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OVERVIEW OF HYDROMETALLURGICAL METHODS FOR PROCESSING ZINC-CONTAINING TECHNOGENIC WASTE

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Abstract

This review examines various hydrometallurgical strategies for recovering valuable metals from zinc-containing industrial wastes, such as basic oxygen steelmaking (BOS) filter cakes, hot filter cakes (HFC), and zinc plant residues. The study analyzes different leaching agents, including organic acids (butyric, citric), inorganic acids (sulfuric, hydrochloric), and complexing agents (thiosulfate, thiourea). Key findings indicate that zinc recovery rates can reach up to 84.6% using selective organic leaching, while associated metals like cobalt, manganese, lead, and silver show recovery efficiencies exceeding 90% under optimized conditions. This paper provides a comparative analysis of recovery rates, selectivity, and methodological advantages to support sustainable metallurgical waste management.

Keywords: BOS filter cakes, hot filter cake (HFC), hydrometallurgy, selective leaching, reductive leaching, zinc recovery, silver recovery, cobalt, manganese, butyric acid, citric acid, thiosulfate, chloride solutions.

Introduction

The global iron and steel industry generates millions of tonnes of dust and residues annually, much of which is categorized as hazardous metallurgical waste due to the presence of heavy metals[1-2]. Basic oxygen furnace steelmaking (BOS) and electric arc furnace (EAF) operations are primary sources of these technogenic wastes. These residues typically contain high concentrations of iron (50–75%) and zinc (0.5–25%), along with significant amounts of cobalt, manganese, lead, and precious metals like silver[1].

Direct recycling of these materials is often hindered by the high zinc content, which causes operational issues in furnaces. Therefore, the selective removal and recovery of zinc and other valuable components are essential for environmental protection and resource conservation[3-5]. Hydrometallurgical methods are preferred over pyrometallurgical routes due to their flexibility, lower energy requirements, and ability to handle low-grade complex materials effectively[7-9].

Methods

The sources describe several hydrometallurgical approaches adapted for specific waste types:

- **Selective Organic Acid Leaching:** Using butyric acid ($CH_3CH_2CH_2COOH$) for BOS filter cakes to achieve high zinc selectivity over iron. Another approach involves citric acid as a reducing agent in sulfuric acid systems for recovering cobalt and manganese. Selective leaching of zinc over iron from three BOS filter cakes by butyric acid was investigated. The effects of acid concentration and L/S stoichiometric ratio were systematically examined. The following conclusions are obtained:

1. Among the three BOS filter cakes, BOS-3 showed the highest removal of zinc by butyric acid, while the best selectivity of zinc over iron was achieved with BOS-2. The BOS-1 filter cake showed the lowest leaching performance of zinc and iron.
2. The optimal leaching conditions for BOS-3 can be selected depending on the priority consideration. Considering both zinc removal and zinc selectivity, 90% L/S stoichiometric ratio and 1.0 M acid concentration for 10 h were chosen as the optimal conditions with 84.6% zinc removal and 20.0% iron loss.
3. BOS-1 probably have the self-sinter behavior resulting from long term stockpile with some exothermic oxidation reactions occurred, and those materials generally have stronger physical properties with harder surface, higher density and strength, and larger grain size which can make the acid leaching very difficult. The zinc leaching from BOS-2 was limited by the franklinite but can reach the maximum by increasing the acid concentration.
4. For the leaching behaviors of zinc and iron from the BOS filter cakes using butyric acid, mineral compositions played a more important role than the leaching parameters[1].

- **Inorganic Acid Leaching:** Standard sulfuric acid (H_2SO_4) systems are used for the primary dissolution of zinc oxide (ZnO), often followed by more aggressive steps to break down zinc ferrites ($ZnFe_2O_4$). It is presumed that zinc leaching from steelmaking dust is related to the fraction of Zn in the form of ZnO because $ZnFe_2O_4$ has a very stable spinel structure that is considerably refractory against leaching [8-11]. However, no specific relationship between the leaching efficiency of zinc and the ZnO fraction has been established. Steer and Griffiths investigated the leaching of zinc from BF slurry with 2.25 wt.% of Zn in the form of ZnO using 1 M prop-2-enoic acid, and 83.1% of zinc was removed [12]. Kelebek et al. found that the fine fraction of BOS sludge contained a greater proportion of $ZnFe_2O_4$ than the coarse fraction, and 81% of zinc removal was achieved for the coarse fraction by leaching with H_2SO_4 while only 29.2% removal was achieved for the fine fraction [13]. It was reported by Vereš et al. that BOS dust contained 9.37 wt.% zinc with 14.5% of the total zinc as $ZnFe_2O_4$ and the remaining portion as ZnO, and the zinc extraction was less than 50% even if the H_2SO_4 concentration was increased to 2.0 M at room temperature [14].

Using H_2SO_4 to leach zinc from BOS sludge with 2.74% of Zn, about 10% of zinc was removed at room temperature and low acid concentration (0.1 and 0.2 M) since only Zn in ZnO was leached out. However, Zn in $ZnFe_2O_4$ was further dissolved at higher temperatures and higher concentrations (1 M), giving increased zinc and iron leaching efficiencies over 50% [15]. So, the characteristics of the steelmaking dusts are closely related to the zinc leaching performance.

Butyric acid ($CH_3CH_2CH_2COOH$), as a 4-carbon short-chain fatty acid, is known to have many applications in the chemical, food, and pharmaceutical industries. It is partially dissociated weak acid, and the stabilization of $CH_3CH_2CH_2COO^-$ could potentially alter the extraction capability as follows.

$$CH_3CH_2CH_2COOH + H_2O = CH_3CH_2CH_2COO^{-} + H_3O^{+} \quad (1)$$

- **Chloride Leaching:** Utilizing calcium chloride ($CaCl_2$) or magnesium chloride ($MgCl_2$) solutions at high temperatures (95 °C) to extract lead and silver from zinc plant residues. The experimental results of leaching Pb–Ag cake in $CaCl_2$ and $MgCl_2$ solu-tions show that the $CaCl_2$ solution enabled a significantly better leaching effici-ency of lead and silver than the $MgCl_2$ solution.

Optimal conditions for lead and silver leaching in $CaCl_2$ solution are: a 3.6 mol dm–3 (400 g dm–3) solution of leaching agent; pH value of leaching 2.0–2.5; temperature of leaching 95 °C; S:L ratio, 1:5 in the reaction mixture and rinsing the solid residue after leaching with hot water. Under these conditions, the efficiency of lead and silver extraction from Pb–Ag cake was approximately 94 %, whereby iron was not extracted but remained in the solid residue[7].

- **Precious Metal Recovery:** Specialized leaching using thiosulfate ($Na_2S_2O_3$) or thiourea ($CS(NH_2)_2$) to recover silver, providing an environmentally friendly alternative to cyanide-based processes. In order to evaluate the potential of the thiourea and thiosulfate leaching for silver recovery from zinc cake, a series of experiments were conducted. The thiourea is more promising of the two leaching agents trialed in terms of recovery efficiency and leaching time. Silver recovery in the thiourea leach system achieved maximum recovery of silver being 94.3%, using 10 g L^{-1} $CS(NH_2)_2$; 4 g L^{-1} Fe^{3+} as $Fe_2(SO_4)_3 \cdot 9H_2O$; 0.5 g L^{-1} $Na_2S_2O_5$; pH = 1; 40% solids, at 30°C in 20 minutes. The leaching rate is initially fast and then decrease with an increase in leaching time. The high initial leaching rate observed with thiourea is probably due to the action of the formamidine disulfide as a result of the oxidation of the thiourea. The formamidine disulfide further decomposes, partially passivating the silver surface by the products of oxidation and precipitation of low-soluble silver salts and the rate of dissolution decreases.

Laboratory scale experiment showed that silver could be extracted almost completely from zinc cake before Waelz processing by means of acid thiourea leaching. This process offered an advantage in hydrometallurgical processing by solving both silver extraction and its recovery problems [2].

Results

The performance of these methods varies significantly based on the mineralogical composition of the waste (Table 1).

Table 1. Comparative Analysis of Hydrometallurgical Processing Methods

Raw Material	Target Element	Lixiviant / Method	Recovery Rate (%)	Focus / Highlight
BOS Filter Cake (BOS-3)	Zn	1.0 M Butyric Acid	84.6%	Selective Zn/Fe leaching
Zinc Plant Residue (HFC)	Zn	0.15 M Sulfuric Acid	81.5%	Selective zinc removal
Zinc Plant Residue (HFC)	Co / Mn	H_2SO_4 + Citric Acid	96.4% (Co) / 90.3% (Mn)	Reductive leaching
Zinc Plant Residue	Ag	Acidic Thiourea	94.3%	Non-cyanide recovery
Pb-Ag Waste Cake	Pb / Ag	3.6 M $CaCl_2$	94.0% (Pb & Ag)	High temp (95°C) chloride leaching
Zinc Cake (KCM Ltd)	Ag	Sodium Thiosulfate	70–74%	Solution regeneration
Zinc Plant Residue	Co	Roasting + H_2SO_4	~94.0%	Multi-stage purification

Silver Recovery Dynamics

Experimental data shows that silver recovery using thiourea is significantly faster and more efficient than thiosulfate. The initial dissolution rate is high, though it may decrease over time due to oxidant consumption and passivation[4].

- **Linear Trend Description (Silver Recovery vs. Time):** (Based on Source) During silver recovery from zinc cakes, recovery rates typically rise sharply in the first 20–60 minutes of leaching. Using thiosulfate, the curve plateaus at approximately 70–74% after 30 minutes. In contrast, thiourea leaching shows a steeper climb, reaching peak recovery (94.3%) within 20 minutes at 30 °C before stabilizing or slightly declining due to reagent decomposition. As a result of thiosulfate leaching of the zinc cake at 25 g/l $Na_2S_2O_{3.5}H_2O$, 15 g/l $(NH_4)_2SO_4$, 20 % pulp density, 30 min process duration and pH=6,a solution with chemical composition as presented in Table 3 is obtained.

Table 2. Chemical composition of zinc cake, %

Cu	Pb	Fe	Zn	Ag, g/t
1.27	4.40	27.69	18.10	158

Table 3. Chemical composition of thiosulfate solutions,g/l

Cu	Pb	Fe	Zn	Ag
0.07	0.64	1.81	4.65	0.026

Table 4. Chemical composition of undissolved residue,%

Cu	Pb	Fe	Zn	Ag, g/t
1.14	4.85	31.95	17.00	30

As demonstrated by the obtained experimental results, about 74% of the silver contained in the zinc cake can be recovered by thiosulfate technology and subsequent precipitation with Na_2S to produce silver concentrate. The proposed process diagram can be successfully applied in the end of the cycle of wet recovery of zinc cakes[4].

Discussion

The efficiency of hydrometallurgical recovery is primarily dictated by the mineralogical form of the metals.

- **The Ferrite Problem:** Zinc often exists as ZnO and $ZnFe_2O_4$ (franklinite). While ZnO is easily soluble in most acids, $ZnFe_2O_4$ has a stable spinel structure that is refractory to standard leaching. Sources indicate that selective leaching with butyric acid effectively removes Zn from ZnO but leaves $ZnFe_2O_4$ in the residue, which explains why recovery rates for some samples (like BOS-2) are limited to ~55%.
- **Selectivity and Reagent Efficiency:** Organic acids like butyric acid provide a "hydrophobic film" effect on iron-containing phases, which minimizes iron dissolution and maximizes the Zn/Fe ratio in the leachate. Reductive leaching using citric acid is vital for metals like cobalt and manganese (found as $Co(OH)_3$ and MnO_2), as it shifts them into soluble divalent states.

- **Waste Aging:** Long-term storage of waste (e.g., BOS-1) leads to "self-sintering," creating a harder surface and larger grains that significantly reduce leachability.

Conclusion

The comprehensive analysis of hydrometallurgical methods for processing various zinc-containing technogenic wastes allows for the following expanded conclusions:

- **Efficiency of Selective Leaching for BOS Wastes:** The study confirms that the age and storage conditions of basic oxygen steelmaking (BOS) filter cakes are critical factors for zinc recovery. Fresh waste (BOS-3) demonstrates the highest susceptibility to organic acid treatment, achieving a zinc recovery rate of 84.6% using 1.0 M butyric acid. However, a significant challenge remains in the form of iron loss (up to 20%), which occurs when aiming for maximum zinc extraction. For aged materials like BOS-2, a higher acid concentration (1.5 M) ensures superior selectivity, limiting iron loss to a negligible 0.47% while still recovering over half of the zinc content.
- **The Impact of Mineralogical Composition:** The presence of zinc ferrite ($ZnFe_2O_4$) significantly limits the efficiency of standard leaching processes. While zinc oxide (ZnO) is easily dissolved, the stable spinel structure of franklinite requires more aggressive conditions or pre-treatment. In long-term stockpiled wastes (BOS-1), self-sintering and exothermic oxidation reactions create a hard surface and larger grain sizes (majority >1 µm), rendering the material almost refractory with zinc recovery falling below 10%.
- **Advanced Recovery of Associated Metals (Co, Mn, Pb, Ag):** For complex zinc plant residues such as hot filter cakes (HFC), a multi-stage approach is most effective. Reductive leaching using a combination of sulfuric and citric acid proves to be highly efficient for recovering cobalt and manganese, reaching efficiencies of 96.4% and 90.3%, respectively. For precious metals like silver, non-cyanide alternatives such as thiourea demonstrate superior kinetics, achieving 94.3% recovery in just 20 minutes, compared to the 70–74% typically seen with thiosulfate systems.
- **Optimal Process Parameters and Industrial Scalability:** The extraction of lead and silver from waste cakes is most successful in high-concentration chloride environments. Using 3.6 M calcium chloride ($CaCl_2$) at 95 °C with a solid-to-liquid ratio of 1:5 allows for a leaching efficiency of approximately 94% for both metals. These results highlight that temperature, reagent concentration, and the specific choice of lixiviant (e.g., preference of $CaCl_2$ over $MgCl_2$) are decisive for the economic viability of the process.
- **Environmental Significance:** The transition to organic acids (butyric, citric) and non-cyanide reagents (thiourea, thiosulfate) represents a shift towards more environmentally benign metallurgical practices. By selectively removing zinc and other heavy metals, these hazardous industrial by-products are transformed into high-quality iron-bearing materials suitable for recycling back into the steelmaking process, thereby supporting the principles of a circular economy.

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