

Preparation and characterisation of ferrite grade zinc oxide from zinc ash

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ABSTRACT

Ferrite grade zinc oxide was prepared through aqueous processing of zinc ash followed by calcination. Zinc was quantitatively dissolved in sulphuric acid medium. The ferrous iron present in the leach solution was oxidised with hydrogen peroxide followed by precipitation of total iron by pH adjustment to 4.5 with dilute sodium hydroxide solution. Copper was removed by cementation using zinc dust. Zinc hydroxide was precipitated from the purified zinc sulphate solution with precipitating agents such as ammonia, ammonium carbonate, sodium carbonate and urea. A typical hydroxide obtained with ammonia as the precipitating agent was characterized by IR, XRD and TG-DTA. It was found that during precipitation pure zinc hydroxide was not obtained but ammonium zinc sulphate $((\text{NH}_4)_2\text{Zn}(\text{SO}_4)_2)$ and hydrated hydroxyl zinc sulphate $(\text{ZnSO}_4 \cdot 3\text{Zn}(\text{OH})_2 \cdot 4\text{H}_2\text{O})$ had precipitated. Calcination temperature of $\sim 940^\circ\text{C}$ was required to prepare zinc oxide from the precipitate. In order to obtain the desired particle size and surface area, pulverisation was done. A complete flow-sheet has been developed. © 2004 SDU. All rights reserved.

Keywords: Zinc ash; Zinc oxide; Precipitation; Calcination

1. INTRODUCTION

Zinc oxide (ZnO) finds applications in a variety of products which include inks, rubber, oil, greases, ferrites, cosmetics, pharmaceuticals, food additives, lacquers, ceramics, textiles and glass. In paints, zinc oxide serves as an acid buffer as well as a pigment and the oxide also supplies zinc in animal feeds and is a fertilizer supplement used in zinc deficient soils (Maczek and Kola, 1980; Kola, 1982). Its chemical action in cosmetics and drugs is varied and complex but based upon its fungicidal activity, it promotes wound healing.

Zinc oxide is prepared commercially by two methods, the American (or direct) process (Maczek and Kola, 1980; Kruger and Pullenberg, 1981) which uses zinc ore and concentrate, and the French (or indirect) process (Veltmann and Weir, 1982) which uses zinc metal. In the direct process an initial high-temperature reduction ($1000\text{-}1200^\circ\text{C}$) of a zinc-containing material (as oxide) is carried out using coal. The zinc vapour and the CO gas are then oxidized to zinc oxide and carbon dioxide above the reaction bed or at the furnace exit. In the indirect process the zinc is boiled, and the resulting vapor is oxidized by combustion in air under defined conditions. Due to the increased specificity with respect to surface area and purity for ferrite industry and other applications, zinc oxide is produced using wet chemical processes which include sol-gel, micro-emulsion and hydrothermal technique (Lu *et al.*, 1997; Li *et al.*, 1999; Zou *et al.*, 1999; Kaneko *et al.*, 2000; Rodriguez-Patz *et al.*, 2001; Mondelaers *et al.*, 2002; Pal *et al.*, 2002). Zinc ash is an important secondary source of zinc. Preparation of zinc metal/zinc powder from zinc ash following aqueous processing route has been reported (Thorsen and Grislingas, 1981; Brooks 1986; Nirdosh *et al.*, 1988; Gogia *et al.*, 1995). In the present work a complete flow-sheet for preparation of high pure ferrite grade zinc oxide from zinc ash using different unit operations of leaching, purification, precipitation and calcination has been developed.

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2. EXPERIMENTAL

The zinc ash was analysed by wet chemical method. It contained 81.32% Zn, 7.4% Pb, 0.83% Fe, and 0.062% Cu. The dissolution experiments were carried out in a one liter capacity beaker. Known volume of sulphuric acid was placed in the beaker and the solution was stirred with a stirrer fitted with a motor whose speed could be adjusted with a controller. Required quantity of dried zinc ash sample was added to the acid solution and the reaction was allowed to continue for a predetermined time. The leach slurry was filtered and the leach liquor was analysed for zinc, copper and iron by atomic absorption spectrophotometer (AAS). The ferrous iron of the leach solution was oxidised to ferric form by hydrogen peroxide and was precipitated from the leach liquor by raising the pH. Copper was removed by cementation. The zinc hydroxide was precipitated from the purified solution with various precipitating agents such as ammonia, ammonium carbonate, sodium carbonate and urea. The hydroxide slurry so obtained was filtered, washed till free of alkali and the precipitate was allowed to dry at 100°C for 24 hours in an air oven and then calcined at required temperature to prepare zinc oxide. Size reduction of ZnO was carried out in a Pulveriser (Sieb Technique Malheim, Germany). The time for pulverisation was kept as five minutes each time.

The particle size was determined using a Malvern Particle Size Analyser and for some samples surface area was estimated by BET method. X-ray diffraction (XRD) patterns of zinc hydroxide/oxide were obtained with a Phillips Powder Diffractometer Model PW 3710 in a range of 10 to 70° (2 θ) at a scanning rate of 1°/min using a Ni-filtered Cu target. The TG-DTA study on a typical zinc hydroxide sample was carried out using a Shimadzu TD-40 Thermal Analyser. The IR spectra was obtained by Bruker Spectrophotometer Model Vector-22 using standard procedure.

3. RESULTS AND DISCUSSION

3.1. Leaching of zinc ash

The dissolution tests were carried out at room temperature using different acid concentrations and pulp density. The results given in Table 1 show that by keeping the initial acid concentration as 40% for 33% pulp density, quantitative dissolution of zinc from zinc ash takes place.

Table 1
Results on dissolution of zinc from zinc ash

Expt. no	Pulp density (% wt/vol)	Acid conc. (% vol/vol)	Leaching time, (hour)	Zn dissolution (%)
1	20	1.4	2	48.5
2	20	5.0	2	79.5
3	20	7.5	2	79.0
4	20	10	2	79.4
5	33	40	4	99.9

3.2. Purification of leach solution

Two hundred ml of leach solution obtained under conditions of experiment 5 of Table 1 was diluted prior to purification. The composition of diluted solution was: Zn 28.6g/l, Fe 1.2g/l, Cu 1.41ppm. Ferrous iron was oxidised to ferric iron with the addition of 5ml of hydrogen peroxide and pH of the solution was raised to 4.5 with sodium hydroxide wherein total iron precipitated as hydroxide. Copper was removed by cementation using zinc dust. The iron and copper contents after purification were 5 and 0.3ppm respectively. In subsequent experiments the leach solution was purified without dilution.

3.3. Precipitation and characterization of precipitated zinc hydroxide

The iron and copper free leach liquor containing zinc sulphate was taken and the pH was raised to 7.5 using ammonia for zinc hydroxide precipitation. The slurry was filtered and the precipitate was washed till free from sulphate and alkali and was dried at 100°C for 24h.

The IR spectra of precipitated compound is shown in Fig. 1. The broad peaks at 3487cm⁻¹ and 3079cm⁻¹ can be ascribed to stretching mode of bonded -OH and ammonium ion (Nakamoto, 1963; Rochester, 1973). The sharp peak at 1629cm⁻¹ is due to water angular deformation and adsorbed ammonium ion. The peak at 516cm⁻¹ is due to water angular deformation in plane (Rochester, 1973). The small peak at 1456cm⁻¹ is attributed to ammonium ion angular deformation. The sharp peak at 1115cm⁻¹ correspond to the stretching mode of SO₄ while the peak at 601cm⁻¹ correspond to bending mode of SO₄. The band at

654 cm^{-1} can be attributed to Zn-N vibrational stretching and the peak at 437 cm^{-1} is due to Zn-O vibrational stretching (Nakamoto, 1963). Some of the peaks remained unresolved. From the IR spectra it is inferred that the precipitated compound contains both ammonium ions and sulphate besides presence of water of hydration and compounds with Zn-O and Zn-N bondings.

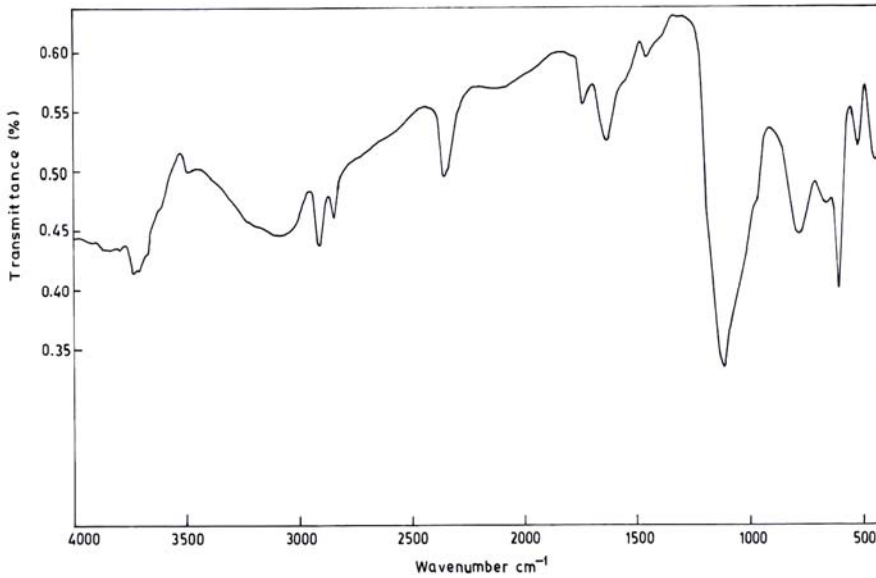


Figure 1. IR spectra of the precipitated hydroxide. Conditions: Purified ZnSO_4 solution, precipitating agent ammonia, pH 7.5, temp. ambient

To know the presence of crystalline phases, XRD pattern of the precipitated compound was taken. Fig. 2 shows that there are no peaks corresponding to any form of pure form Zn(OH)_2 . The peaks correspond to two compounds viz., a double salt of zinc and ammonium sulphate $(\text{NH}_4)_2\text{Zn(SO}_4)_2$ (JCPDS, 1971a) and hydrated zinc hydroxyl sulphate, $\text{ZnSO}_4 \cdot 3\text{Zn(OH)}_2 \cdot 4\text{H}_2\text{O}$ (JCPDS, 1971b). The formation of these compounds may take place as given below:

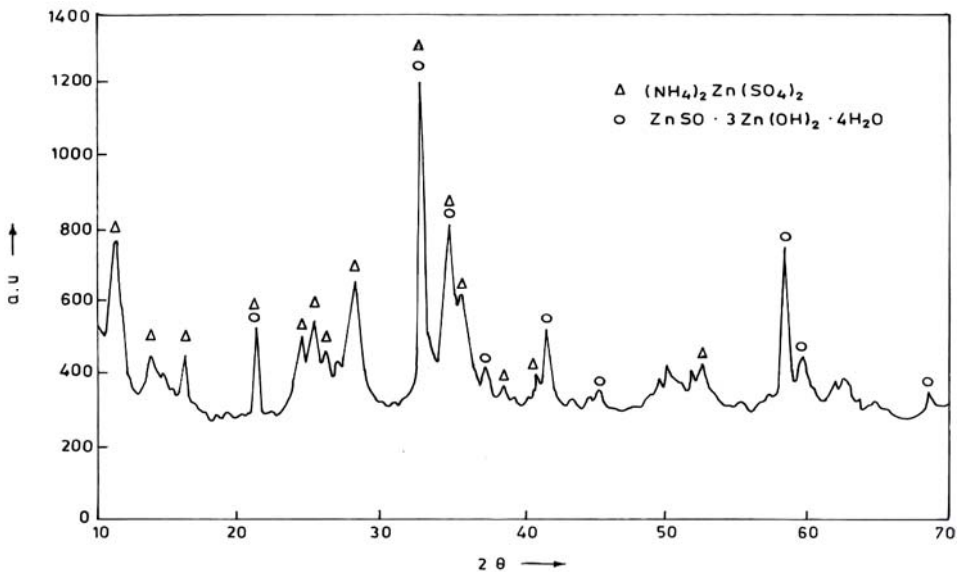
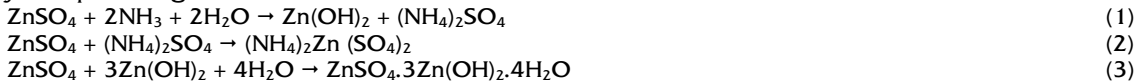


Figure 2. XRD pattern of the precipitated hydroxide (same conditions as mentioned in Fig. 1)

The TG-DTA trace given in Fig. 3 shows a total weight loss of 32%. The endo peak in the region 90-120°C accompanied with 3.6% weight loss corresponds to loss of adsorbed water. The endo-peak at 260°C accompanied by 9.5% weight loss corresponds to weight loss due to loss of water of crystallisation from hydrated hydroxyl zinc sulphate (Bailar Jr, 1973). The endo-peak at 380°C is due to decomposition of ammonium sulphate (Mackenzie, 1970) associated with the double salt of zinc and ammonium sulphate. The weight loss in the region 700 to 900°C may be attributed to both dehydroxylation of zinc hydroxide from the compound $ZnSO_4 \cdot 3Zn(OH)_2$ (Bailar Jr., 1973) and decomposition of zinc sulphate. Though the regions of weight loss and endothermic peaks can be identified but It is difficult to quantitatively estimate the distribution of these compounds in the precipitate.

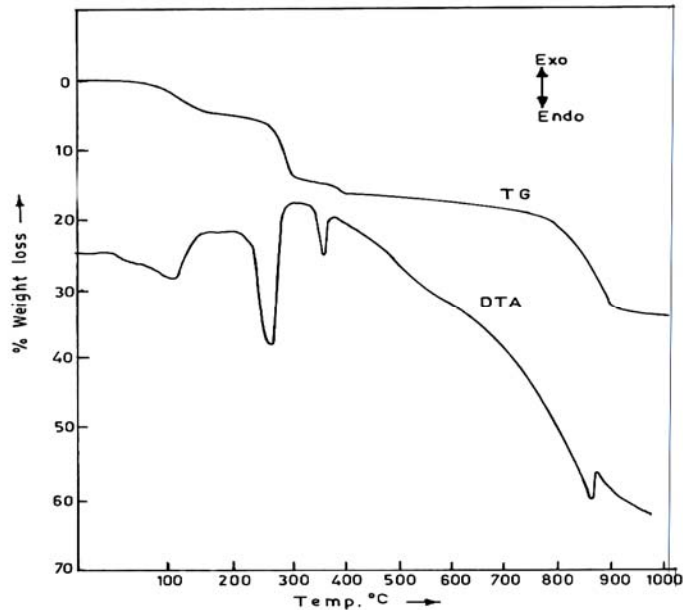


Figure 3. TG-DTA traces for the precipitated hydroxide (same conditions as mentioned in Fig. 1)

3.4. ZnO preparation

From the TG-DTA trace, it was observed that the weight loss from the precipitate continued till 900°C, hence it was essential to calcine the precipitate at $\geq 900^\circ\text{C}$ to obtain ZnO. The precipitate was calcined at 940°C for 2h and analysed. The XRD pattern of ZnO is shown in Fig. 4. All the peaks match with those of ZnO.

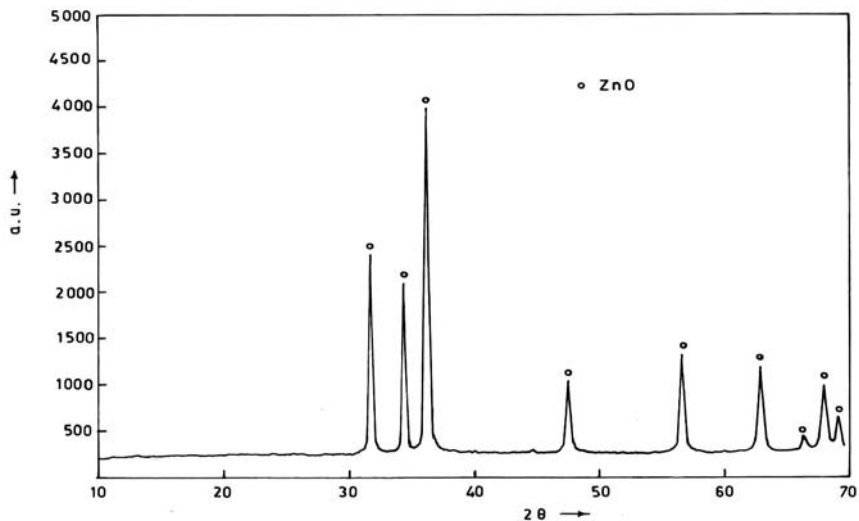


Figure 4. XRD pattern of ZnO (same conditions as mentioned in Fig. 1)

The analysis of synthesised sample is compared with the ferrite grade ZnO in Table 2. It is observed that the impurity levels in the sample prepared from zinc ash are comparable to ferrite grade zinc oxide.

Table 2
 Comparison of zinc oxide analysis prepared in the present work with the specifications required for ferrite industry

Parameters	%ZnO (this work)	%ZnO (used for ferrite)
Moisture (110°C)	0.09	0.21
Loss on ignition (1000°C)	0.03	0.13
Matter insoluble in conc. HCl	0.0	0.04
Matter soluble in water	0.16	0.72
Silica (as SiO ₂)	0.01	0.02
Copper oxide (as CuO)	0.0003	0.0005
Lead oxide (as PbO)	0.0033	0.001

3.5. Particle size analysis

Besides impurities, the particle size and surface area are also important for the ferrite grade zinc oxide. The particle size and specific surface area as determined by Malvern Particle Size analyser were D₅₀: 16.97 microns and 0.47m²/cc respectively whereas the requirement of particle size for ferrite industry is 1-2 microns with surface area of 5 to 6.5m²/g. With a view to reduce the particle size and increase the specific surface area, additives such as sodium lauryl sulphate (SLS) and ethanol were added individually to the hydroxide slurry. Turbidity was observed with SLS and the particle size increased to 83.43 microns and the specific surface area decreased to 0.25m²/cc. In case of addition of ethanol though decrease in particle size and increase in surface area was observed (the particle size D₅₀ was 6.23 microns and the specific surface area was 1.24m²/cc) but still the particle size could not be reduced as desired.

3.6. Particle size and surface area of ZnO prepared by calcination of precursors precipitated at different pH

In order to study the effect of pH on particle size and surface area of zinc oxide, zinc hydroxide was precipitated from zinc sulphate solution (prepared from purified solution after dissolving ZnO in H₂SO₄ as described in Sec. 3.2) at 6.5, 7.0 and 7.5 pH. Ammonia was used as the precipitating agent. The hydroxide was washed till free from alkali and sulphates. The precursors so obtained were roasted at 940°C to prepare ZnO. The particle size analysis and surface areas of zinc oxide samples produced at different pH's is given in Table 3. pH of 6.5 to 7.0 seem to be better with respect to particle size and surface area.

Table 3
 Comparison of particle size and surface area obtained from precursors of ZnO prepared at different pHs (ammonia as the precipitating agent)

Sl No	pH of pptn	Surface area, m ² /cc	Particle size, μm
1	6.5	1.24	9.17
2	7.0	1.06	8.93
3	7.5	0.47	16.97

3.7. Comparison of particle sizes and surface areas of ZnO prepared from zinc hydroxide samples obtained using various precipitating agents

The nature of precursor zinc hydroxide may affect the physical properties of the final product, therefore a number of precipitating agents such as sodium carbonate, urea and ammonium carbonate were used to prepare samples of zinc hydroxide which were calcined at 940°C to obtain zinc oxide. The particle sizes and surface areas of zinc oxide samples are compared in Table 4.

Table 4
 Effect of precipitating agent on particle size and surface area of ZnO

Sl No	Nature of precipitating agent	Surface area (Malvern) m ² /cc	Average particle size μm (D ₅₀)
1	Ammonia	0.47	16.97
2	Sodium carbonate	0.19	78.04
4	Ammonium carbonate	1.62	4.70
5	Urea	0.56	16.26

It is observed that both particle sizes and surface areas are dependent on the nature of precipitant. Calcination of precipitate obtained by using ammonium carbonate as the precipitant yielded zinc oxide having smallest particles (4.7 μm) with largest surface area as 1.62 m^2/cc whereas precipitation with sodium carbonate yielded a product with maximum particle size (78 μm) and minimum surface area (0.19 m^2/cc).

3.8. Reduction of particle size by pulverisation

Further attempts were made to decrease the particle size and increase surface area by disintegrating the particle through pulverisation. The ZnO prepared by using ammonia as the precipitation agent for Zn(OH)₂, and calcining it at 940°C, was pulverised single, twice, four and five times. The particle size decreased to 2.04, 1.37 and 1.34, 1.33 microns by one, two, four and five times pulverisation. The specific surface areas also increased to 3.93, 5.02, and 5.1 m^2/cc with one, two and four times pulverisation respectively. The results show that upto second pulverisation the particle size decreased and further pulverisation did not have much effect. Table 5 compares results obtained after fourth pulverisation using various precipitants for obtaining ZnO precursor. The chemical analysis of all the three samples was comparable with that of standard compound. The XRD patterns of these samples were similar showing peaks only for ZnO. It is observed from these results that the highest surface area was obtained when ammonium carbonate was used to precipitate zinc hydroxide from purified zinc sulphate solution. A schematic flowsheet for production of ferritic grade ZnO is shown in Fig. 5.

Table 5
 Comparison of particle sizes and surface areas of ZnO samples after four times pulverisation using different precipitating agents during hydroxide precipitation

Sl No	Nature of precipitating agent	Surface area		Particle size, μm
		Malvern analyser, g^2/cc	BET, m^2/g	
1	(NH ₄) ₂ CO ₃	6.1	4.94	1.06
2	Na ₂ CO ₃	6.1	4.35	1.06
3	NH ₃	5.1	3.36	1.34

4. CONCLUSIONS

Zinc from zinc ash was quantitatively dissolved in sulphuric acid. Ferrous iron present in the leach solution oxidized to ferric iron followed by precipitation of total iron as ferric hydroxide after adjusting the pH to 4.5 with sodium hydroxide. Copper was removed through cementation by zinc dust. For precipitation of zinc from zinc sulphate solution, precipitating agents such as ammonia, ammonium carbonate, sodium carbonate and urea were used. IR and XRD studies were carried out on the precipitate obtained by using ammonia and it was revealed that the precipitate contained double salt of ammonium. The TG-DTA trace indicated weight loss till a temperature of ~900°C.

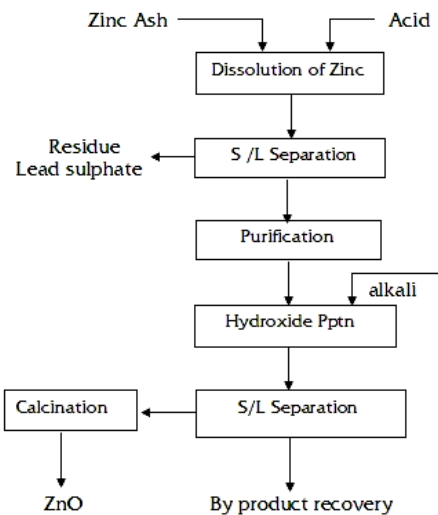


Figure 5. Schematic flowsheet for production of zinc oxide from zinc ash

Hence a temperature of ~940°C was chosen for preparation of ZnO from the precipitate. Pure ZnO matching in chemical analysis, surface area and particle size for ferrite grade was prepared. To obtain the requisite particle size of ZnO and surface area, pulverisation was essential. A complete flow sheet has been developed.

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