

Recovery of High Purity Zinc Oxide through Dry and Wet Processes from Low-Quality Dross Containing Zinc

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Abstract

In this study, nano-grade zinc oxide powder was produced through a dry/wet fusion process of zinc dross generated by a melting process using an electric furnace and collected through a dust collector. The process of recovering nano sized zinc oxide powder consists of vapor distillation to recover Zn by mixing cast iron soluble dust and cokes, selective leaching of $Zn(NO_3)_2$ through the addition of HNO_3 , and recovery of nano zinc oxide powder through NH_3 neutralization. The vapor distillation process was maintained for 1 hour at $700^\circ C$ with cast iron melting dust : cokes = 1 : 1 weight ratio. Thereafter, the deposited Zn was recovered, and the concentration of Zn and 30% HNO_3 was maintained at room temperature in a 1 : 6 molar ratio, and then neutralized and dried by introducing a concentration of 28% NH_3 to recover pure ZnO. Through the above process, finally, a purity of 99.99%, an average particle size of 150nm, and a plate-shaped ZnO nano powder were prepared.

Keywords: dry distillation; acid leaching; zinc oxide; nano powder, wet process

1. INTRODUCTION

ZnO is a compound semiconductor with 3.37eV band gap energy, and its bond energy at room temperature is 60meV, which is greater than thermal energy (2626meV), that it has established a broad market as it is used in piezoelectric body, cosmetics, and white pigment^[1]; it is recently drawing attention as a high value material with great potential in optoelectronic device such as solar battery, laser, and LED, and nano-structured ZnO for electronic, optical, and catalytic sensor^[2-6].

However, Korea is dependent on the import of zinc mineral, which is the raw material of ZnO, and needs to establish a stable supply system for the survival of domestic industry in the global market. For this, many studies have been conducted on ways to collect zinc from zinc scraps, but there are still many difficulties in commercializing zinc collection. In Korea, zinc is collected from electric arc furnace dust through dry processing, and a typical dry processing includes the production of metal zinc using Waelz Kiln and Plasma method^[7,8]. Iron scrap is the raw material used by dry electric arc furnace steel manufacturers, and while most of it is dissolved in the refining process into products, some elements contained

in the scrap such as zinc turn into dust with the supplementary materials added in electric arc furnace refining process and are discharged outside the furnace^[9]. In electric arc furnace steelmaking process, about 15~25kg of dust is known to be generated per 1 ton of crude steel^[9, 10]. Since over 100,000 ton of ZnO (grade 60~67%) can be produced from over 400,000 ton of steelmaking dust (Zn grade about 28%) that is generated per year, Befesa Zinc Korea Co., Ltd. has been developing and commercializing Waelz Kiln Process-based HKZ Process since 2013^[11]. Waelz method puts and reduces steelmaking dust pallets and cokes in a large capacity rotary kiln and produces ZnO at a high recovery rate, but contains considerably large amounts of impurities such as Pb, Cl, Na, K, and Fe, and has high fuel cost. In addition, Plasma method can directly collect metal zinc that is produced through smelting reduction, but has high power consumption and low zinc purity^[12]. Electrolytic method in wet process includes the use of alkaline leaching solution or acidic leaching solution^[13].

Method using alkaline leaching solution uses ammonium chloride to collect high purity zinc, but zinc recovery rate is low at 50%^[14]. Also, according to study result by Havlik et al., diluted sulfuric acid was used for about 70~80% recovery rate by solid-liquid ratio condition^[15]. Study by Hwang et al. reported of selective extraction of Zn by liquid surfactant membrane process and synthesis of high purity zinc oxide powder^[16]. In addition, studies on the recovery of Zn and ZnO from low grade Zn-containing scrap are mostly about dry process such as Waelz method and Plasma method, and wet process using alkaline and acidic leaching solutions, but with low purity or recovery rate of Zn or ZnO collected, development of dry/wet fusion process may be necessary.

In this study, high purity ZnO was produced through dry thermal reaction and wet leaching continuous process. First, 2N-grade Zn was collected from low-grade Zn-containing scrap through dry distillation. Collected Zn powder was produced into high purity nano ZnO through acid distillation and neutralization. Produced ZnO was analyzed through XRD, XRF and TEM.

2. MATERIALS

Material used in this study is iron dross, an oxide layer that is

produced as the uppermost part of molten metal is in contact with air while producing zinc ingot. Fig. 1 and Table 1 display the results of phase analysis and composition analysis of raw sample where phase analysis was performed by XRD (X-Ray Diffraction) and composition analysis was performed by EDS (Energy Dispersive X-ray Spectroscopy). As a result of XRD analysis, raw sample existed in the form of ZnO, Zn, Zn(OH)₂, and ZnS. As a result of composition analysis, content of Zn is 64.7%, O is 13.41%, Na is 10.7%, C is 7.54%, Cl is 2.32%, S is 1.10%, Al is 0.33%, Si is 0.13%, and Ca is 0.1% in the raw sample.

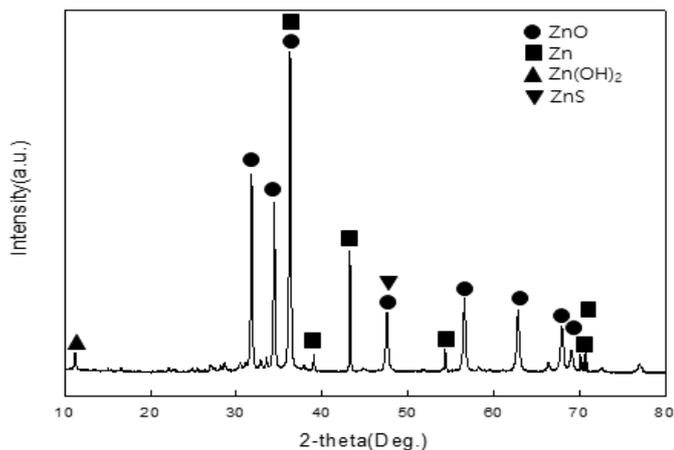


Fig. 1. XRD pattern of zinc dross

Table 1. Chemical compositions of raw material

| | | | | | |
|---------|------|-------|------|------|------|
| Element | Zn | O | Na | C | Cl |
| wt. % | 64.7 | 13.41 | 10.7 | 7.54 | 2.32 |
| Element | S | Al | Si | Ca | |
| wt. % | 1.1 | 0.33 | 0.13 | 0.1 | |

3. EXPERIMENT METHOD

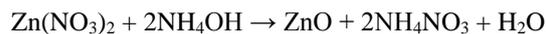
3.1. Vapor Distillation

To collect Zn from the raw sample selectively, zinc dross was combined with the reducing agent, cokes, and inserted into electric arc furnace. Zn and cokes in zinc dross were reacted for reduction reaction as well as deposition recovery of Zn.

Vapor deposition experiment was conducted in Ar gas (300cc/min) atmosphere from 30°C to 1100°C at 10°C/min heating rate, and mix proportion of zinc dross and cokes was added at 3 conditions of 9:1, 8:2, and 7:3. Reaction time was 1 hour, 2 hours, and 3 hours.

3.2. Acid Leaching

30% HNO₃ was added to leach ZnO selectively after collecting vapor deposited Zn powder, and 28% ammonia water was added for neutralization to collect nano ZnO powder. Reaction formulas of acid leaching and neutralization are as follows.



Acid leaching was done under 4 conditions of Zn : nitric acid molar ratio (1:4, 1:5, 1:6, 1:7), and acid reaction was done under 4 conditions (30 minutes, 40 minutes, 50 minutes, 1 hour).

3.3. Neutralization Reaction

ZnO is an amphiprotic solution that dissolves in strong acid and strong alkali, and when ammonia water is unsaturated in neutralization, ZnO yield decreases as solution is acidic, and when supersaturated, ZnO yield decreases as solution is basic and purity decreases due to residual ammonia water. Therefore, ammonia water was experimented under 10 conditions by adding 10ml starting from the volume ratio of ZnO and ammonia water 100ml:10ml.

When ammonia water is added to zinc nitrate, ZnO powder is created, and neutralization time is when nucleation occurs. Particle size was expected to be smaller with longer neutralization time, and particle size of ZnO was measured under 5 conditions of 1 hour, 2 hours, 3 hours, 4 hours, and 5 hours of neutralization. To measure, SEM (Scanning Electron Microscope) analysis was performed.

3.4. Water Leaching

After neutralizing zinc nitrate into ZnO, water leaching was performed to remove residual NH₄NO₃. NH₄NO₃ is easily dissolved in water and ZnO is not dissolved in water, and this property was used to separate them. Table 2 displays the difference in solubility of water between NH₄NO₃ and ZnO.

Table 2. The variation in solubility of water between NH₄NO₃ and zinc oxide at elevated temperatures

| Materials | NH ₄ NO ₃ | Zinc Oxide |
|---------------------|---|------------|
| Solubility in water | 118g/100ml(0°C) 150g/100ml(20°C) 297g/100ml(40°C) 410g/100ml(60°C) | Insoluble |

For number of leaching, NH₄NO₃ and ZnO solution and distilled water at room temperature were experimented at 1, 2, and 3 times. To measure, XRD (X-Ray Diffraction) analysis was performed.

4. RESULT AND DISCUSSION

4.1. Vapor Distillation

After vapor deposition of zinc dross, amount of zinc deposited in condenser was calculated to measure the recovery rate. Result of experiment according to the mix proportion of zinc dross and cokes is displayed in Table 3. Based on the calculation of zinc amount, process time and cokes content are proportional to recovery rate, and the optimum process time of

3 hours and cokes content of 30% was drawn from the result of experiment.

Table 3. Recovery rate by vapor deposition process time and cokes content

unit: wt.%

| Cokes content (wt.%) | Time | | |
|----------------------|-------|-------|-------|
| | 1 | 2 | 3 |
| 10 | 70.46 | 83.30 | 92.22 |
| 20 | 74.23 | 86.57 | 96.83 |
| 30 | 77.38 | 87.96 | 97.10 |

XRD (X-Ray Diffraction), EDS (Energy Dispersive X-ray Spectroscopy), and XRF (X-Ray Fluorescence) analyses were performed for phase analysis and composition analysis of recovered powder, which the results are displayed in Fig. 2. Based on XRD analysis result, Zn only existed as Zn phase, and based on EDS and XRF results, zinc with over 99.3% purity was recovered.

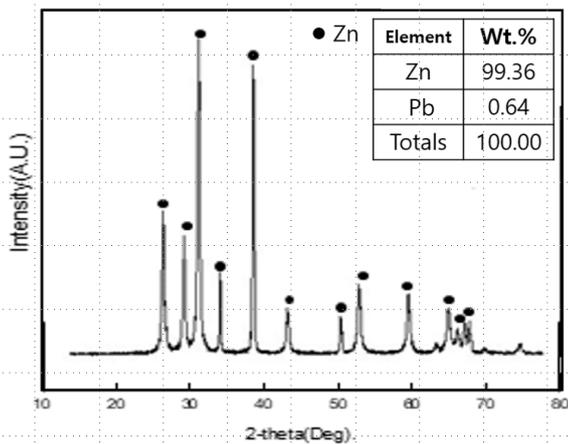


Fig. 2. Result of XRD pattern of recovered zinc

4.2. Acid Leaching

During the acid leaching for selective leaching of zinc nitrate, the retention period was set at 1 hour. Existence of acid leaching was confirmed through the existence of residual Zn after leaching the recovered Zn powder in nitric acid for 1 hours.

As a result, residual zinc powder was confirmed in the solution when leached at the zinc: nitric acid molar ratio of 1:4 and 1:5, but no residual zinc powder when leached at the molar ratio of 1:6 and 1:7, confirming complete leaching of zinc powder. Based on the result, the optimum molar ratio of 1:6 between zinc powder and nitric acid was obtained.

After obtaining the optimum zinc-nitric acid molar ratio of 1:6, an experiment was conducted to obtain the optimum acid leaching time, and existence of acid leaching was confirmed through the existence of residual zinc after the time identically set as the previous experiment.

Based on the result, residual zinc powder was confirmed at acid leaching time of 30 minutes and 40 minutes, and at 50 minutes, leaching was almost completed but residual zinc was confirmed when the outside temperature was lower than room temperature.

When acid leaching time was 1 hour, it was completely leached regardless of outside temperature, which concluded the optimum condition of acid leaching of zinc-nitric acid molar ratio at 1:6 and acid leaching time of 1 hour.

4.3. Neutralization Reaction

In order to compare ZnO recovery rate based on volume ratio of zinc nitrate and ammonia water, neutralization retention time was set at 1 hour. Recovery rate was compared by measuring the mass of powder through decompression filtration of crystals that are created when ammonia water is added. Result of ZnO recovery rate based on volume ratio of zinc nitrate and ammonia water is displayed in Fig. 3.

As a result, there was no recovery at the volume ratio of 100ml: 10ml and 100ml: 20ml, and ZnO recovery rate increased as more ammonia water was added. However, recovery rate decreased from 100ml: 60ml, and ZnO could not be recovered from 100ml: 80ml, as it did not exist.

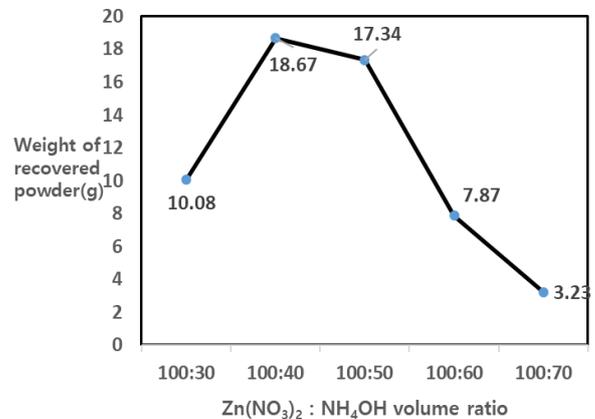


Fig. 3. Amount of recovered powder per Zinc nitrate: Ammonia water ratio

Experiment was conducted under 5 conditions by increasing by 1 hour starting from 1 hour to observe changes in particle size of ZnO based on neutralization time, and the result is displayed in Figure 4.

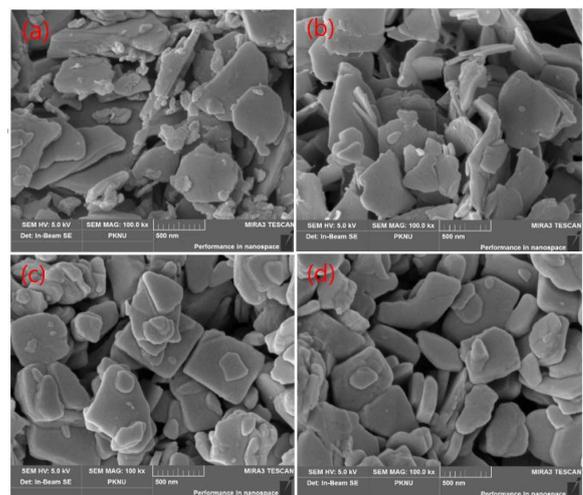


Fig. 4. Particle size of zinc oxide with reaction time: (a) 1hr (b) 2hrs (c) 3hrs (d) 4hrs

As a result, particle size of ZnO powder was below 500nm when neutralization time was 3 hours, 4 hours, and 5 hours. However, the change in particle size was small starting from 3 hours, which concluded the optimum condition of neutralization at volume ratio between zinc nitrate and ammonia water at 100ml:40ml, and neutralization time of 3 hours.

4.4. Water Leaching

To examine the effects of number of water leaching, experiment was conducted under 3 conditions of 1, 2, and 3 times at 1 hour process, and the result is displayed in Fig. 5.

When water leaching process is repeated 1 time and 2 times, NH_4NO_3 was detected in powder, but when the process was repeated 3 times, no NH_4NO_3 was detected in the recovered powder. Therefore, the optimum number of leaching is 3 times.

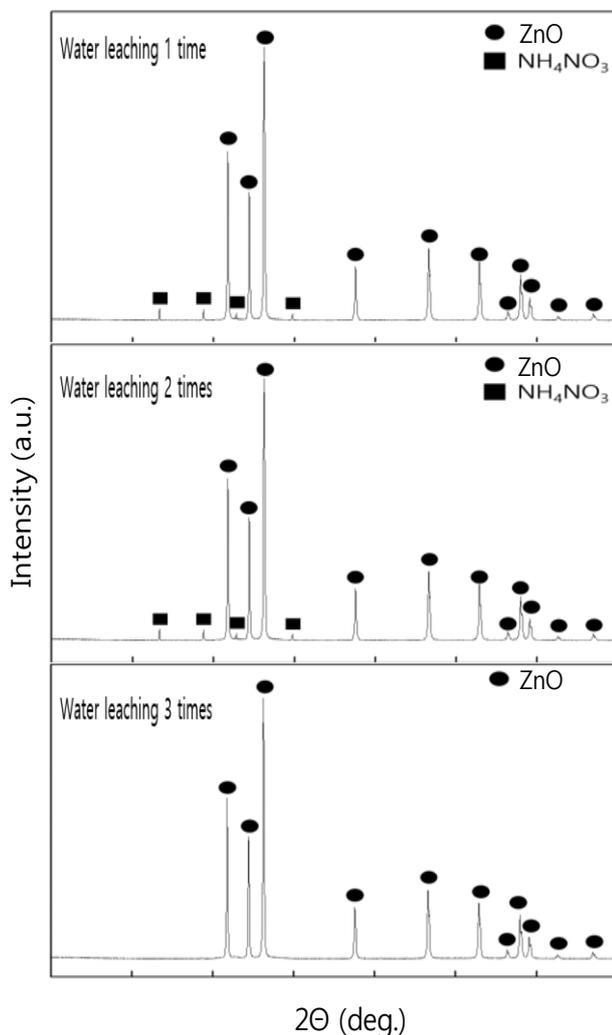


Fig. 5. XRD pattern of the number of water leaching

The final recovered ZnO powder was analyzed through XRF and TEM for ZnO purity and particle size, and the results are displayed in Table 4 and Fig. 6. Based on XRF and TEM results,

ZnO with over 99.9% purity and average particle size of 150nm or below was recovered.

Table 4. Analysis of recovered zinc oxide examined by XRF.

unit: wt.%

| Element | Content |
|---------|---------|
| ZnO | 99.92 |
| NiO | 0.08 |
| Totals | 100 |

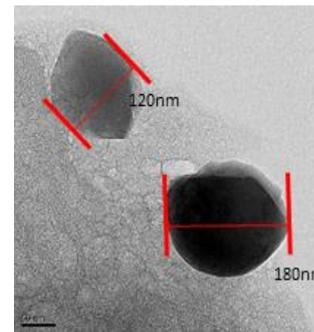


Fig. 6. TEM analysis of recovered Zinc oxide

5. CONCLUSIONS

This study is on the recovery of high purity nano ZnO powder from zinc dross through dry/wet fusion process, and aimed to obtain optimum conditions for vapor deposition, acid leaching and neutralization, and water leaching. Results of experiments are summarized as follows.

1. Optimum condition of zinc recovery through vapor deposition obtained is iron dross-coke mix proportion of 7:3, reaction temperature of 1100°C, and reaction time of 3 hours, and zinc with over 99.3% purity was recovered.
2. Optimum condition of acid leaching for recovered zinc powder was zinc-nitric acid molar ratio of 1:6 and acid leaching time of 1 hour.
3. Optimum condition of neutralization is ZnO-ammonia water volume ratio of 100ml: 40ml and neutralization time of 3 hours.
4. Optimum number of water leaching to remove NH_4NO_3 to after acid leaching and neutralization is 3 times.
5. Final recovered ZnO powder through vapor deposition, acid leaching and neutralization, and water leaching is nano-grade high purity ZnO with over 99.9% purity and average particle size of 150nm or below.

ACKNOWLEDGEMENTS

This work was supported by a Research Grant of Pukyong National University (2019)

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