

# Studies on the Preparation of Zinc Oxide from Galvanizing Plant Waste

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Received September 16, 2013; Revised October 30, 2013; Accepted December 01, 2013

**Abstract** Galvanizing plant waste (zinc dross) containing 27.66% zinc was leached in HCl solutions. Zinc in solution was precipitated as Zn(OH)<sub>2</sub> by adding ammonium hydroxide. The product was characterized by atomic absorption spectroscopy, thermogravimetric analysis, x-ray diffraction analysis, and scanning electron microscopy. X-ray diffraction analysis confirmed that when heated at 500°C, the product possesses hexagonal zincite structure. Scanning electron microscopy confirmed that the shape of zinc oxide particles was spherical and compares well with the standard product. A maximum of 93.7% zinc contained in the dross could be extracted and converted to zinc oxide having a purity of 98.8%.

**Keywords:** *galvanizing plant waste, zinc dross, acid-leaching, zinc oxide*

**Cite This Article:** M Mahbubur Rahman, Md. Rakibul Qadir, AJM Tahuran Neger, and ASW Kurny, "Studies on the Preparation of Zinc Oxide from Galvanizing Plant Waste." *American Journal of Materials Engineering and Technology* 1, no. 4 (2013): 59-64. doi: 10.12691/materials-1-4-1.

## 1. Introduction

Recovery and recycling of value materials from industrial wastes reduces the amount of wastes to be finally disposed and thus reduce the waste disposal problems. These wastes usually also contain value materials that can be recovered and reused. Thus recovery of value materials from industrial wastes is important both from economic and environment points of view. Zinc is listed by the Environmental Protection Agency (USA) as one of the 129 priority pollutants [1]. In humans, prolonged excessive exposure to zinc can lead to deficiencies in iron and copper, nausea, fever, headache, tiredness, and abdominal pain [2].

Zinc oxide has wide applications as white pigment, ceramic glaze, lubricants, ointments, adhesive, sealants, and in rubber tires, dry cell batteries, ferrites, fire retardants and an opaque base in cosmetics [1,3]. It is also used in catalysis and as adsorbent in steam reforming process [4,5]. Addition of ZnO improves the resistance of concrete against water [6], fine particles of zinc oxide have antibacterial action [7] and are added into various materials including cotton fabrics, rubber, food packaging, etc [8]. It is also a component in tape (called zinc oxide tape) used in athlete's bandage to prevent soft tissue damage during workouts [9].

Among the vast variety of the available methods for metal recovery, hydrometallurgical method can be a viable wet technique [1]. Promising results can be obtained by combining methods like conventional liquid-liquid extraction, ion exchange, and/or electrochemical separations used for some metals [5,10].

A lot of work has been done on the recovery of metallic zinc from galvanizing plant wastes. Hydrometallurgical processes developed for the recovery of metallic zinc from galvanizing plant wastes involve [11] leaching in a suitable reagent followed by precipitation, solvent extraction, electrochemical reduction etc. However, only one method [12] could be found in published literature for the preparation of zinc oxide from galvanizing plant dross. The method describes the production of high purity ZnO powder (99.78 – 99.91 percent pure) by oxidizing zinc vapor in oxygen atmosphere. The galvanizing plant waste (zinc dross) was mixed with a reducing agent (e.g., coke, activated carbon) and heated to vaporize zinc.

## 2. Materials and Methods

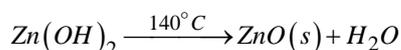
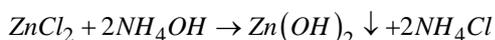
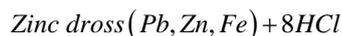
The galvanizing plant waste used for this investigation was collected from one galvanizing plant located at Chittagong, Bangladesh. Analytical grade hydrochloric acid (Merck Germany), ammonium hydroxide (Merck Germany), sodium hydroxide (Merck Germany) and hydrogen peroxide (Merck Germany) used in these experiments were collected from local market.

### 2.1. Experimental Procedure

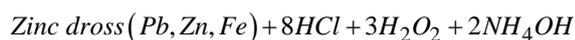
The dross was leached in hydrochloric acid solutions of different concentrations for different periods of time in a round bottom flask. The round bottom flask, fitted with a reflux condenser, was heated by a mantle heater to a fixed temperature and the solution was stirred continuously by a mechanical stirrer. The leach liquor was filtered and concentrated to such a point that precipitation begins on

cooling. The residue was separated by filtration. Lead was separated from the leach liquor as lead chloride. The filtrate was diluted and pH was maintained at 3.9 to 4.0 by adding NaOH. Then H<sub>2</sub>O<sub>2</sub> (1% of total volume) was added to a nearly boiling solution. Iron was precipitated from the leach liquor and was separated by filtration. The filtrate was diluted to a certain volume and ammonium hydroxide was added slowly to a hot agitated solution until precipitation of Zn(OH)<sub>2</sub> was complete. The precipitates were filtered and washed with distilled water for several times for purification. It was then heated at 140°C in an oven to a constant weight.

A series of reactions take place during the preparation of zinc oxide and may be represented as follows:



Overall reaction:



Four sets of experiments were performed by varying (i) concentration of acid (ii) time of reaction (iii) concentration of oxidizing agent (H<sub>2</sub>O<sub>2</sub>) and (iv) solid/liquid ratio. In each experiment approximately 10g

dross was subjected to react with 10 ml conc. hydrochloric acid (the latter was diluted to different concentrations) at a fixed temperature 95°C for different periods of time. The product in each case was washed carefully, separated, dried and analyzed.

Quantitative analyses of zinc dross and the prepared product were carried out by atomic absorption spectroscopy (AAS, Instrument: VARIAN, AA 240 FS, Australia). The phase composition of the prepared zinc oxide was determined by x-ray diffraction analysis (Instrument: BRUKER X-ray Diffractometer model 'Advanced D8'). Morphological analysis of the prepared product was carried out on a 2600SN Hitachi (Japan) Scanning Electron Microscope equipped with Germanium detector and Diamond window. The thermal behavior of the product obtained was evaluated by using a DTA/TG instrument (Model-DTA/TG 6300, Series-EXSTAR 6000, Brand-SII, Seiko Instrument Inc., Japan). The thermogravimetric and differential thermal analyses were carried out in N<sub>2</sub> atmosphere with a heating rate of 20°/min. The temperature difference between an inert (Alumina) reference and the sample was recorded and mass loss was calculated from the thermogravimetric curve.

### 3. Results and Discussion

The chemical analysis of zinc dross used in this study is shown in Table 1. This table also shows the chemical composition of the other raw materials such as hydrochloric acid, ammonium hydroxide and hydrogen peroxide used in this study.

Table 1. Assay of raw materials

Name of raw materials	Zinc dross			Hydrochloric acid	Ammonium hydroxide	Hydrogen peroxide
Parameter	Lead	Zinc	Iron	HCl	NH <sub>4</sub> OH	H <sub>2</sub> O <sub>2</sub>
Percentage	71.82	27.66	0.17	34.76	32.77	27.55

The effect of time of leaching on percent yield of zinc oxide is shown in Table 2. In each case, 10 g zinc dross was leached in 50 ml 1.904M hydrochloric acid solution at a temperature 95°C with constant agitation. The percent yield increased gradually upto 87 percent in 3 hrs. It can also be seen that the amount reacted mass increased with an increase in time, but the percent yield remained

unchanged. This may be explained as follows: leaching of zinc in dross was nearly complete in 3 hrs, but lead contained in zinc dross continued to react with HCl to produce lead chloride thus increasing the amount of reacted mass. The percent purity of these samples was nearly 97.

Table 2. Effect of period of leaching on the extent of yield of zinc oxide

No. of Expt.	Period of leaching (hrs)	Unreacted zinc dross, (g)	Reacted zinc dross, (g)	Amount of precipitated Iron (mg)	Percent removal of iron	Amount of ZnO produced	Percent purity as ZnO	Percent yield
01	0.5	8.1691	1.8309	7.2900	42.88	2.0323	97.1	58.96
02	1.0	7.7069	2.2931	7.7468	45.57	2.5224	97.3	73.18
03	2.0	7.5654	2.4346	10.1264	59.57	2.6782	96.8	77.70
04	3.0	7.2563	2.7437	8.5862	50.51	3.0181	97.1	87.56
05	4.0	5.9727	4.0275	6.9890	41.11	3.0194	97.2	87.60
06	5.0	5.7946	4.2054	6.8986	40.58	3.0187	96.9	87.58
07	10.0	3.3349	6.6651	3.2358	19.03	3.0205	96.8	87.63

Condition: Solid/liquid ratio: 1:5, Conc. of oxidizing agent: 0.801, Conc. of precipitating agent: 2.72 M, Mode of reaction: Closed and stirring

Table 2 also shows that the percent removal of iron increased during first 2 hrs of leaching and then decreased. It is well known that a metal in a solution can replace a metal lower in the reactivity series

[<http://en.wikipedia.org/wiki/Reactivity-series>] by a single displacement reaction. In these experiments both zinc and iron react with hydrochloric acid and produce zinc chloride and iron chloride. After sometime, when free acid

becomes unavailable some metallic zinc from zinc dross reacts with iron chloride to produce metal iron and zinc chloride. As a result after 2 hrs, the amount of iron in the leached solution decreased with an increase of leaching time.

In each of this set of experiments 10g sample was used. Thus the reacted solution may contain a maximum 17mg of iron (the sample of dross contains 0.17 percent iron). But a maximum of around 10mg (60 percent) iron could be removed (Table 2). This also could be attributed to the displacement reaction that takes place during leaching operation.

Table 3 shows the effect of concentration of  $H_2O_2$  (oxidizing agent), in the range 0.405M to 1.215M, on the precipitation of iron. These experiments were carried out at 95°C with 50 ml 1.904M hydrochloric acid and 10g dross. The pH was maintained at around 4.0. It can be seen that the removal of iron was maximum when the concentration of  $H_2O_2$  was 0.810M. Concentrations of  $H_2O_2$  higher than 0.810M did not enhance the extent of removal significantly. The removal of iron was not significant when the concentration of  $H_2O_2$  was less than 0.810M.

**Table 3. Effect of concentration of  $H_2O_2$  on the iron removal during zinc oxide preparation**

No. of Expt	Unreacted zinc dross, g	Reacted zinc dross, g	Conc. of $H_2O_2$ , M	Amount of precipitated iron, mg	Percent removal of iron	Amount of zinc oxide produced	Percent purity as ZnO	Percent yield
08	7.2649	2.7351	0.405	4.9069	28.86	3.0211	97.5	87.65
09	7.2658	2.7342	0.810	8.6261	50.74	3.0185	97.3	87.57
10	7.2655	2.7345	1.215	8.6270	50.75	3.0182	96.8	87.56

Condition: Solid/liquid ratio: 1:5, Period of leaching: 3 hrs, Conc. of precipitating agent: 2.72 M, Mode of reaction: Closed and stirring.

To confirm if zinc contained in the dross reacted first with the acid followed by the reaction of lead, further experiments were carried out and the results are shown in Table 4. This table shows the effect of solid/liquid ratio on the percent yield of zinc oxide. It can be seen that the percent yield remains the same even when the amount of

reacting zinc dross is different for the same amount and concentration of acid. This may be attributed to the fact that according to the reactivity series zinc from a mass of zinc-lead-iron reacts first and subsequently lead reacts with hydrochloric acid. This is in good agreement with the relative positions of the two metals in the reactivity series.

**Table 4. Effect of liquid/solid ratio on the extent of yield of zinc oxide**

No. of Expt.	Zinc dross taken, g	Solid/liquid ratio	Unreacted zinc dross, g	Reacted zinc dross, g	Amount of zinc oxide produced, g	Percent purity of ZnO	Percent yield
11	10	1:5	3.3351	6.6649	2.1855	97.1	63.40
12	05	1:10	2.8126	2.1874	1.1006	97.4	63.86

Conditions: Conc. of HCl: 1.9046M, Temperature: 95°C, Period of leaching: 3 hrs, Conc. of precipitating agent: 2.72 M, Mode of reaction: Closed and stirring

The effect of concentration of acid in the range 0.4761 – 2.3808M on percent yield of zinc oxide is shown in Table 5. In this series of experiments 10 ml concentrated hydrochloric acid were diluted to 0.4761M, 0.9523M, 1.4429M, 1.9046M and 2.3808M concentrations and all

other leaching parameters were kept the same. It can be seen that the percent yield is the highest (nearly 94 percent) with 0.9523M HCl, the yield decreased with an increase in the concentration of acid.

**Table 5. Effect of concentration of acid on the percent yield of zinc oxide**

No. of Expt.	Conc. of acid, M	Un-reacted zinc dross, g	Reacted zinc dross, g	Amount of zinc oxide produced, g	Percent purity of ZnO	Percent yield
13	0.4761	8.3882	1.6118	2.0081	96.8	58.231
14	0.9523	7.0910	2.9090	3.2290	97.2	93.6797
15	1.4429	7.2080	2.7920	3.1001	96.6	89.9401
16	1.9046	7.2818	2.7182	3.0172	97.1	87.5350
17	2.3808	7.4189	2.5811	2.8650	97.3	83.1194

Condition: Solid/liquid ratio: 1:5, Temperature: 95°C, Period of leaching: 3 hrs, Conc. of precipitating agent: 2.72 M, Mode of reaction: Closed and stirring

Figure 1 shows the DTA/TG curves of the prepared product after drying at 140°C. Both the TG and DTG patterns of Figure 1 contain two peaks at around 276°C and 730°C. But the DTA pattern in Figure 1 contains three peaks at around 27°C, 494°C and 730°C. The sample subjected to DTA/TG was a complex  $Zn_5(OH)_8Cl_2$  containing associated water molecule. The peaks at 276°C and 730°C are associated with weight loss, while there is no loss at 494°C. According to published literature

([http://en.wikipedia.org/wiki/Zinc\\_chloride\\_hydroxide\\_monohydrate](http://en.wikipedia.org/wiki/Zinc_chloride_hydroxide_monohydrate)) the complex decomposes at 494°C Thus the weight loss at 276°C may be associated with the loss of water molecule and that at 730°C to the volatilization of  $ZnCl_2$ , while the peak at 494°C in the DTA pattern to the decomposition of the complex. But in Figure 2, (recorded after drying the compound at 500°C), no change in mass was observed.

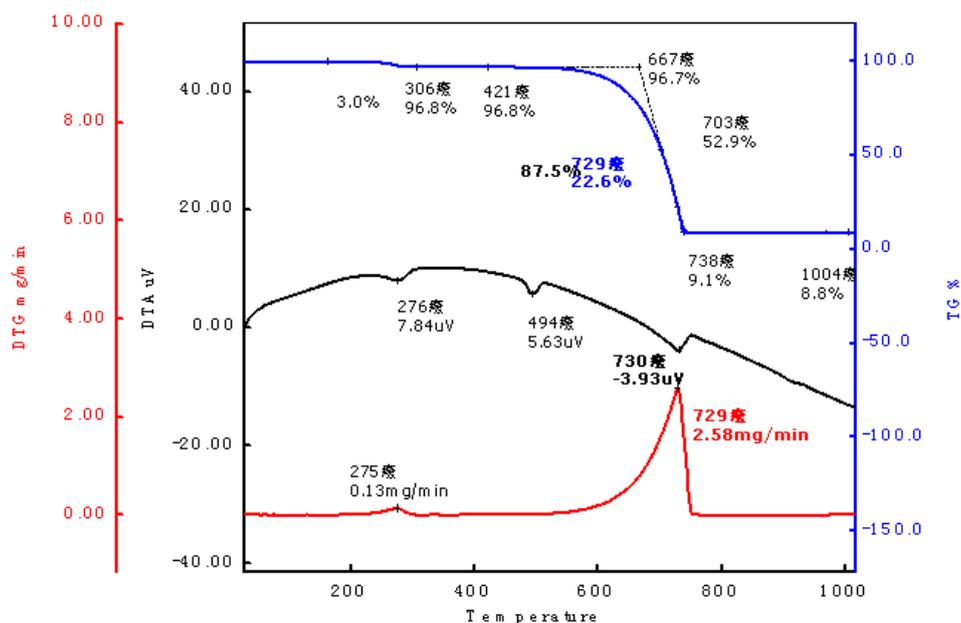


Figure 1. DTA/TG/DTG curves of the product dried at 140°C

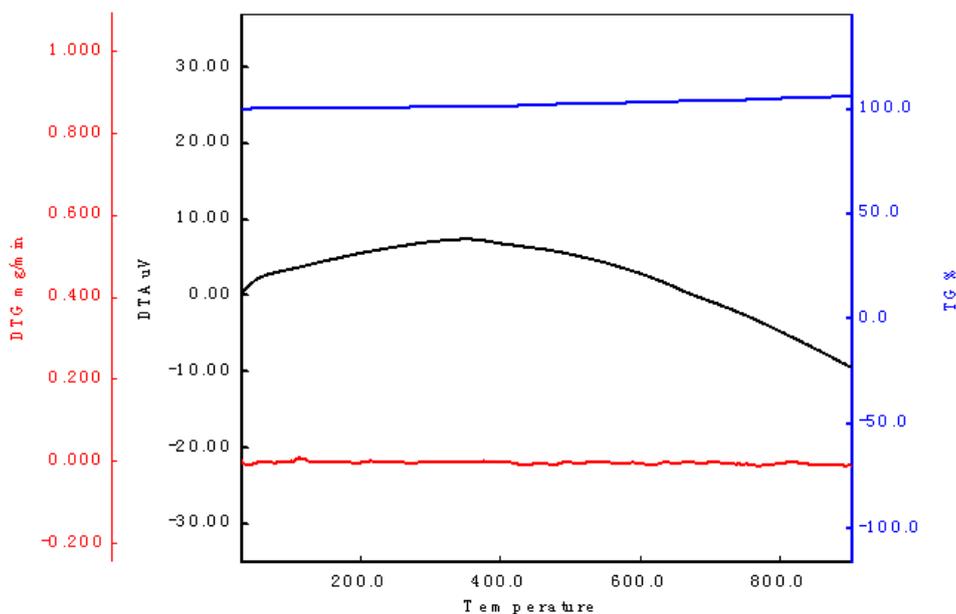


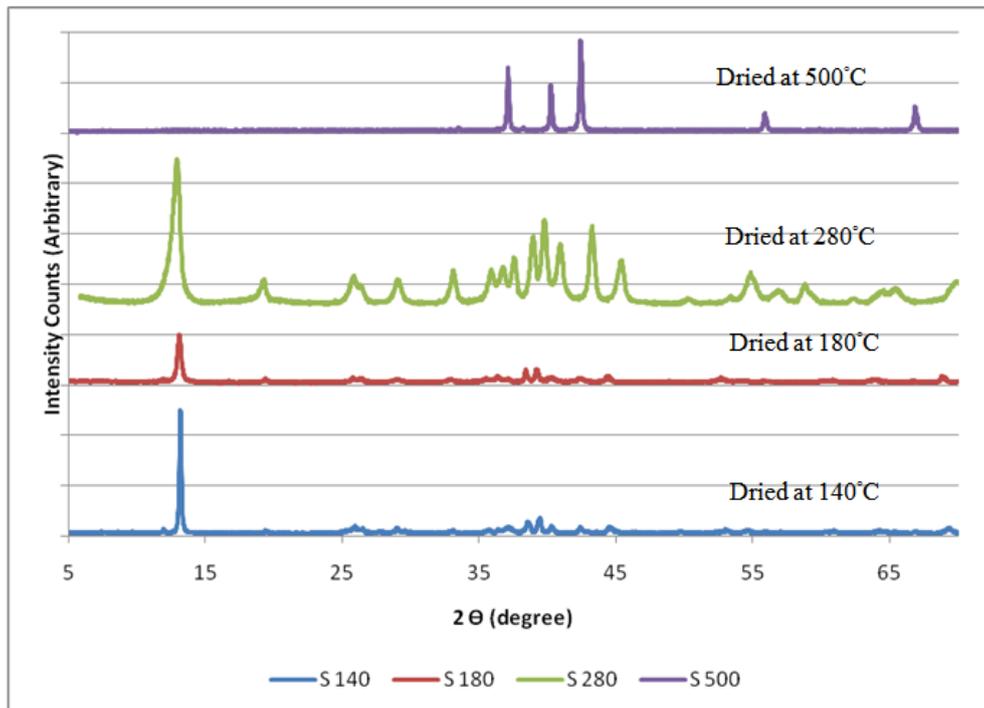
Figure 2. TG/DTA/DTG curves of the product dried at 500°C

A sharp and high intensity peak was observed at a  $2\theta$  value of less than 15 degree in the x-ray diffraction patterns recorded on samples dried at 140, 180 and 280°C (Figure 3). In addition, there were few broad and low intensity peaks at  $2\theta$  values below 36 degrees. These peaks neither matched the peaks of standard ZnO (PDF file no: 01-089-7102), nor those of standard Zn(OH)<sub>2</sub>. These peaks were completely absent when the compound was dried at 500°C. A careful analysis of these patterns showed that the diffraction lines match completely with those of a complex Zn<sub>5</sub>(OH)<sub>8</sub>Cl<sub>2</sub>·H<sub>2</sub>O [Zinc chloride hydroxide complex, known as Simonkolleite: Crystal structure: Rhombohedral; space group: R-3m(166) having cell constants  $a = 6.34000$ ,  $b = 6.34000$ , and  $c = 23.66000$ , PDF file no. 00-007-0155]. The x-ray diffraction lines of the compound in Figure 3 dried at 500°C matched completely with the lines of standard ZnO (PDF file no: 01-089-7102). The x-ray diffraction patterns of the

compound dried at 500°C could be indexed to the hexagonal zincite structure, space group: primitive - P63mc (186), having cell constant  $a = 3.24950$ ,  $b = 3.24950$  and  $c = 5.20690$  and  $\alpha = \beta = 90$ ,  $\gamma = 120$ . Table 6 summarizes the XRD spectrum results of ZnO which almost perfectly match with the results of standard ZnO.

Table 6. Assignment of Miller indices to the product ZnO

Sl. No.	2 theta, degree	Intensity, nm	d-spacing, nm	hkl
01	37.1102	557	2.81915	100
02	40.2455	393	2.60345	002
03	42.4063	999	2.47570	101
04	55.8655	197	1.91107	102
05	66.8282	285	1.62475	110

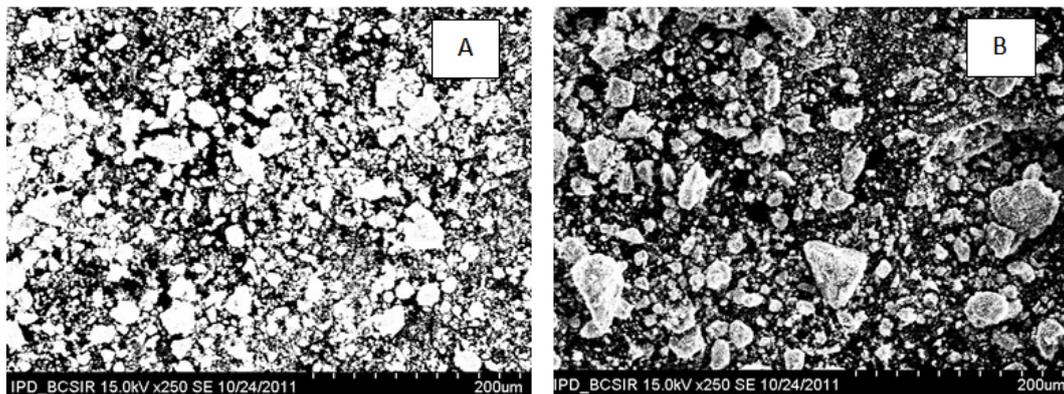


**Figure 3.** X-ray diffraction patterns of the product dried at 140°C, 180°C, 280°C & 500°C respectively (bottom to top)

It has been reported that  $\text{Zn}(\text{OH})_2$  is converted to ZnO at 120°C [1]. The zinc containing precipitate formed in this study required a much higher temperature for transformation, which is perhaps another proof that the product formed was not  $\text{Zn}(\text{OH})_2$ .

Morphology of the prepared zinc oxide was examined under a scanning electron microscope and compared with the morphology of a standard product of E Merck, Germany. The morphology of the prepared product

[Figure 4A] compares very well that of the standard product of E Merck [Figure 4B]. The ASTM "grain-size number" or "index number" [calculated as  $n = 2^{N-1}$  where  $n$  is the number of grains per square inch when viewed at a magnification of 100X, and  $N$  is the ASTM "index number" or "grain-size number" of the prepared product and the standard were quite close, 22.83 and 23.27 respectively. The shapes of particles of these two samples were spherical and agglomerate among themselves.



**Figure 4.** SEM images of compound formed and standard sample (X 250)

## 4. Conclusion

ZnO could be prepared from galvanizing plant zinc dross by simple leaching followed by precipitation. X-ray diffraction study has shown that a hexagonal zincite structure is obtained only after heating to 500°C. Nearly 93.7 % zinc contained in the dross could be leached out and converted to zinc oxide having a purity of 97 percent. Scanning electron microscopic investigation confirmed that the particles are spherical and agglomerate among themselves.

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