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ANALYSIS OF PROCESSING METHODS FOR ZINC-CONTAINING INDUSTRIAL WASTES: A COMPREHENSIVE REVIEW

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Abstract Zinc (Zn) is the fourth most produced metal globally, yet its extraction and recycling generate significant volumes of hazardous technogenic waste[1,2]. This article provides a comprehensive analysis of methods for recovering zinc from various industrial residues, including electric arc furnace dust (EAFD), Ni-Cd cakes, basic oxygen steelmaking (BOS) filter cakes, and zinc ferrites. Drawing on experimental data from the sources, we evaluate pyrometallurgical techniques such as carbothermic reduction in iron baths and reduction roasting, alongside hydrometallurgical flowsheet involving selective leaching and solvent extraction. Key findings indicate that while iron-bath processes achieve recovery rates exceeding 99.9%, hydrometallurgical routes offer superior selectivity for high-purity metal recovery[3]. The role of zinc ferrite ($ZnFe_2O_4$) as a primary barrier to recovery and mechanical insights into its decomposition are discussed.

Keywords: zinc, cobalt, manganese, reductive leaching, residue, citric acid, high iron bearing zinc calcine, zinc ferrite, reduction roasting, soluble zinc, magnetic susceptibility

Introduction

Zinc is vital for steel galvanization and alloy production, with an annual output of approximately 13 million tons[2,4]. However, the global recycling rate remains low at 33%, leading to the accumulation of hazardous wastes. These waste residues contain toxic but valuable heavy metals. Due to the potential release of toxic heavy metals into the surface and ground water, these waste residues are classified into a hazardous category. Therefore, such wastes are securely stored inside the industrial premises, encroaching valuable land mass[2]. For instance, electric arc furnace (EAF) steel production generates 10 to 25 kg of dust (EAFD) per ton of steel, containing up to 43% Zn. Other significant wastes include filter cakes from purification stages (Co and Ni-Cd cakes) and BOS filter cakes.

The complexity of these materials lies in their mineralogy. Zinc is often bound in the stable spinel structure of zinc ferrite **(**$ZnFe_2O_4$**)**, which is insoluble in standard dilute acids. Environmental regulations classify these wastes as hazardous (e.g., US EPA K061) due to the presence of heavy metals like Pb, Cd, and Ni, necessitating advanced recycling technologies to prevent environmental contamination and recover value.

2. Materials and Methods

The analysis covers several distinct methodologies identified in the sources:

- **Carbothermic Iron-Bath Reduction:** Experimental studies used a carbon-saturated iron melt as a reducing agent for molten ZnO-containing slag at temperatures between 1400 °C and 1500 °C.

1. Preheating of the graphite crucible to the desired temperature (1420 C to 1530 C)
2. Feeding of the iron master alloy and the synthetic slag mixture
3. Melting and temperature homogenization
4. Feeding of the pure ZnO (> 99 pct)
5. Slag sampling in defined time intervals
6. Temperature reference measurements to calibrate the pyrometer (a minimum of three) 7. Chemical analysis of slag samples.

The graphite crucible was covered by a perforated cover (hole diameter 60 mm) to prevent excessive heat losses and achieve a homogenous temperature distribu-tion across the melt. At the bottom of the furnace a pyrometer continually recorded the crucible surface temperature. A custom-made furnace controller (PID algorithm) regulated the furnace power to ensure a constant crucible temperature and therefore isothermal conditions within the crucible. Additionally, three to four temperature measurements per experiment were recorded with commercially available type-S immersion thermocouples (Minkon GmbH, Erkrath, Germany), these measurements were used in the kinetic model. After cooling to room temperature, the slag samples were ground in a vibration mill, fixed to adhesive tape and analyzed using energy-dispersive X-ray spec-troscopy within a scanning electron microscope. The chemical analyses were recalculated and normalized to account for the corresponding oxidic forms (Ca to CaO, Si to SiO2, Al to Al2O3, Zn to ZnO and Fe to FeO) of the measured elements. The reduction of ZnO from the slag and the Fe oxidation into the slag influence the total slag mass and consequently the chemical analysis. To account for these changes in the kinetic model, effective FeO and ZnO concentrations (Figure 2) are calculated in Eqs. [8] and [9]. The measured FeO and ZnO concentrations are multiplied with the ratio of slag building compounds at the start (t = 0) and each sampling time (t). The effective FeO and ZnO concentrations are subsequently denoted as [ZnO] and [FeO].

- **Reduction Roasting:** High-iron bearing zinc calcine was treated with a gas mixture of CO and $CO2$ to selectively decompose ferrites at 750 °C. In this study, the reduction roasting–leaching–mag-netic separation process was proposed for recovering zinc and iron from high iron bearing zinc calcine. The key of the process lies in the control of the reduction roasting conditions causing the selectively decomposi-tion of zinc ferrite into zinc oxide and magnetite with weak reducing agent. After the roasting pretreatment, zinc leaching rate can be increased significantly by the conventional low acid leaching process and the magne-tite enriched in leaching residues will be able to be recovered effectively through magnetic separation pro-cess[3]. The main reactions occurring in the roasting process are as follows

$3ZnFe_2O_4+CO(g)=3ZnO+{}_2Fe_3O4+CO_2(g)$ (1)

$ZnFe_2O_4+CO(g)=ZnO+{}_2FeO+CO_2(g)$ (2)

- **Hydrometallurgical Processing:** Ni-Cd cake was treated using a mixture of HCl and $H2SO4$ with $H2O2$ to selectively leach Zn and Ni while precipitating Fe and Ca. A complete process has been developed to recover high purity solutions of zinc and nickel from Ni-Cd cake waste residue generated in a zinc processing plant in Iran. The process flowsheet is given in Figure

10. The main advantage of the process is that leaching of metals has been carried out using lixiviant containing minimum but maximum utilization of acid. The process has been designed such that iron was removed in-situ during leaching. Zinc and nickel from the leach solution were recovered by solvent extraction after removing cadmium through the cementation process. For solvent extraction, a mixture of HDEHP and TEHA was used as extractant. During solvent extraction process, TEHA did not directly participate but helped in the extraction of zinc by scavenging the H+ ion released by HDEHP. Therefore, it was not required to add NaOH solution for maintaining the equilibrium pH. However, for solvent extraction of nickel, a little amount of sodium hydroxide was required to be added as nickel extracts at high equilibrium pH (4.8). In the above process, more than 95% of zinc and nickel were recovered with more than 99% purity. The high pure solutions of zinc and nickel could be used for the preparation of value added products like metal powders and salts for targeted applications. The effluent generated could be disposed of after the removal of impurity metals by neutralization[7].

- **Sintering and Tableting:** BOS filter cakes were tableted with coke breeze (3–9 wt%) to create a localized reducing atmosphere within a sinter bed. Zinc removal by sintering of a filter cake generated in basic oxygen steelmaking was examined in tablet testing and millipot sintering under simulated commercial sinter plant conditions. According to the out-comes of this investigation, it is feasible to recycle zinc bearing dusts by sintering. The major findings are summarized below:

Coke and metallic iron in filter cake play the role of reductant in zinc removal during sintering. Zinc removal from the filter cake tablets increased with an increase in temperature and decrease in oxygen partial pressure. In a nitrogen atmosphere at 1300 °C, zinc removal from a tablet reached 24.6%. Addition of coke breeze into the filter cake tablets in the range of 3 to 9 wt% increased zinc removal from 60.6% to 91.4% at 1300 °C in an atmosphere of 0.5 vol% oxygen. In millipot sintering, when loading a filter cake blend with a coke rate of 7.43 wt%, zinc removal was very low (~21%). Increasing the coke rate to 9.43 wt% enhanced local zinc removal to 69.6%, and zinc was moved downward farther in the sintering bed.

When the filter cake was loaded into the millipot in the form of tablets, addition of coke in the tablets improved zinc removal. Zinc removal from the tablets reached 66.7% with a coke rate of 11 wt% in the filter cake.

The proposed mechanism of zinc removal from filter cake during sintering is as follows. Reductants such as carbon and CO reduce ZnO and $ZnFe_2O_4$ to zinc vapour during the sintering process. Some of the zinc vapour which diffuses out from the filter cake particle is convected away, while the remaining vapour is either re-oxidized (to ZnO and $ZnFe_2O_4$) and deposited on the surface of solid materials or dissolved into molten phase or liquefied to zinc on the particle surface at low temperature and then re-oxidized to ZnO.

Zinc removal from the filter cake in millipot sintering was affected by the deposition of zinc oxide on the materials close to the wall with lower temperature. However, this negative effect (wall effect) would be negligible in a commercial sinter plant. It is suggested that filter cake be loaded at the bottom of a commercial sinter bed so as to minimize the deposition of zinc within the bed and maximize the removal of zinc[6].

- **Solid-State Interaction:** Pure and industrial zinc ferrites were mixed with CaO or MgO (ratios 1:1 and 1:2) and heated up to 1200 °C to facilitate zinc displacement. 1. It was established that CaO and MgO substitute ZnO from synthetic ZnFe2O4 and zinc ferrite included in zinc cake – residue from zinc hydrometallurgy.

2. The amount of the obtained free ZnO increases with the increasing of temperature, duration and amount of used CaO and MgO. The most favorable results were obtained with a ratio of ZnFe2O4 - CaO = 1:2, t = 1200 °C and duration of 60 min, where the maximum amount of extracted free ZnO is 74.1%. Under the same conditions and ratio using MgO the obtained free ZnO is 49.7%.

3. On the basis of XRD analysis and Mössbauer spectroscopy it can be concluded that both CaFe2O4 and Ca2Fe2O5 form as a result of the solid state interactions in the ZnFe2O4-CaO system.

4. Mixed zinc-magnesium ferrites are obtained in the exchange reaction between MgO and ZnFe2O4 which is confirmed by Mössbauer spectroscopy.

5. The results obtained give grounds to argue that the use of CaO and MgO (or intermediate products containing them) in the Waeltz-process can lead to a more complete and more rapid reduction of zinc ferrite with a corresponding improvement of technical and economic parameters of the process[4].

- **Column Leaching:** Used to evaluate the transport of heavy metals (Ni, Co, Cd) from purification residues under varying pH (5–7) and flow conditions. For studying of filter cake properties, three parameters of acid flow rate, input pH and time were studied using column leaching tests. Statistical analysis was achieved with the SPSS 14 software for Ni dissolution as:

R=0.081pH+0.077Q-0.641t For the Ni dissolution, time was found the effective parameter for the transport to the environment. For Co dissolution the sta-tistical analysis show:

R=-0.028pH-0.024 Q+0.863 t For Co dissolution, time and input pH was found respectively, the effective parame-ters for the transport to the environment. Statistical analysis was resulted for Cd disso-lution as:

R=-0.102pH-0.092Q+0.632t For Cd dissolution, time and input pH was found respectively, the effective parame-ters for the transport to environment[5].

3. Results

The comparative performance of these methods is summarized in the table below.

Table 1. Comparative Analysis of Zinc Recovery Methods from Technogenic Wastes

Processed Product	Recovery Method	Technical Highlighting	Zinc Recovery Rate
EAF Dust (EAFD)	Carbothermic (Iron Bath)	Combined metallothermic (Fe) and carbothermic (C) reduction	> 99.9%
Ni-Cd Cake Waste	Hydrometallurgy (SX)	HDEHP + TEHA extractant system; no NaOH needed	> 95%
High-Fe Zn Calcine	Reduction Roasting	Selective decomposition into ZnO and magnetic Fe_3O_4	~ 90%
BOS Filter Cake	Sintering (Tablets)	Localized CO atmosphere inside coke-added tablets	60.6% – 91.4%
Zinc Cake (Ferrite)	Solid-State Interaction	CaO displacement of Zn at 1200 °C	~ 74.1%
Co Filter Cake	Column Leaching	pH and time-dependent solubility studies	Varies by metal

3.1. Pyrometallurgical Kinetics

In the iron-bath process, the mass transfer coefficient (MTC) of ZnO reduction increased fourfold from 1400 °C to 1500 °C. A critical insight is that liquid iron itself acts as a reductant, contributing 25% to 50% of the overall reaction mechanism. For BOS filter cakes, the addition of coke is vital; without it, zinc removal is only ~24.6%. In reduction roasting, the optimal atmosphere was found to be 8% CO and 45% CO_2, which prevents the over-reduction of iron to metallic Fe, keeping it in the magnetic Fe_3O_4 phase for later separation.

3.2. Hydrometallurgical and Leaching Outcomes

Leaching Ni-Cd cake with a HCl/H_2SO_4 mixture achieved 96.7% Zn, 98% Cd, and 98% Ni recovery. The solvent extraction (SX) stage utilized TEHA as a proton scavenger, which maintained the equilibrium pH at 2.0 without the need for external alkali addition. The column leaching tests on Co filter cakes demonstrated that Ni, Co, and Cd mobility is highly sensitive to the pH of the input solution (simulating acid rain) and time, with nickel showing significant dissolution over 30 days.

4. Discussion

The sources highlight that the success of any method depends on its ability to overcome the stability of the zinc ferrite phase.

4.1. The Ferrite Decomposition Mechanism Research on solid-state interactions shows that CaO is more effective than MgO in displacing zinc from ferrites. The addition of CaO leads to the formation of calcium ferrites ($CaFe_2O_4$ and $Ca_2Fe_2O_5$), releasing ZnO for subsequent acid leaching. In pyrometallurgical roasting, the selective conversion of $ZnFe_2O_4$ to Fe_3O_4 allows for the recovery of iron as a magnetic concentrate (53.2% Fe) while zinc is leached at rates of ~90%.

4.2. Industrial Application and Environmental Considerations

- **Pyrometallurgy:** The iron-bath process is superior for total zinc recovery (>99.9%) and producing marketable slag, but it is energy-intensive. Sintering BOS cakes in tablets at the bottom of the sinter bed is recommended to prevent the re-oxidation and recirculation of zinc within the plant.
- **Hydrometallurgy:** This route is ideal for recovering high-purity products (e.g., Ni and Zn sulfates) with lower capital costs. However, the management of impurity transport (as seen in column leaching) is essential for environmental safety in stockpile management.

5. Conclusion

This review of multiple technogenic waste processing methods concludes that:

1. Carbothermic reduction in a metal bath provides the highest zinc recovery efficiency (>99.9%).
2. Selective reduction roasting allows for the dual recovery of zinc and a magnetic iron concentrate.
3. Hydrometallurgical circuits using HDEHP/TEHA systems offer an environmentally friendly alternative for purifying zinc and nickel from complex residues.
4. Breaking the zinc ferrite bond via chemical displacement (CaO) or selective roasting is the key to unlocking the value in these hazardous industrial wastes.

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