HSR (LONDON),
HOUGHTON STREET REVIEW JOURNAL
ISSN: 2058-5519|Impact factor-15.9
http://houghtonstreetreview.com/index.php/hsr

Development of a Resource-Efficient Technology for Producing Zinc Electrolyte from Metallurgical Industrial Waste

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doi:https://doi.org/10.5281/zenodo.24354522

Abstract. The article investigates the processes involved in the comprehensive processing of metallurgical industrial waste for the production of zinc electrolyte. The Waelz process for metallurgical waste jointly blended with current zinc plant cakes was studied, resulting in the production of zinc-bearing Waelz oxides (fumes). The leaching behavior of the obtained Waelz oxides and the subsequent hydrolytic purification of zinc-bearing solutions from impurity components were examined. An improved technological flowsheet for the hydrolytic purification of solutions was developed using an iron-containing solution as an additional reagent. It was established that its addition promotes more effective removal of harmful impurities that adversely affect the electrolytic deposition of zinc. The proposed technological solutions are aimed at improving the purification efficiency of zinc electrolyte, ensuring the stability of the electrowinning process, and enhancing the comprehensive utilization of zinc production waste.
Keywords: zinc, zinc electrolyte, Waelz process, metallurgical waste, zinc cake, sludge.

The declining content of valuable components in mineral raw materials worldwide, together with the steady increase in the cost of fuel, energy, and natural resources, makes the recovery of non-ferrous metals from industrial waste, its integrated processing, and its reuse as a secondary raw material increasingly important. For this purpose, the blending of sludge generated during the scrubbing of sulfur dioxide (SO_2) gases at a zinc plant with zinc cake was studied, followed by roasting of the mixture to transfer zinc into the fume phase. The experimental methodology was developed in two successive stages to optimize the technological parameters of the jarosite process using ammonium salts. A zinc recovery of 17.02% from the residues was achieved under the following conditions: pH = 1.5 (H_2SO_4 concentration: 190 g/L), temperature: 90 °C, $(NH_4)_2SO_4$ consumption: 800 mg, and reaction time: 300 minutes. [1–4]

Within this process, it is necessary to obtain a highly purified zinc sulfate solution because, during electrolysis, zinc ions are less noble than hydrogen ions. Therefore, solution purification is one of the most important technological stages in zinc hydrometallurgical production. [2, pp. 445–461] The authors consider ways to improve the hydrolytic purification of zinc electrolyte solutions obtained by leaching zinc calcine, with the aim of improving electrolyte quality and ensuring efficient electrolysis. [3]

To determine the optimum blending conditions for the Waelz processing of zinc cake, a 1 kg charge was prepared. Industrial waste was added at 1, 2, 4, 8, 12, and 16% of the total charge mass. After Waelz

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processing, the masses of the resulting clinker were 700, 710, 695, 680, 690, and 600 g, respectively. The zinc contents in the initial charge were 18.25, 17.87, 17.63, 17.13, 17.01, and 15.93%, while the corresponding copper contents were 0.840, 0.840, 0.836, 0.807, 0.790, and 0.610%. After Waelz processing, the zinc content in the clinker ranged from 0.45 to 0.75%, while the copper content was 1.19–1.20%.

Based on the experimental data, the clinker yield, zinc recovery (volatilization), and copper enrichment factor were calculated to evaluate the effect of industrial waste content in the charge on Waelz process performance. The values of these indicators for each charge composition are presented in Table 1.

Effect of industrial waste content in the charge on clinker yield, zinc recovery, and the copper enrichment factor

Industrial waste, %	Clinker mass, g	Clinker yield, %	Zn recovery, %	Cu enrichment factor
1	700	70,0	97,70	1,43
2	710	71,0	97,62	1,43
4	695	69,5	97,63	1,44
8	680	68,0	97,62	1,49
12	690	69,0	97,57	1,52
16	600	60,0	97,74	1,97

The relationship between the copper enrichment factor in the clinker and the industrial waste content in the charge is shown in Figure 1.

The graph shows that the copper enrichment factor increases steadily from 1.43 to 1.97, indicating copper concentration in the clinker as the proportion of industrial waste increases. This is because zinc volatilizes intensively, whereas copper is almost entirely concentrated in the clinker.

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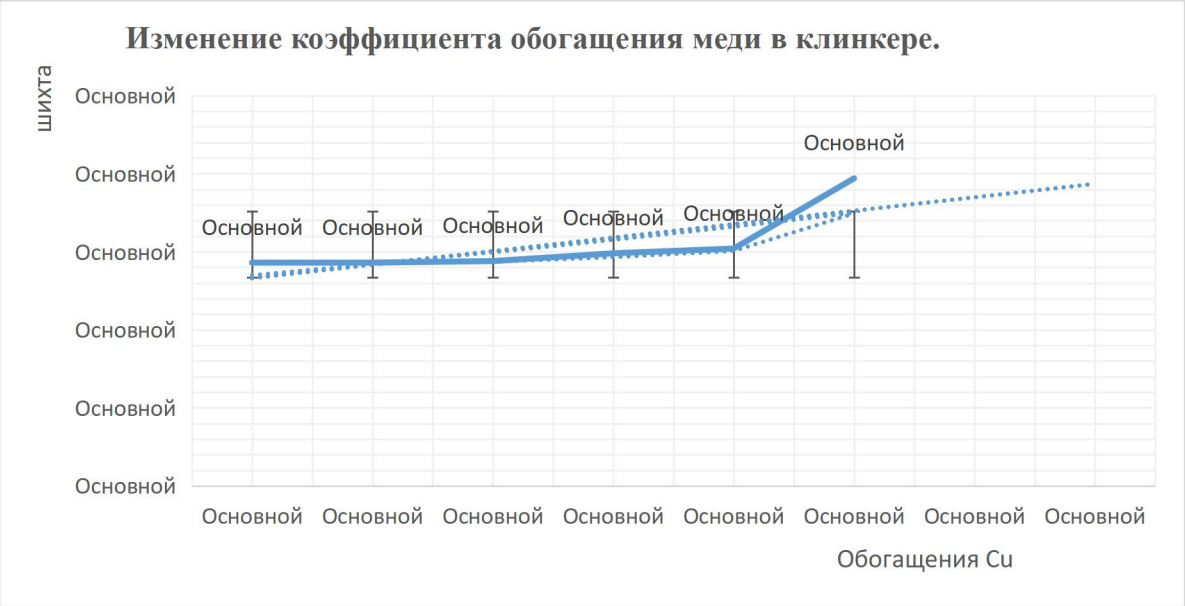

Figure 1. Dependence of the copper enrichment factor on the industrial waste content in the charge

Zinc recovery remains high in all experiments, amounting to 97.6–97.7%, which confirms the effective removal of zinc from the charge during the Waelz process.

Thus, increasing the industrial waste content to 16% promotes maximum copper concentration in the clinker while maintaining a high zinc recovery rate. However, if the optimization criterion is to obtain a sufficient amount of clinker with a high copper concentration, the most rational range is 8–12% industrial waste. Within this range, a high level of zinc volatilization (>97.5%) and stable copper enrichment are achieved without a significant decrease in clinker yield.

Copper behavior was monitored by chemical analysis using the following methods:

1. 1. Inductively coupled plasma atomic emission spectrometry (ICP-ARCOS).
2. 2. DDK KFK-ZOMZ-3.01 photoelectric colorimeter.
3. 3. Complexometric determination of copper using 0.005 N sodium thiosulfate.
4. The data obtained using the ICP-ARCOS instrument are presented below.

The results of the analysis performed using the ICP-ARCOS atomic emission spectrometer are presented as analytical signals of copper and zinc recorded at their respective analytical lines. The obtained signals are shown in Figures 2 and 3.

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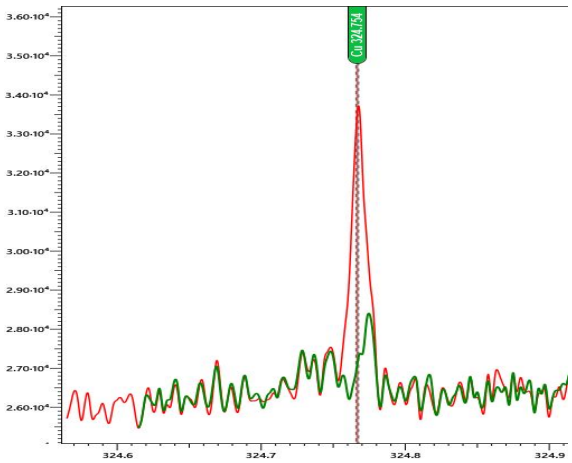

Figure 2. Analytical signal of copper at a wavelength of 324.754 nm.

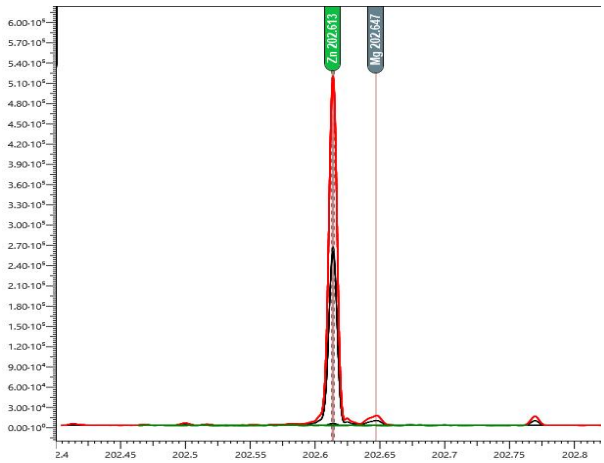

Figure 3. Analytical signal of zinc at a wavelength of 202.613 nm

The research results established that the optimum proportion of industrial waste blended with current zinc cakes for the Waelz process is 8–12%. At this component ratio, zinc-bearing fumes are formed efficiently and the technological process proceeds stably. Increasing the industrial waste proportion to 16% reduces the clinker yield and disrupts the established temperature regime of the Waelz furnaces, adversely affecting the process performance. Therefore, the industrial waste content in the charge should be maintained at 8–12%.

The parameters of neutral leaching of zinc-bearing fumes are presented in Table 2.

Table 2

Ferrous iron content in the mixture of Waelz fume and recycled zinc solution

Parameter	Value
Iron (Fe^{2+})	Not more than 60 mg/L
Initial H_2SO_4 concentration	120–150 g/L
H_2SO_4 after pulp formation	10–15 g/L
Slurry specific gravity	1300–1320 g/L

The fumes are leached using a sulfuric acid solution with an initial H_2SO_4 concentration of 120–150 g/L. When the fumes are mixed with spent electrolyte, the concentration of free sulfuric acid decreases to 10–15 g/L. The slurry is then neutralized until a stable pH of 4.8–5.2 is reached. The process is carried out at 70–75 °C for 2.5–3 hours.

The average impurity concentrations in the neutralized solution after three-stage purification are presented in Table 3.

Table 3

Ferrous iron content in the neutral zinc-bearing solution

Parameter	Value
Iron (Fe^{2+})	12–20 mg/L
pH	4.8–5.2

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Slurry specific gravity	1280–1300 g/L

During leaching and subsequent neutralization, ferrous iron (Fe^{2+}) is oxidized to ferric iron (Fe^{3+}). At pH 4.8–5.2, ferric iron undergoes hydrolysis and transfers to the solid phase as hydroxide compounds, precipitating together with associated impurities. The residual Fe^{2+} concentration in the solution is 12–20 mg/L, indicating effective iron removal from the solution.

It was established that the optimum proportion of industrial waste in the charge blended with current zinc cakes is 8–12%, ensuring efficient production of zinc-bearing fumes while maintaining a stable temperature regime during Waelz processing. Increasing the waste proportion to 16% reduces the clinker yield and disrupts the temperature regime of the Waelz furnaces.

A technological flowsheet for leaching zinc-bearing fumes has been developed and proposed. It uses spent electrolyte as the leaching reagent, followed by neutralization of the slurry to pH 4.8–5.2. During this process, ferrous iron (Fe^{2+}) is oxidized to ferric iron (Fe^{3+}), which then undergoes hydrolysis and precipitates together with associated impurities. This improves the purification of the zinc-bearing solution and creates favorable conditions for subsequent zinc recovery.

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