Hydrometallurgical Process for Zinc Recovery from C.Z.O. Generated by the Steelmaking Industry with Ammonia–Ammonium Chloride Solution

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Abstract: In this research, some experimental steps were investigated to recover zinc contained in crude zinc oxide (C.Z.O.). In the first stage, the C.Z.O. was treated in NH₃–NH₄Cl–H₂O solution to dissolve the metals. The optimized leaching conditions in batch experiments were obtained: agitation speed 250 rpm, concentration of ammonia and ammonium chloride 2.5 mol/L and 5 mol/L, respectively, time 30 min, temperature 40 °C, and L/S = 6 mL/g. The extraction percentage of zinc was over 81% under the optimized leaching conditions. The kinetic study indicates that zinc extraction from the C.Z.O particles was very rapid. In the second stage, the solution from the leaching process was purified by adding zinc dust to the solution. The Cu, Cd, Pb, Sb, and As could be reduced to levels of 0.03, 0.09, 0.87, 0.22, and 0.12 mg/L after the purification process. Finally, the electrowinning process was used to recover dissolved Zn from the final solution. The zinc content in the electrowon zinc was more than 99.99%.

Keywords: crude zinc oxide; steel dust; ammonia-ammonium chloride; zinc; secondary resource

1. Introduction

In 2013, more than 1.6 billion tons of crude steel was produced all over the world [1]. Approximately 0.08–0.12 tons of dust containing iron, zinc, cadmium, lead, fluoride, and chloride is generated per 1 ton of steel produced. Cadmium, lead, fluoride, and chloride are hazardous species [2]. A significant and ongoing mass of dust bearing zinc and other hazardous species is therefore produced in the steelmaking industry. The zinc-bearing dust main originates from electric arc, blast, and converter furnaces. Only 45–50% of the electric arc furnace dust is recycled, while the rest is sent to landfills. A large number of hydrometallurgical processing studies of these dusts have been undertaken by researchers. Because of the deportment of zinc to lowly soluble franklinite, the zinc extractions of the approaches based on leaching were low [3–5]. The Waelz process is widely used to dispose of furnace dusts when the zinc content is higher than approximately 15–20%. In the 21st century, the Waelz process is used more widely than ever before. In this process, zinc-bearing dust is reductively heated in a rotary kiln to approximately 1200 °C [6–8]. Zinc, lead, chloride, and fluoride are volatilized and collected as fine particles in the dust collection system. ZnO is the main zinc-containing phase formed by the Waelz process. It represents one source of crude zinc oxide (C.Z.O.). C.Z.O. ash materials from the Waelz process usually contain alkali metals, chlorides, and fluorides [9]. Sulfuric acid leaching-electrowinning and the imperial smelting process are often used to treat the crude zinc oxide [10]. Sulfuric acid leaching cannot selective extract zinc into a solution as iron dissolves readily in acid, so iron removal can subsequently be difficult [11]. Furthermore, the
presence of chlorides during zinc sulphate E.W. can lead to anodic chlorine evolution, which can cause worker health problems, increase the corrosion rate of the anode, and reduce the quality of cathode zinc [12]. In addition, the stripping of cathode zinc is heavily compromised even when the concentration of fluorides is several hundreds of ppb [13].

Ammonia, together with various ammonium salt solutions, are used to leach zinc oxide ores and zinc secondary sources [14–17]. The zinc(II) ion forms strong ammonia complexes in lixivium, while other metals, such as iron, remain in the residue. R. X. Wang et al. investigated the NH₃–NH₄Cl–H₂O system for the production of electrolytic zinc [18]. S. H. Yang et al. calculated the thermodynamic data in the system of Zn–NH₃–NH₄Cl–H₂O and plotted the solubility of ZnO in the system [19,20].

Although there are many studies on the leaching of zinc from steel plant dust, studies on the entire process, including leaching, purification, and electrowinning, are relatively few in number. The flow sheet for extracting zinc from steel plant zinc-bearing dust is presented in Figure 1 [20]. The aim of this paper is to present the characterization of a C.Z.O. material, the leaching of this C.Z.O. by NH₃–NH₄Cl–H₂O solution, followed by solution purification and electrowinning.

![Flow sheet](image)

**Figure 1.** The principal flow sheet for extraction and recovery of high-purity zinc from steel plant zinc-bearing dust.

### 2. Experimental

#### 2.1. Material

The chemical composition of C.Z.O. used for experiments is given in Table 1. The XRD pattern and scanning electron microscopy–energy dispersive spectroscopy (SEM–EDS) analysis of C.Z.O. are presented in Figure 2, pattern (d) and Figure 3, pattern (a), respectively. The material was a fine powder that was used without further treatment. The other chemicals used in the experiments were analytical reagent grade. All solutions were prepared using deionized water. After leaching, the residue was separated by vacuum filtration, washed with dilute ammoniacal solution, and dried at 60 °C.

#### 2.2. Experimental Setup and Procedure

Batch leaching, kinetic leaching, and purification were conducted using a magnetic stirring apparatus and a stirring speed of 250 rpm. The setup was placed in a thermostatic water bath, and the reaction temperature was maintained constantly within a temperature range of ±0.5 °C. Batch
leaching tests were performed in a 1 L beaker. Here, 500 mL of ammonia–ammonium chloride solution was heated to the specified temperature; then, C.Z.O. was added. The factors studied were the concentration of ammonia, concentration of ammonium chloride, liquid-to-solid ratio (L/S), and temperature. Kinetic leaching tests were performed in a 2 L beaker. Samples of approximately 5 mL were taken from the solution at times of 1, 3, 8, 18, 28, 38, 48, and 58 min. Each sample was filtered quickly.

Purification tests were performed in a 1 L beaker. Here 500 mL of lixivium was heated to the specified temperature; then, zinc powder was added. DC constant voltage power supply (It6720, ITECH, Nanjing, China) was used in the electrowinning tests. Electrowinning tests were performed in a 3 L custom-made rectangular (16 cm × 12 cm × 16 cm) container to minimize ammonia volatilization. Here, 2500 mL of purified solution (Zn–NH₃–NH₄Cl–H₂O) was heated to the specified temperature; then, electrowinning commenced. The cathode and anode plate was a titanium and graphite plate, respectively.

2.3. Analyses and Detection

The concentration of zinc in solution was determined by EDTA titration. The concentration of copper, cadmium, lead, and antimony in solution was determined with a TAS-990 flame atomic absorption spectrophotometer (Beijing Persee General instrument Co, Ltd., Beijing, China). The concentration of arsenic in solution and impurities content in the cathode zinc were determined by a SPECTRO BLUE SOP (ICP-OES) instrument (Thermo Electron Corporation, Waltham, MA, USA). The chemical phase analyses results were provided by Changsha Research Institute of Mining and Metallurgy based upon a selective leaching method metallurgy. XRD measurements of the residue and C.Z.O. were carried out using a RIGAKU-TTRIII instrument (Rigaku corporation, Tokyo, Japan) with a Cu/ka X-ray source at 40 kV and 250 mA. The surface morphology of the residue and C.Z.O. was examined using a JEOI JSM-6360LV instrument (EDAX Inc., New York, NY, USA) operating at 20 kV. The elemental composition of the residue and C.Z.O. was examined using a Genesis 60S energy dispersive spectroscopy system (EDS) (EDAX Inc., New York, NY, USA).

3. Results and Discussion

3.1. Characterizations of C.Z.O.

The chemical analyses of the samples are shown in Table 1. The sample contains an average of 50.25% zinc, 18.9% oxygen, 9.3% chlorine, 0.18% fluorine, 1.32% lead, 3.71% cadmium, and 6.18% iron. The content of chlorine in the sample was very high. Chlorine would need to be removed as it is a harmful impurity in zinc sulfate E.W., but it was not a problem in an ammonia–ammonium chloride process.

| Zn  | F   | Mg  | Al  | Si  | P   | S   | Cl  | K   | Ca  | Ti |
|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|----|
| 50.25 | 0.18 | 0.04 | 0.11 | 2.31 | 0.03 | 0.33 | 9.26 | 0.90 | 0.43 | 0.07 |
| Pb  | Sn  | Cd  | Br  | O   | Cu  | Ni  | Fe  | Mn  | Cr  |    |
| 1.32 | 0.07 | 3.71 | 0.14 | 18.9 | 0.05 | 0.02 | 6.18 | 0.37 | 0.04 |    |

3.2. XRD Analyses

The X-ray diffraction (XRD) pattern of the C.Z.O. is presented in Figure 2d. This revealed that the zinc-containing phases in C.Z.O. were simonkolleite (Zn₅(OH)₈Cl₂·H₂O), zincite (ZnO), and franklinite (ZnFe₂O₄). After being leached in different conditions (Figure 2a–c), the zinc-containing phases in the leach residue were franklinite (ZnFe₂O₄), willemite (Zn₂SiO₄), and some residual zincite (ZnO). Almost all of the zinc present in ZnO and that in Zn₅(OH)₈Cl₂·H₂O was dissolved.
3.3. Mineralogical Composition Analyses

The data obtained from zinc-containing mineral phase analyses are presented in Table 2. The raw material and residue weight is 10 g and 5 g, respectively. The mineral phases containing zinc in the C.Z.O. consist of those with water-soluble zinc 5.6%, zinc oxide 39%, franklinite 4.5%, and zinc sulfide 0.12%. From the XRD analyses (Figure 2), it was shown that zinc can be readily extracted from $\text{Zn}_5(\text{OH})_8\text{Cl}_2\cdot\text{H}_2\text{O}$. The extraction percentage of zinc from the zinc oxide was 84% as a small portion of ZnO was unleached. It was difficult to extract zinc from franklinite and zinc sulfide in the ammonia–ammonium chloride process.

| Phase                | Water-Soluble Zinc | Zinc Oxide | Franklinite | Zinc Sulfide | T Zinc |
|----------------------|--------------------|------------|-------------|--------------|--------|
| Before leached       | 5.6                | 39         | 4.5         | 0.12         | 49.22  |
| After being leached  | 0.11               | 12.85      | 7           | 0.23         | 20.19  |

| Extraction percentage | 99 | 84 | 22 | 4 | 80 |

- Before leached,
- After being leached twice,
- Concentration of ammonia and ammonium chloride 2.5 mol/L and 5 mol/L respectively, L/S 50 mL/g, reaction time 58 min and leaching temperature 40 °C.
- Includes ZnSO$_4$ and ZnCl$_2$.
- Includes Zn$_5$(OH)$_8$Cl$_2$H$_2$O and ZnO.
- Includes ZnFeO$_4$ and ZnSiO$_4$.

3.4. SEM Analyses

SEM with EDS analysis was used to analyze the particle morphology and surface composition of the C.Z.O. and leach residue. The results are presented in Figure 3. The SEM analyses showed that the spherical structure of the C.Z.O. was destroyed both at the surface and inside the particles. It was assumed that the leaching reaction took place via three steps: ammonia and chloride adsorption to the surface and inside, reaction on the surface and inside the particle, and desorption of the soluble zinc species. The concentration of zinc in the residue from EDS analyses was high, which is consistent with the interaction of the X-rays with unleached ZnO. The surface of the residue...
particles contained a large amount of iron and silicon. Combined with XRD analysis, the main phases were zinc ferrite and zinc silicate. There may also have been small amounts of amorphous silicon oxide. Zinc oxide was mixed with these minerals or was wrapped.

![Figure 3](imagelink)

**Figure 3.** Results of the scanning electron microscopy–energy dispersive spectroscopy (SEM–EDS) analyses of the C.Z.O. and leach residue: (a1, a2) SEM–EDS analyses of C.Z.O. (b1, b2) SEM–EDS analyses of leach residue under the following conditions: concentrations of ammonia and ammonium chloride 2.5 mol/L and 5 mol/L, respectively, L/S = 50 mL/g, temperature 40 °C, time 58 min.

### 3.5. Kinetics

The kinetics experiment of zinc leaching from C.Z.O. is presented in Figures 4 and 5. The initial total concentration of ammonia (ammonia/ammonium chloride = 1/2) and solution temperature varied between 3–7.5 mol/L and 30–60 °C, respectively. The main chemical reactions during the leaching process are expressed in Equations (1)–(4) as follows:

\[
\text{Zn}(\text{OH})_6\text{Cl}_2\cdot\text{H}_2\text{O} + 5n\text{NH}_4^+ = 5\text{Zn}(\text{NH}_3)_n^{2+} + 2\text{Cl}^- + (5n - 8)\text{H}^+ + 9\text{H}_2\text{O}(n = 1-4) \tag{1}
\]

\[
\text{Zn}(\text{OH})_6\text{Cl}_2\cdot\text{H}_2\text{O} + (5m - 2)\text{Cl}^- = 5\text{ZnCl}_{m-2}^{2-} + 8\text{OH}^- + \text{H}_2\text{O}(m = 1-4) \tag{2}
\]

\[
\text{ZnO} + p\text{NH}_4^+ = \text{Zn}(\text{NH}_3)_p^{2+} + (p-2)\text{H}^+ + \text{H}_2\text{O}(p = 1-4) \tag{3}
\]

\[
\text{ZnO} + q\text{Cl}^- + 2\text{H}^+ = \text{ZnCl}_{q-2}^{2-} + \text{H}_2\text{O}(q = 1-4) \tag{4}
\]

It is clear that the leaching of zinc from the C.Z.O. particles was very rapid. The time required to obtain 73% extraction of zinc was less than 1 min. Reasons for the rapid leaching rate were the small
particle diameter (<10 µm) and clear access of the lixiviant to the reacting surfaces, both external and internal to the particle (SEM). Combining the mineralogical composition and XRD analyses, it was clear that the dissolution of Zn$_5$(OH)$_8$Cl$_2$·H$_2$O and ZnO were both very rapid. The extraction percentage of zinc subsequently increased slowly at times longer than 1 min. Zinc oxide was mixed with these minerals or was wrapped to make that mass transfer greatly hindered. Zinc oxide in residue was difficult to be dissolved due to kinetics reasons. Figure 4 displays the effect of temperature on zinc extraction kinetics. The mass of the solid, the volume of solution, and the total ammonia concentration were kept constant at 20 g, 1000 mL, and 7.5 mol/L, respectively. Increasing the temperature from 30 to 60 °C had a greater effect on the extraction percentage of zinc. The extraction percentage of zinc increased from 80.1% to 88.5% as ZnO dissolution increased. The rate of zinc extraction also increased with the temperature increasing from 30 to 60 °C.

![Figure 4](image.png)

**Figure 4.** Effect of temperature (mass of solid 20 g, volume of solution 1000 mL, concentration of ammonia and ammonium chloride 2.5 mol/L and 5 mol/L, respectively).

The effect of the total concentration of ammonia is presented in Figure 5. Increasing the concentration of total ammonia from 3 to 7.5 mol/L had a small effect on the extraction of zinc. The extraction increased from 78.6% to 81.6% when the concentration of total ammonia increased from 3 to 7.5 mol/L. This was because all of the concentrations of total ammonia were at a sufficiently high level given that the L/S ratio in the kinetics experiments was much higher than for batch experiments. The initial rate of zinc extraction also increased when the total concentration of ammonia increased from 3 to 7.5 mol/L.

![Figure 5](image.png)

**Figure 5.** Effect of total ammonia concentration (ammonia/ammonium chloride = 1/2). Mass of solid 20 g, volume of solution 1000 mL, temperature 40 °C.
3.6. Batch Experiment

The results of batch leaching of zinc from C.Z.O. are presented in Figures 6–9. The initial total concentration of ammonia, L/S, and solution temperature varied from 3–7.5 mol/L, 4–8 mL/g, and 30–60 °C, respectively.

**Figure 6.** Effect of L/S (time 30 min, concentrations of ammonia and ammonium chloride, 2.5 mol/L and 5 mol/L respectively, temperature 40 °C).

**Figure 7.** Effect of total ammonia concentration (ammonia/ammonium chloride = 1/2). Time 30 min, L/S 6 mL/g, temperature 40 °C.

**Figure 8.** Effect of temperature (Time 30 min, L/S 6 mL/g, concentrations of ammonia and ammonium chloride, 2.5 mol/L and 5 mol/L respectively).
Figure 9. Effect of time (Concentrations of ammonia and ammonium chloride, 2.5 mol/L and 5 mol/L, respectively, L/S 6 mL/g, temperature 40 °C).

The effect of L/S is presented in Figure 6. Increasing L/S from 4 to 5 had a noticeable effect on the extraction of zinc. However, when the L/S was greater than or equal to 5, the effect was diminished. The extraction of zinc increased from 79.9% to 81.5% when L/S increased from 5 to 7 mL/g, but the concentration of zinc in solution decreased from 80.4 to 52.4 g/L.

The effect of total concentration of ammonia is presented in Figure 7. Total concentration of ammonia had a noticeable effect on the extraction of zinc. The maximum extraction of zinc, ~80%, was reached in the solution with 7.5 mol/L total ammonia. When the concentration of ammonium chloride was more than 5 mol/L, ammonium chloride crystals were readily formed.

The effect of solution temperature is presented in Figure 8. The extraction of zinc increased from 76.8% to 82.9% when temperature increased from 30 to 60 °C. When the temperature reached 50 °C, ammonia volatilized from the solution, producing a very strong, pungent odor in the laboratory. Therefore, the temperature of experiments had to be lower than 50 °C.

The effect of leaching time is presented in Figure 9. The results show that leaching zinc into the solution was a very fast process. The dissolution of zinc at 40 °C reached equilibrium within the first 30 min.

3.7. Purification of Lixivium

Prior to this work, significant work on purification and electrowinning had been done by our team [20].

The optimum condition determined in batch experiments for zinc extraction from C.Z.O. was determined to be: L/S = 6, stirred at 250 rpm for 30 min, 7.5 mol/L total concentration of ammonia, and 40 °C. The zinc and main impurity content in lixivium in the optimum condition is presented in Table 3.

Table 3. Zinc and main impurity content in lixivium (mg/L).

| Zn  | Cu | Cd | Pb  | Sb | As |
|-----|----|----|-----|----|----|
| 69.2| 34.3|53.7|637  |5.6 |0.17|

3.7.1. Removal of Sb and As

Hydrogen peroxide addition was used to enable the removal of Sb and As. An addition of 2 mL/L of H₂O₂(30%) to the leaching process occurred after 15 min. Ferrous iron, Sb, and As in the solution were oxidized to enable co-precipitation of ferric iron with the oxidized Sb and As species.
The experimental results indicate that the contents of Sb and As in the lixivium were reduced to 0.22 mg/L and 0.12 mg/L or less, respectively.

### 3.7.2. Removal of Cu, Cd, and Pb

Cementation of Cu, Cd, and Pb using a two-stage countercurrent cementation process using zinc powder was carried out. The total dosage of zinc powder in this two-stage countercurrent cementation process was 1.6 g/L. Cu, Cd, and Pb were easily removed under the conditions of 40 °C and stirred at 250 rpm for 30 min for both cementation stages. The content of the lixivium after removal of Sb, As, Cu, Cd, and Pb is presented in Table 4.

| Zn (g/L) | Cu  | Cd  | Pb   | Sb   | As   |
|----------|-----|-----|------|------|------|
| 69.4     | 0.03| 0.09| 0.82 | 0.22 | 0.12 |
| 69.2     | 0.02| 0.08| 0.87 | 0.21 | 0.12 |
| 69.6     | 0.03| 0.04| 0.76 | 0.19 | 0.1  |

### 3.8. Electrowinning

The lixivium after purification was used for electrowinning. The condition for electrowinning was as follows: zinc concentration more than 30 g/L, electrode space 3.5 cm, current density 400 A/m², and temperature 40 °C. The zinc and main impurity content in the cathode zinc is shown in Table 5. The zinc content in the electrowon zinc was more than 99.99%, and the contents of impurities, such as Cu, Cd, Fe, Sb, and As, were all lower than 0.0007%, while lead was lower than 0.008%. The electrowon zinc product is shown in Figure 10.

| Zn (%) | Cu | Cd | Pb  | Sb  | As | Fe |
|--------|----|----|-----|-----|----|----|
| 99.9930| 0.1|    | 6.0 | 0.5 | -  | 0.5|
| 99.9907| 0.2| -  | 8.0 | 0.4 | -  | 0.7|
| 99.9916| 0.4| -  | 7.0 | 0.6 | -  | 0.4|

▲: below detection limits.

**Table 4.** Zinc and main impurity content in the lixivium after purification (mg/L).

**Table 5.** Zinc (%) and main impurity contents (×10³ %) in cathode zinc.

**Figure 10.** Electrowon zinc product.
4. Conclusions

The chemical and mineralogical properties of C.Z.O. indicate that it was composed of approximately 50.25% zinc, in which 78% of the total zinc was ZnO and Zn(OH)Cl·H2O. SEM, EDS, XRD, and mineralogical composition analyses results showed that the leaching reaction takes in three steps: adsorption to the surface and inside, reaction on the surface and inside of the particle, and desorption. Zinc existing in ZnO and Zn(OH)Cl·H2O was easily extracted with the NH3·NH4Cl·H2O system, and dissolution speed was very rapid. The percentage extraction of zinc was over 81% in batch experiments. The Sb and As could be reduced to 0.22 mg/L and 0.12 mg/L by NH4 and Cl in three steps: adsorption to the surface and inside, reaction on the surface and inside of the particle, and desorption. Zinc existing in ZnO and Zn(OH)Cl·H2O was easily extracted with the NH3·NH4Cl·H2O system, and dissolution speed was very rapid. The percentage extraction of zinc was over 81% in batch experiments. The Sb and As could be reduced to 0.22 mg/L and 0.12 mg/L by addition of H2O in the leaching process. The Cu, Cd, and Pb could be removed effectively by a two-stage countercurrent cementation process using zinc powder. The zinc content in the electrowinning zinc was more than 99.99%.

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