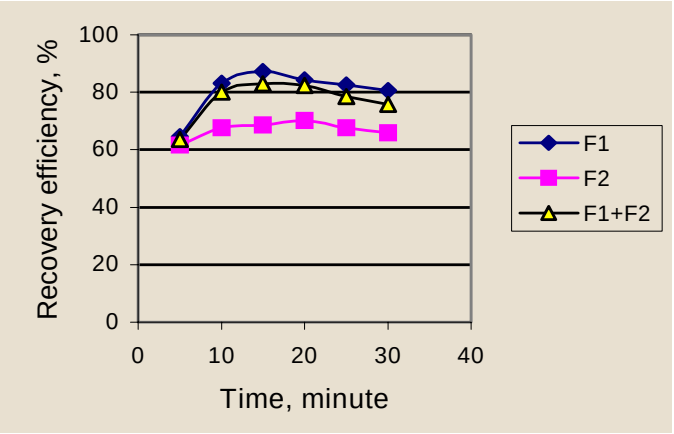

Fig.4 Effect of Time on Zinc Recovery from the Blended Fractions of the Ash without Flux, for 15 minute (Gradually Heating)

This can be attributed to that for the short time (less than 15 minute) although zinc began to melt, however its particles have a little chance to agglomerate and collect completely and so the yield is low. Heating for longer times leads to partial oxidation of zinc particles as the atmospheric oxygen can penetrate the slag layer to the molten zinc. From the previous Figures it is clear that the recovery process is time and temperature dependent.

Recovery of Zinc From Dust

The effect of ammonium chloride concentration on the recovery efficiency (R. E.) is reported in Figure 5. It is clear that at zero flux, R. E. value was zero, the R. E. values increase directly with increase of the flux content and attain its maximum value of 70.6 % with 20 % ammonium chloride, further increase in the flux results in lowering the R.E. The role of flux on the recovery can be explained as follows; in absence of flux zinc metal is easily oxidized at elevated temperatures by atmospheric oxygen. The oxide film separates the individual droplets of molten metal particles from one another, and hence prevents them from coalescing together to form ingots. Ammonium chloride was then added to act as a fluxing agent forming a coating film on the molten surface and preventing it from atmospheric oxygen [3]. At temperature of 340°C, ammonium chloride begins to sublimate and equal volumes of ammonia and hydrogen chloride are evaporated [17]. The generated vapors of the flux form an insulation film around the molten zinc and prevent any further atmospheric oxidation. Also the reaction between the hydrogen chloride gas and zinc oxide layer to form a molten zinc chloride layer (with melting

point of 383°C) takes place. This helps coalescing of zinc droplets to collect together forming ingot [18], and so higher R .E. value of zinc metal is achieved. On the other hand excess ammonium chloride yields a corresponding excess hydrogen chloride vapors which attack more zinc leading to the decreases of the R. E. values.

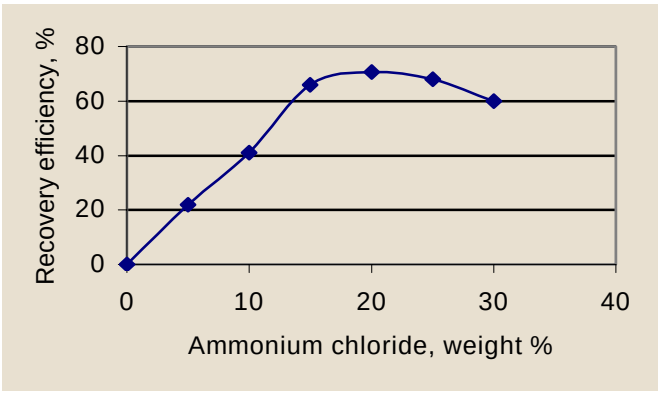

Fig.5 Effect of Ammonium Chloride Concentration on the Recovery of Zinc from Dust
temperature = 600 °C, time = 30 minute

Effect of temperature and time on the R. E. values by using 20 % ammonium chloride flux is demonstrated in figures 6 and 7 respectively. It can be seen that the maximum R. E. values were achieved at 600 °C for 30 minute of thermal treatment. The dust slag formed (slag 2) was collected by skimmed and directed to the hydrometallurgical treatment.

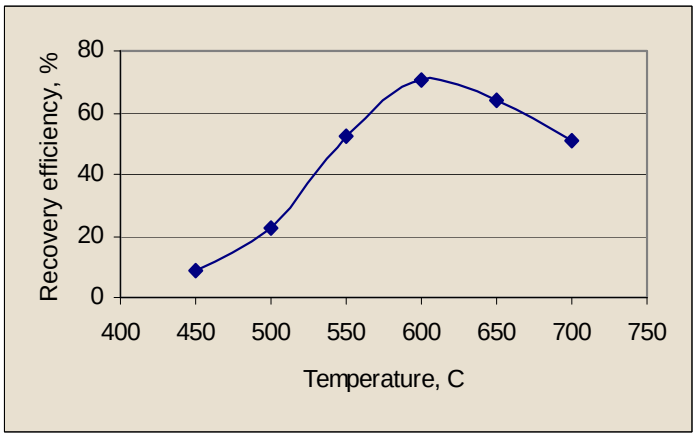

Fig.6 Effect of Temperature on the Recovery of Zinc from Dust
time = 30 minute, with 20% ammonium chloride flux

Chemical Composition of the Produced Zinc

Table (V) shows the chemical composition of the recovered zinc ingots from zinc ash, slag and dust. It is clear that zinc content in the ingots from these materials is higher than 99 % which meets the standard specifications for zinc in galvanization processes.

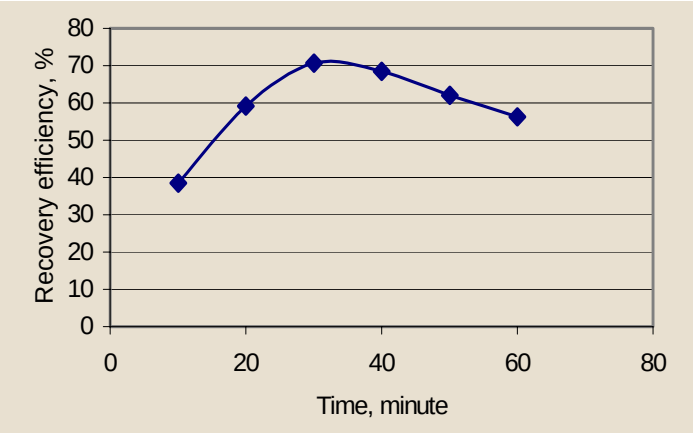

Fig.7 Effect of Heating Time on the Recovery of Zinc from Dust
Temperature = 600 °C, with 20% ammonium chloride flux

Conclusion

The outputs of this study can be summarized in the following:-

- The coarse fraction of zinc ash having particle diameter of +0.9 mm with zinc content amounting to 93.2 % was successfully treated by pyrometallurgical processes.
- The fine fraction of the ash with the particle diameter of –0.9 mm and zinc content of 78.5 % gave a very low yield with pyrometallurgical treatment, so it is better treated by hydrometallurgical processes.
- Zinc was recovered from the coarse ash at 600 °C for 15 minutes, with a recovery efficiency value of 83 %.
- Zinc was recovered from the dust by adding 20 % NH_4Cl at 600 °C for 30 minutes, with a recovery efficiency value of 70.6 %.
- The purity of the recovered zinc metal is about 99.2 %.
- The prices of the products are competitive to the market price as the materials and energy consumption are low.

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