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Hydrometallurgical Recovery of Zinc from Fine Blend of Galvanization Processes

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Abstract: In many factories, which are working in the field of steel industry, there are galvanization units in which steel products are galvanized for corrosion protection. About 15% of the total amount of the used zinc are accumulated as zinc ash and dust at the surface of molten zinc bath and in the chimney respectively. In a previous work, zinc was successfully recovered from the coarse ash by applying pyrometallurgical processing. In this work, zinc fine blend (of fine ash and flue dust) was hydrometallurgically treated using sulfuric acid. Two alternative techniques were applied for producing zinc sulfate salt or pure zinc metal. In the first technique, the salt was separated from the leach solution as zinc sulfate hydrate ($ZnSO_4 \cdot H_2O$). It was crystallized by concentrating the leach liquor to a density of $1.52\,g/cm^3$. The purity of the produced zinc sulfate was 99.5%. In the second technique, the leach solution has been purified with respect to the soluble impurities using precipitation. The electrowinning technique was applied for producing a pure zinc metal from the purified solution. Electrolysis was performed at ambient temperature (25–28°C) with current density (c.d.) of $40\,mA \cdot cm^{-2}$. The recovery of zinc proceeds down to a concentration of $50\,g \cdot l^{-1}$ with acceptable cathodic current efficiency of 96.5%, and energy consumption for the electrolysis step of 2.75 KWh/Kg. The zinc purity in the deposit obtained from the electrolysis was 99.9%.

Keywords: Zinc recovery, fine ash and dust, leaching, crystalization, electrowinning

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INTRODUCTION

This study deals with the recovery of zinc as sulfate salt or pure zinc metal from secondary resources, namely zinc ash and dust, obtained during the galvanization processes of steel. These wastes are usually composed of variable composition of metallic zinc and zinc oxide and may contain from 70 to 96% total zinc. Thorsen et al. (1) developed a process for zinc and/or zinc sulfate recovery from zinc ash skimmed from galvanizing baths, flue dusts of zinc smelting, and Waelz processes. A liquid organic phase containing a cation exchanger (the commercial carboxylic acid Versatic 911) was efficient for zinc extraction from the leach liquor. Concentrated sulfuric acid was used for stripping of zinc, as sulfate, from the organic phase. Several sulfuric acid leaching processes have been investigated to recover zinc selectively from waste materials such as baghouse dust in iron and steel making, or from ash of galvanization process (2–10). The leaching steps were carried out by hot concentrated sulfuric acid so as to generate dissolved zinc sulfate and precipitation of iron with other insoluble impurities. Zinc was recovered from leach solutions as a pure zinc sulfate by vaporization and crystallization, or precipitated as basic zinc carbonate (8). Zinc plant residue was blended with sulfuric acid and subjected to roasting, water leaching, and finally NaCl leaching (11). Saleh and Hassaan (12) studied the recovery of zinc from blast-furnace dust by roasting followed by leaching with ammonium sulfate.

Zinc can be electrodeposited from acid baths including sulfate and chloride (13, 14). The sulfate electrolysis has grown steadily to be the most widely applied method of zinc extraction today. Zinc is recovered from sulfate electrolyte by an electrowinning process in which zinc is electrodeposited on aluminum cathodes while oxygen is evolved at lead anodes. Saba and El-Sherief (15) reported that the minimum zinc concentration at which electrowinning should be stopped is around $40\,\mathrm{g\,l^{-1}}$. The negative effects of impurities on the electrowinning of zinc from acid sulfate electrolytes were studied by many investigators in recent years (16–18). Organic additives such as glue, gum Arabic, and gelatine are usually added to the electrolytic bath to counteract the harmful effects of metallic impurities. They improve cathode zinc quality for deposits from solutions containing various amounts of impurity. Afifi et al. (19) showed that gelatine has an improving effect on the current efficiency and cathode zinc quality, the best choice of concentration is in the range of $2–5\,\mathrm{mg\,l^{-1}}$. Zinc electrowinning is very sensitive to the presence of impurities in the electrolyte. Electropositive ions co-deposit on cathode zinc and make the product impure. The purification process of zinc electrolyte has been studied by many authors (20–25).

The aim of this work is to recover zinc from the fine blend accumulated from steel galvanization process. The study investigated the production of zinc sulfate or pure zinc metal from leach solution by crystallization or electrowinning, respectively.

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. It is skimmed manually from the surface of the galvanizing bath and kept in iron tanks. A sample of 50 Kg ash was supplied by a steel pipes company.

b. Zinc dust

During the same processes of galvanization, flue dust of fine particles is accumulated in the chimney. The dust is collected regularly and stored in separate tanks. A sample of about 50 Kg of the dust was also supplied by the same company.

Chemicals

Chemicals used in this work were of pure grade (ADWICK Chemicals).

Method of Recovery

Zinc fine blend (ash and flue dust) were used for recovery of zinc. Figure 1 shows the process flow chart for the hydrometallurgical recovery of zinc from the fine blend using sulfuric acid as a leaching agent. The produced leach liquor was either concentrated for producing of zinc sulfate crystals, or purified and electrowinned for producing a pure zinc metal.

Leaching

Leaching of zinc blend sample with H_2SO_4 was performed in a 1000 ml three necked glass reactor provided with a thermometer and a reflux condenser. The slurry was agitated with a mechanical stirrer for the required time, and filtered with polypropylene filter cloth having 75 μm (200 mesh) size.

Crystallization

Concentration (evaporation) of the leach liquor for zinc sulfate crystallization was performed in a 1000 ml Pyrex round flask placed on heating mantle provided with a temperature regulator. The vapors were condensed by

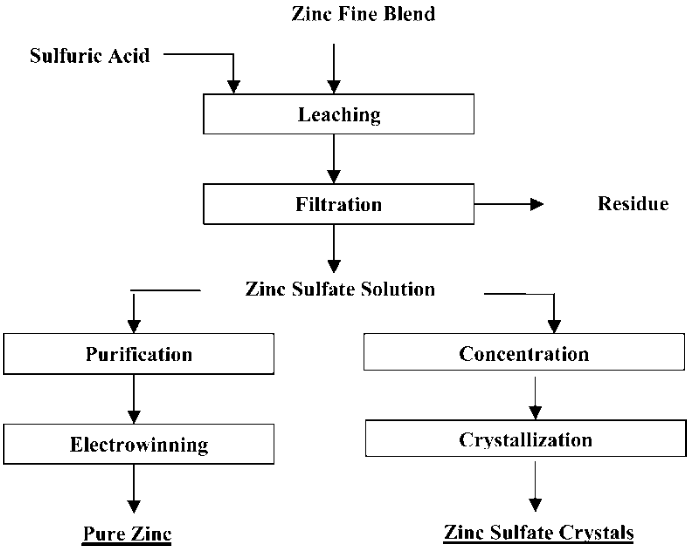


Figure 1. Process flow chart for hydrometallurgical recovery of zinc from zinc fine blend.

means of a glass water condenser and the condense was received in a graduated glass cylinder.

Iron Removal and Purification

The leach solution has been purified with respect to the soluble impurities for electrodeposition of zinc metal. Iron is released into the solution mostly as Fe^{2+} during leaching. It was precipitated in a separate step as ferric hydroxide (26). Oxidation took place by sparging air into solution. Manganese dioxide is added to assist oxidation. At this stage $1.0\,g\,l^{-1}$ of manganese dioxide was added to the solution and the pH was adjusted at 4.5–5.2 using calcium hydroxide. Air was passed through the solution for 2 h, where the color was changed to brown yellow, during which the temperature was maintained between 60–80°C. The solution was then filtered. The above step was repeated to ensure that iron concentration in solution reached the acceptable level. The filtered solution was analyzed for zinc and other minor constituents. The chemical analysis of the leach solution before purification and after the removal of iron is shown in Table 5. After the removal of iron, the next step was to precipitate copper, cadmium, and other impurities. Zinc dust was used to precipitate electropositive impurities from zinc solution by the cementation process.

$$M^{2+} + Zn = Zn^{2+} + M$$

The first purification stage was carried out at 65–75°C by adding 0.5 $g\,l^{-1}$ of zinc dust. Most of the copper, and nickel together with some of the cadmium were precipitated. The filtered solution was then cooled and treated again with another 0.5 $g\,l^{-1}$ of zinc dust to remove the remainder of the cadmium and any other metals still remaining. The solution has been filtered after each stage. The final composition of the leach solution after all purification stages also shown in Table 5.

Electrolytic Cell

The electrolytic cell was a 1 litre rectangular Pyrex glass vessel. It was covered with a Perspex glass lid bearing the electrodes. The temperature was controlled and maintained via thermostatic water bath. A contact thermometer and a relay were used. A peristaltic pump (Cole-Parmer Instrument Company, Master Flex L/S, model 7518-00) was used for maintaining the flow rate of the electrolyte at 40 $ml\,min^{-1}$. The anode was surrounded by a perforated polypropylene bag to collect and separate any anodic slimes that may be deposited during electrolysis. Aluminium sheets were used as cathodes. A sheet of an alloy of lead and 4% antimony was used as an insoluble anode.

Physico–Chemical Properties

X-ray diffraction analysis was used to determine the phases of zinc ash, dust, and produced salts. X-ray fluorescence as well as atomic absorption analysis were used to determine the chemical composition of the raw materials and products. Energy dispersive X-ray analysis (EDX) and ICP-MS were used to analyze the electrodeposits obtained from the leaching solutions. Scanning electron microscope (SEM) was used for inspection of surface morphology of the deposits.

Current Efficiency Calculation

The cathodic current efficiency of the process studied could be defined as the ratio of the weight of metal actually deposited by passing a definite quantity of electricity to the maximum weight that would be deposited by that quantity of electricity in accordance with Faraday's law:

$$W = \frac{ItM}{nF}$$

where I denotes the current passed in Amperes, t is time in second, M is molecular weight, n is number of electrons involved in the reaction, and F is equal to 96500 C.

If w‘ is the weight of metal actually deposited at the cathode, then;

$$\text{(CE)}\ \textit{Current efficiency} = \left[\frac{W'}{W}\right]100$$

Energy Consumption Calculation

The electric energy consumption is the power required to electrodeposit a unit weight of zinc, so it is of an extremely high importance. The electric energy consumption (EC) per kilogram of zinc was calculated from

$$EC = \frac{VI\ t}{W}$$

where V denotes the anode-cathode voltage.

RESULTS AND DISCUSSION

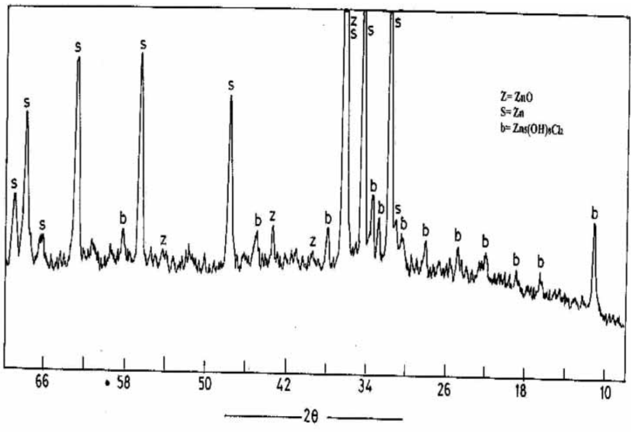
The XRD plots in Fig. 2 shows that the main constituents of each of the fine ash and the dust are zinc metal and zinc oxide (ZnO). The ash and the dust have nearly the same grain size (100% of >0.90 mm). Both fractions were mixed to one blend by the ratio of their industrial production as 2 : 1 by weight, respectively. The chemical analysis of the ash, dust and their blend are listed in Table 1. Zinc content ranged from 82.6 to 90.8%, where the iron content was about 1.0%.

Leaching of the Fine Zinc Blend

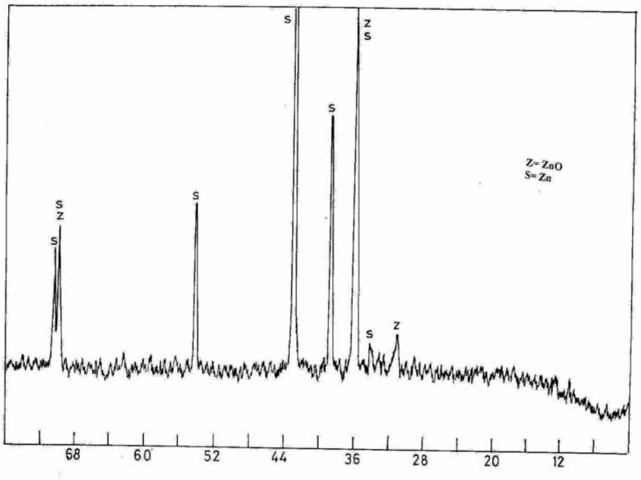
The fine blend sample was treated with sulfuric acid to dissolve its zinc content as zinc sulfate. The different parameters affecting the leaching process were systematically studied to recover as much zinc as possible from the sample. The stoichiometric amount of H_2SO_4 was calculated according to the following equation:

$$\mathrm{Zn} + \mathrm{H_2SO_4} \longrightarrow \mathrm{ZnSO_4} + \mathrm{H_2}$$

A series of experiments was carried out to study the effect of H_2SO_4 concentration on zinc recovery and the results are shown in Fig. 3. The leaching was conducted at solid: liquid (s/l) ratio of 1/4, for 60 minutes at 80°C. About 99% of zinc was recovered using 3.2 M H_2SO_4 (corresponding to 1 stoichiometry). Under the same conditions, about 91% of iron was also dissolved. At higher acid concentration as 3.68 M, the zinc recovery is slightly increased to 99.34%. Further increase in acid concentration leads to negligible



a) zinc ash



b) zinc dust

Figure 2. X-ray diffraction of zinc ash and zinc dust.

increase in the Zn recovery. Subsequent experiments were conducted at 3.68 M H_2SO_4 which is equivalent to 1.2 stoichiometric amount of H_2SO_4.

The effect of s/l ratio on the recovery of zinc from the mixed zinc sample is shown in Fig. 4. The test was conducted at 80°C for 1 h with 3.68 M H_2SO_4. The results reveal that the recovery of zinc increased with increasing the liquid ratio, i.e. increasing the amount of H_2SO_4 added. Almost all of the zinc was dissolved at solid/liquid ratio of 1/4, in which the recovery reached >99.3%. More addition of H_2SO_4, (s/l of 1/5 and 1/6) increased the recovery of zinc to 99.9%. Solid/liquid ratio of 1/4 was selected as the optimum condition and was applied to subsequent experiments.

Table 1. Chemical composition of zinc ash, dust, and their blend

	Weight%		
Constituent	Ash	Dust	Blend
Fe	1.1	0.85	0.91
Pb	0.0036	0.0034	0.0035
Cd	0.002	0.0024	0.002
Ni	0.0032	0.0028	0.003
Cu	0.0016	0.0018	0.001
Mn	0.012	0.01	0.01
Silica + insoluble	2.90	3.00	2.92
Zn	82.6	90.8	85.3

Leaching of the zinc blend sample was carried out at different time periods, and results of zinc recovery are shown in Fig. 5. It is clear that the reaction was very fast as more than 98% of zinc was recovered after only 15 minutes, further increase in time leads to a slight increase in zinc recovery. Time of 30 minutes was selected as optimum retention time at which 99.2% of zinc was recovered. Leaching experiments were carried out at room temperature (about 25°C) which was elevated through addition of the acid. The reaction temperature was recorded at different time periods as shown in Table 2. The reaction is exothermic and the temperature reached

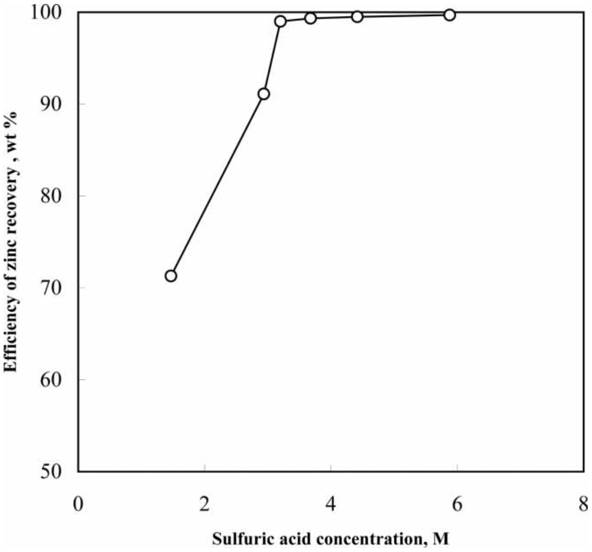


Figure 3. Effect of sulfuric acid concentration on zinc recovery from the fine blend by leaching with sulfuric acid.

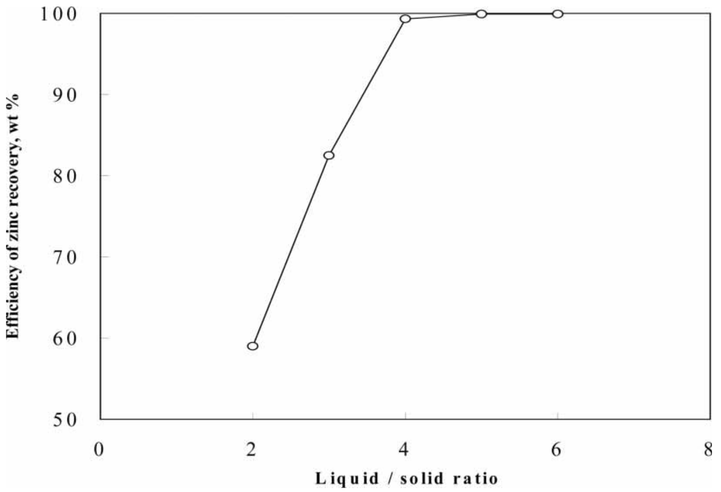


Figure 4. Effect of solid/liquid ratio on zinc recovery from the fine blend by leaching with sulfuric acid.

75°C as soon as the total amount of zinc sample is added to the sulfuric acid solution. After 30 minutes, the temperature of the pulp decreased from 75°C to 50°C. It is worth mentioning that, sulfuric acid was diluted to the required concentration and cooled down to the room temperature before the leaching experiment. To study the effect of the surrounding temperature, the reaction

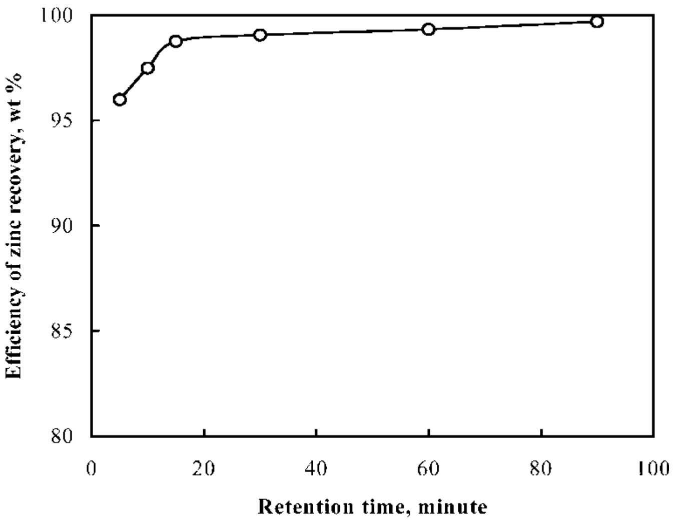


Figure 5. Effect of retention time on zinc recovery from the fine blend by leaching with sulfuric acid.

Table 2. Reaction temperatures at different time periods

Time, min.	Temperature, °C
0	75
5	69
10	64
15	60
20	57
25	54
30	51

mixture was put in a water bath adjusted at constant temperature. It was noticed that, leaving the reaction pulp at room temperature is sufficient to give 99.9% reaction efficiency but raising temperature more than 50°C is not recommended because zinc sulfate has low solubility tendency in water at temperature higher than 50°C (27).

Concentration and Crystallization

Zinc sulfate solution was concentrated by evaporation and crystallized on cooling. The crystals formed may contain different amounts of water of crystallization based on the concentration conditions. Zinc sulfate forms three hydrated compounds, the hepta-hydrate $ZnSO_4 \cdot 7H_2O$, the hexa-hydrate $ZnSO_4 \cdot 6H_2O$ and the mono-hydrate $ZnSO_4 \cdot H_2O$. The solubility of zinc sulfate in water is given in Table 3 (28).

It is clear that the solubility of zinc sulfate in water increases by raising the temperature to 50°C reaching its maximum solubility of 74 g/100 ml H_2O, after that it decreases gradually reaching 60.6 g/100 ml H_2O at 100°C.

Zinc sulfate pregnant liquor of 1.3 g/cm^3 density was concentrated under vacuum to different densities from 1.35 to 1.5 g/cm^3 to study the effect of liquor density on the productivity efficiency by cooling to room temperature (25–30°C). The obtained data are listed in Table 4. The results reveal that, the productivity efficiency increased from 0.0033 $ZnSO_4$ g/cm^3 liquor at density of 1.35 g/cm^3 to 0.401 $ZnSO_4$ g/cm^3 liquor at density of 1.521 g/cm^3.

Table 3. Solubility of zinc sulfate in water (28)

Temperature, °C	0	10	20	30	40	50	60	80	100
Solubility, (g/100 ml H_20)	41.9	47.6	54.2	61.6	70.1	74.0	72.1	65.9	60.6

Table 4. Effect of liquor density on the productivity efficiency of $ZnSO_4$ crystal

Density	Weight of $ZnSO_4$ g/cm^3
1.357	0.0033
1.3792	0.00599
1.4028	0.00587
1.442	0.0584
1.448	0.138
1.4808	0.21013
1.4912	0.29683
1.5186	0.2928
1.5117	0.3583
1.521	0.40146

Crystals precipitated from different concentrated solutions (at different densities) were examined by X-ray diffraction spectrometer. The X-ray data reveal that for all liquor concentrations with density values $<1.52\,g/cm^3$, different forms of zinc sulfate hydrate were crystallized. Thus, it was difficult to produce one specific hydrate form from liquors with density values $<1.52\,g/cm^3$. However by concentrating zinc sulfate in the liquor to $0.4\,g/cm^3$ at a density of $1.52\,g/cm^3$, only the mono-hydrate ($ZnSO_4 \cdot H_2O$) form was produced.

Electrowinning Process

The zinc content and free sulfuric acid of the final leach solution obtained were adjusted to suit the electrolysis step. Mixture of $10\,mg\,l^{-1}$ gelatine and $20\,mg\,l^{-1}$ lignin sulfonate were added to the bath to improve the morphology of the deposited zinc. Electrolysis was performed at ambient temperature, 25°C and current density of $40\,mA\,cm^{-2}$. An insoluble lead anode and pure aluminum cathode were used. During the electrowinning process, zinc concentration in the electrolyte decreased as the zinc is cathodically deposited. The corresponding acid is liberated and consequently, the free acid is increased. The exhausted electrolyte is reused in another leaching step. Experiments were performed to determine the least zinc concentration in the electrolyte at which electrowinning should be stopped. At the end of each experiment, the amount of zinc deposited was determined, current efficiency was calculated and the quality of the deposit was investigated.

Figure 6 shows both the current efficiency and the energy consumption of zinc electrodeposition process. The process was performed at $40\,mA\,cm^{-2}$, in the presence of $10\,mg\,l^{-1}$ gelatine and $20\,mg\,l^{-1}$ lignin sulfonate. The

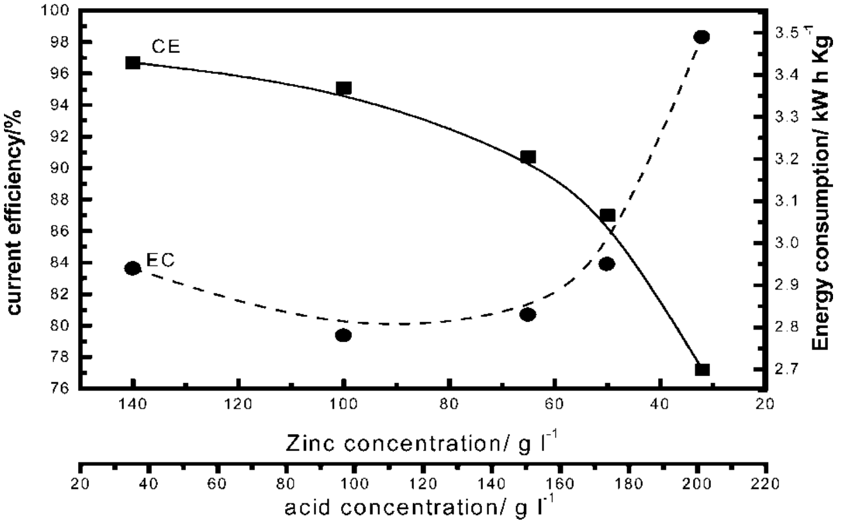


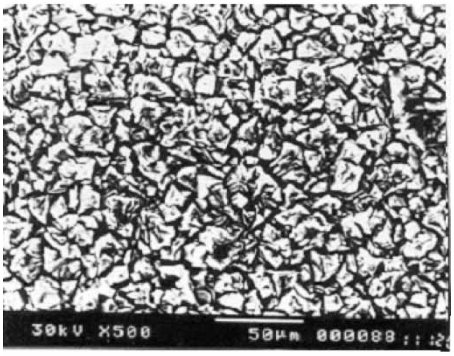
Figure 6. The current efficiency (CE) and electric energy consumption (EC) of zinc electrodeposition process at 40 mA cm^{-2} in the presence of 10 mg l^{-1} gelatine and 20 mg l^{-1} lignin sulfonate.

cathodic efficiency started at 96.5% and reached 90.7% for a solution containing 65 gl^{-1} Zn^{2+} and 150 gl^{-1} H_2SO_4. The electric energy consumed for the production of 1 kg of Zinc was calculated. It records a minimum of 2.75 kWh/kg for a solution containing 100 gl^{-1} Zn^{2+} and 97.5 gl^{-1} H_2SO_4. The energy consumption remains at an acceptable value of 3 kWh/kg for the solution containing 50 gl^{-1} Zn^{2+} and 170 gl^{-1} H_2SO_4.

Gelatine and lignin sulfonate have a smoothing effect on zinc electrodeposits when used in proportions equal to 10 and 20 mg l^{-1} respectively. The cathodic zinc deposits obtained become more fine-grained. The positive effect of additives on the structure of cathodic zinc seems to be related to the formation of an adsorption layer, which increase the cathodic polarization of zinc and thus improves the quality of the metal deposit. SEM inspected the surface morphology of deposits electrowon from the leaching solution in the presence of organic additives. The surface morphology of zinc deposited from an additive-free solution and a similar, containing 10 mg l-1 gelatine and 20 mg l-1 lignin sulfonate are compared (Figs. 7-a and 7-b). The chemical analysis of the produced zinc deposit is shown in Table 6. The purity of the produced zinc was 99.9%.

From the aforementioned results, it is seen that in the electrowinning process, electrorecovery of zinc can be achieved successfully from the electrolyte down to a concentration of 50 g l^{-1} of zinc concentration with acceptable current efficiency, energy consumption, and deposit morphology. Below this concentration, the current efficiency decreased

a) Without additives



b) With additives

Figure 7. SEM of cathodic zinc deposited at $65\,\mathrm{g\,l^{-1}}$ Zn and $150\,\mathrm{g\,l^{-1}}$ H_2SO_4.

sharply, and energy consumption increased. Accordingly, solutions with the range of zinc concentration $< 50\,\mathrm{g\,l^{-1}}$ should be transferred to the leaching vessel, to make use of its high acid content, for further dissolution of raw material.

Table 5. Typical composition ranges of nonpurified and purified solutions produced from leaching of zinc blend

Constituent	Before purification/$\mathrm{g\,l^{-1}}$	After iron removal/$\mathrm{g\,l^{-1}}$	After purification/$\mathrm{g\,l^{-1}}$
Zn	154	152.8	153.3
Fe	7.098	0.026	0.014
Pb	0.00735	0.0004	0.0002
Cd	0.0049	0.0008	0.00004
Ni	0.007	0.0013	0.0001
Cu	0.0028	0.00043	0.00005
Mn	0.00455	0.066	0.065

Table 6. Chemical composition of zinc deposit produced by electrolysis

Element	$65\,g\,l^{-1}$ Zn, $150\,g\,l^{-1}$ H_2SO_4 from zinc blend, wt%
Al	0.0025
Mn	0.002
Fe	0.0029
Ni	0.0021
Cu	—
Cd	0.0006
Total	0.01
% Zinc balance	99.99
% Zinc(EDX)	99.9

CONCLUSIONS

Zinc fine blend was hydrometallurgically treated using sulfuric acid as a leaching agent. Two alternative products, zinc sulfate or purified zinc metal, were obtained. Zinc sulfate hydrate ($ZnSO_4 \cdot H_2O$) was crystallized by concentrating the produced liquor to a density of $1.52\,g/cm^3$ with zinc purity of 99.5%. In the second technique, the leach solution thus obtained has been purified and electrowinned for producing a pure zinc metal. Electrolysis was performed at ambient temperature (25–28°C) with current density of $40\,mA \cdot cm^{-2}$. The recovery of zinc proceeds down to a concentration of $50\,g \cdot l^{-1}$ with acceptable cathodic current efficiency of 96.5%, energy consumption of 2.75 KWh/Kg. The zinc purity in the deposit obtained from the electrolysis was 99.9%. The two techniques converted the low value waste ash and dust to valuable products those have extensive uses.

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