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Utilization of Galvanizing Flue Dust Residue: A Sustainable Approach towards Complete Material Recycling

Jana Pirošková [1,*], Jakub Klimko [1], Silvia Ružičková [1], Martina Laubertová [1], Vladimír Marcinov [1], Erika Múdra [2], Marek Vojtko [2] and Dušan Oráč [1]

[1] Institute of Recycling Technologies, Faculty of Materials, Metallurgy and Recycling, Technical University of Košice, Letná 9, 042 00 Kosice, Slovakia; jakub.klimko@tuke.sk (J.K.); silvia.ruzickova@tuke.sk (S.R.); martina.laubertova@tuke.sk (M.L.); vladimir.marcinov@tuke.sk (V.M.); dusan.orac@tuke.sk (D.O.)

[2] Institute of Materials Research, Slovak Academy of Sciences, Watsonova 47, 040 01 Kosice, Slovakia; emudra@saske.sk (E.M.); mvojtko@saske.sk (M.V.)

* Correspondence: jana.piroskova@tuke.sk

Abstract: During hot-dip galvanization, wastes such as bottom dross, zinc ash, spent pre-treatment solutions, and galvanizing flue dust (GFD) are generated. In scientific publications, research devoted to GFD waste recycling is absent, and companies generating this waste require a solution to this complex problem. GFD is often landfilled in hazardous waste landfills. However, it is possible to process this waste hydrometallurgically, where GFD is first leached, the solution is refined, and finally, zinc metal is obtained by electrowinning. During specific environmentally friendly leaching, not all solid GFD is dissolved, and the aim of this study is to process the remaining solid GFD residue. The analysis shows that the GFD residue material mainly contains zinc (42.46%) in the form of oxides, but there is also a small amount of polluting elements such as Al, Fe, and Pb. This study examines the leaching of the samples in HCl and H_2SO_4 under different conditions with the aim of obtaining a solution with a high concentration and high leaching efficiency of zinc. The L/S ratio of 3, 4 M H_2SO_4, and ambient temperature proved to be optimal for the leaching of the GFD residue, where 96.24% of zinc was leached out, which represents a zinc concentration of 136.532 g/L.

Keywords: zinc; dust; galvanizing flue dust; recycling; hot-dip galvanization; leaching

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1. Introduction

Zinc is an essential material used in today's world for various purposes, including the production of batteries and alloys such as brass and bronze. Accounting for over 50% is its use as a corrosion protection coating for steel. Globally, zinc is used to coat up to 95% of steel products, providing corrosion protection [1–3].

The largest producers of zinc are China, with a production of 4.2 million metric tons (2022), Australia, and Peru [4]. The total zinc production in 2022 was nearly 13.33 million metric tons. Global zinc reserves are estimated to be around 250 million metric tons, with the largest reserves in Australia, China, Peru, and Mexico. The largest zinc mining company is Glencore, and one of the top zinc smelting companies is Nyrstar [5].

The high consumption of zinc is leading to a reduction in primary reserves in open deposits, which are currently expected to last for approximately 17 to 20 years. According to the list of critical raw materials from 2023, zinc is economically important for the sustainable development of EU countries because of its widespread use in a variety of industries [6]. The zinc end-of-life recycling input rate (EOL-RIR) is currently 31% [7].

Therefore, it is necessary to look for other secondary sources with a high zinc content and to increase the EOL-RIR. The industries producing waste containing zinc include the hot-dip galvanizing of steel [8–11], secondary copper production [12,13], steel production in electric arc furnaces [14], and zinc batteries [15].

The present article focuses on the processing of galvanizing flue dust (GFD) waste from the hot-dip galvanizing industry.

The technological process of hot-dip galvanizing utilizes immersion of a steel component in molten zinc at 450–470 °C. The galvanizing itself is preceded by the surface pre-treatment of the steel. Surface preparation is an important step, which begins with degreasing, followed by pickling and immersion in flux, with the aim of removing fats, oils, metal oxides, and other contaminants from the steel surface [2,16,17].

As a flux in dry hot-dip galvanizing, an aqueous solution of $ZnCl_2$:$2NH_4Cl$ salts is applied, most often in a 1:2 ratio. The zinc coating is formed by a mutual reaction between molten zinc and steel to form the zinc–iron alloy phase [2,16,17].

The entire technological process, from the cleaning process of the steel component to the galvanizing process, is accompanied by the generation of waste. The largest volume of waste generated by hot-dip galvanizing consists of liquids, which include spent solutions from surface pre-treatment and rinsing; solid wastes are mainly bottom dross and zinc ash, and gaseous wastes are generated not only from the pre-treatment but also from the zinc plating process itself. When a steel component is immersed in the zinc bath, violent reactions occur where particles evaporate in the form of white fumes, which are collected on the filters, producing GFD waste. It is a product of zinc chloride and ammonium chloride decomposition contained in the fluxes [2,16–18].

The fumes are largely composed of ammonium chloride, which decomposes according to Reaction (1) into ammonia and hydrochloric acid, which is very reactive and forms chloride compounds with other metals. The unreacted ammonia and acid are cooled over the bath to form solid NH_4Cl, which is part of the white fumes [19].

$$NH_4CI \rightarrow NH_3(g) + HCl(g) \qquad \Delta G^{\circ}{}_{450} = -21.257\ KJ \tag{1}$$

The diameter of almost 80% of the particles in the fumes is under 1 μm. The significant components of GFD are chlorides originating from the application of chloride solutions or fluxes in the pre-treatment process. The resulting hydrochloric acid from Reaction 1 and the remaining hydrochloric acid on the surface from the surface pre-treatment react with zinc to form zinc chloride and hydrogen gas according to Reaction (2) [17,18,20,21].

$$Zn + 2HCl(ia) = ZnCl_2(g) + H_2(g) \qquad \Delta G^{\circ}{}_{450} = -141.090\ KJ \tag{2}$$

The waste generated in the process of batch hot-dip galvanizing is in relatively low quantities (approximately 1 kg of GFD per ton of galvanized steel) compared to other solid waste, which causes its problematic processing [16,17,22].

Galvanizing flue dust is characterized by its fine grain size, high content of zinc (approx. 30%), chlorine (approx. 10%), ammonia, Fe, and other constituents such as Pb, Cu, Al, Sn, Mg, Ca, and Si [19,23–27]. Due to its higher solubility and content of elements, it is categorized as hazardous waste (K061) according to environmental protection agencies [28,29], which was also confirmed by leachability test [19].

To utilize the material potential of GFD and to prevent landfilling, this type of waste can be processed hydrometallurgically or pyrometallurgically together with zinc ash, as this waste has a similar chemical composition [23–25]. A detailed characterization of GFD was carried out in a previous article [19]. The treatment of GFD is currently the subject of only a small number of scientific studies. The hydrometallurgical processing method is used to obtain various zinc and flux products [23,24]. The leaching of zinc is mainly carried out in hydrochloric acid. The choice of hydrochloric acid is due to the high content of chloride compounds in the GFD waste [23].

In a study, L. Rahman et al. (2017) [23] dealt with the leaching of GFD for ZnO production. The leaching was carried out in HCl solution, where the solid residue was then filtered out, and the solution with Fe^{2+} ions was oxidized by hydrogen peroxide to form iron (Fe^{3+}) to remove Fe. The next step involved the precipitation of zinc with ammonium hydroxide and the production of precipitate zinc hydroxide ($Zn(OH)_2$). The precipitate was dried at 140 °C to form the final zinc oxide (ZnO) product.

In another study, F. Bisol et al. (1999) [24] dealt with the processing of GFD to form a new flux. The leaching of GFD was carried out in hydrochloric acid at 80 °C, with the highest extraction of zinc into the solution. After precipitating the ferric ions (Fe^{3+}) and refining the solution by cementation with zinc powder, the final purified zinc chloride solution containing 150 g/L zinc was further processed by electrolysis to produce electrolytic zinc. The solid final products, ammonium chloride and zinc chloride (new flux) were obtained by crystallization. The authors further concluded that any ammonium chloride that is still present in the electrolyte at a concentration of 30 to 35 g/L does not interfere with the electrolysis process.

G. Thorsen et al. (1981) [30] hydrometallurgically processed various zinc wastes of similar nature to GFD to obtain pure zinc metal. The process based on solvent extraction was carried out using 30% organic carboxylic acid (HX) (Versatic 911). Subsequently, zinc was extracted from the organic phase using sulfuric acid at pH 0.5. The obtained zinc sulfate solution was subjected to zinc electrolysis.

Pyrometallurgical processing of GFD and zinc ash was dealt with by A. Barakat (2003) [25], where an ingot of pure zinc with a purity of 99.2–99.6% zinc was obtained using an efficient method. In order to increase the zinc content, GFD was mixed with zinc dust from an electric arc furnace. The smelting was carried out with and without the addition of flux consisting of zinc chloride and ammonium chloride. The addition of flux to the zinc flux positively affected the efficiency of zinc recovery during smelting. The highest zinc extraction efficiency (70.6%) was obtained at a concentration of 20 wt.% NH_4Cl (1:5, $ZnCl_2$:NH_4Cl).

Scientific publications on GFD processing confirm the possibility of recycling through leaching, refining, with the aim of impurity removal, and electrowinning, with the possibility of obtaining pure metallic zinc. However, during leaching, GFD is not fully leached, and the remaining insoluble solid residue, classified as hazardous waste, must be disposed of in hazardous waste landfills.

The aim of this study is to further improve the efficiency of the GFD recycling process by treatment of solid residues (GFD residue) after leaching. In this article, the GFD residue will be characterized from the point of view of elemental and phase composition; a thermodynamic study will be performed, and the leaching will be verified experimentally. In the following article, the study of solution refining and electrolytic recovery of zinc from the solution will be carried out.

2. Materials and Methods

2.1. Material

Galvanizing flue dust (GFD), which is considered hazardous waste, was collected from the filters in local hot-dip galvanizing plants over a one-month galvanizing period. The obtained galvanizing flue dust waste samples underwent selective hydrometallurgical processing, resulting in the generation of the GFD residue used in this study. A representative sample of 50 g was obtained by systematic sampling and by sample divider, according to a verified method for the purpose of material characterization, and the remaining volume was used for the experiments. The samples used for leaching were sieved on sieves with a mesh size of 0.125 mm without the need for mechanical pre-treatment by crushing or grinding.

2.2. Analytical Methods

Chemical analysis of input GFD residue, intermediates, and liquid samples was performed using an atomic absorption spectrometry (AAS) method with a Varian SpectrAA20^{+} type spectrophotometer (Varian, detection limit: 0.3–6 ppb; slit width: 0.2–1 nm; wavelength: 213.9–422 nm; and lamp current: 4–12 mA, Belrose, Australia). Chlorides were determined by titration using silver nitrate $AgNO_3$ (0.1 M) and K_2CrO_4 indicator (5%) of analytical purity. The phases in the GFD residue were identified by X-ray diffraction phase analysis (XRD). The samples were prepared according to the standardized Panalytical system, which provides a nearly random distribution of the particles. The samples were analyzed using a Philips X'Pert PRO MRD (Co-Kα) diffractometer (Philips, Netherlands) and identified using X'Per HighScore plus software (ver. 3.0a). The morphology and microstructure of the samples were studied using a MIRA3 FE-SEM (TESCAN, USA, resolution: 1.2 nm at 30 kV; 2.3 nm at 3 kV) ZEISS EVO MA15 scanning electron microscope (RSEM, Oxford Instruments, United Kingdom). This equipment also enabled multi-elemental semi-quantitative analysis using energy dispersive spectrometry EDS. Thermodynamic analysis was performed using HSC Chemistry 10 software (Outotec, Espoo, Finland) [31].

2.3. Methodology

The leaching experiments were carried out in an 800 mL glass beaker placed in a thermostatically controlled water bath. The experiments published in this study were performed at a laboratory temperature between 25–30 °C using a constant 400 rpm stirring speed. Aqueous solution of 4 M H_2SO_4 sulfuric acid and 4 M HCl hydrochloric acid were used as leaching reagents in the first leaching experiments at L/S from 5 to 1. In the second series of experiments, only H_2SO_4 with an L/S ratio of 3 was employed, while the concentration was varied from 0.5 M to 1 M, 2 M, and 4 M.

The volume of the leaching reagent was 400 mL, and the weight of the GFD residue varied according to the L/S ratio. The total duration of the experiments was 30 min with sampling times of 1, 3, 5, 10, 15, and 30 min in the first series of experiments and 10 min with sampling times at 1, 3, 5, and 10 min in the second series of experiments. The volume of the liquid sample for AAS analysis was 10 mL, from which 5 mL were diluted in 45 mL of weak H_2SO_4 solution in order to stabilize the samples. Leaching efficiencies were calculated with respect to volume changes caused by sampling and the amount of solution taken by previous sampling.

3. Results and Discussion

3.1. Composition of Zinc Galvanizing Flue Dust Residue

Table 1 summarizes the results of the AAS analysis, presenting the chemical composition of the GFD residue. Figure 1 illustrates the morphology of the sample, confirming that it is a fine-grained material with a grain size of up to 20 µm. Figure 2 displays the EDS analysis of the individual spectra A, B, and C of the GFD morphology from Figure 1. The chemical composition analyzed using the EDS method does not show the analyzed graphite content because it should not be present in the sample and was only used as a powder for the purpose of analysis. The XRD analysis diffractogram is shown in Figure 3. In order to identify potential marketable products from GFD residue, a calculation was performed, and the results are presented in Table 2.

According to the chemical analysis, the GFD residue is characterized by a significant zinc content ranging between 40% and 45%. Based on the origin of the galvanizing flue dust waste, it can be assumed that the phase present in GFD residues is a mixture of oxides and chlorides since the presence of oxygen and chlorine was also confirmed by the EDS analysis. It was not possible to clearly identify the specific phase representation of zinc, which would correspond to 40% zinc by phase XRD analyses, which may be attributed to the amorphous nature of the zinc phases. The diffractogram (Figure 3) contains relatively low peaks, with most of the peaks covered by franklinite ($ZnFe_2O_4$), and the remaining peaks were identified as $PbAl_2O_4$. In addition to zinc, the presence of aluminum, iron, or lead was also confirmed by AAS analysis. In addition to franklinite and $PbAl_2O_4$, these elements are also considered to be present as oxides or chlorides. Copper appeared in the SEM–EDS analysis as potentially present, marked in red, but AAS analysis did not confirm its content. The calculations of the value of the GFD residue elements (Table 2) confirmed that only zinc can be considered as a marketable product (1029.87 $/t), and other present elements are classified as impurities, for which removal from the leach solution will be subject to future research.

Table 1. Content (%) of elements in the GFD sample analyzed by AAS.

Element	Zn	Al	Fe	Cu	Si	Pb	Mn	Ca	Cl^- **	Residue
Content (%)	42.46	2.51	1.17	<LoD *	0.25	0.20	0.07	0.03	16.42	36.89

* LoD—Limit of Detection ** Analyzed by titration.

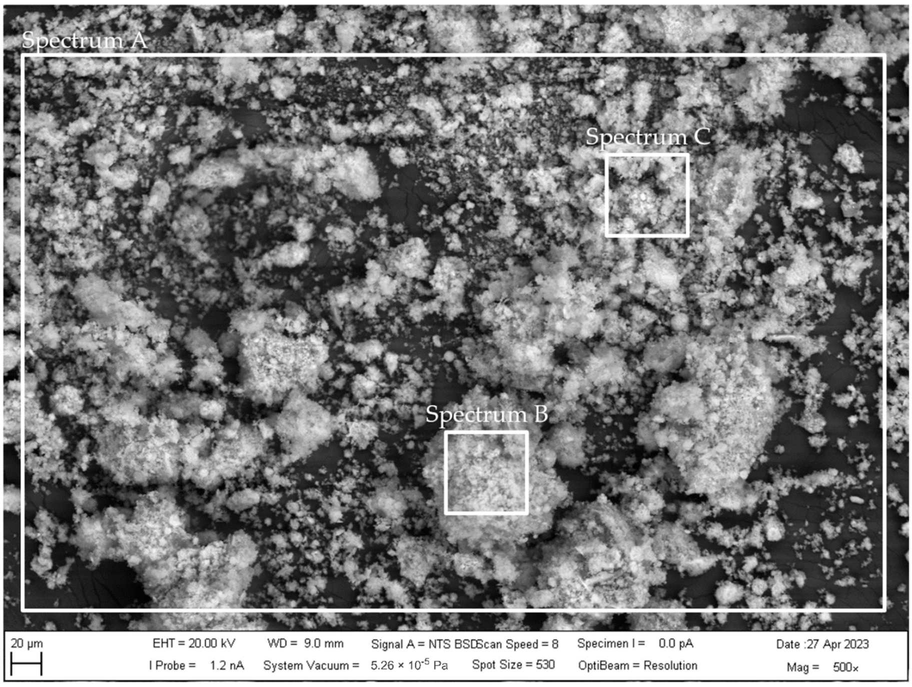
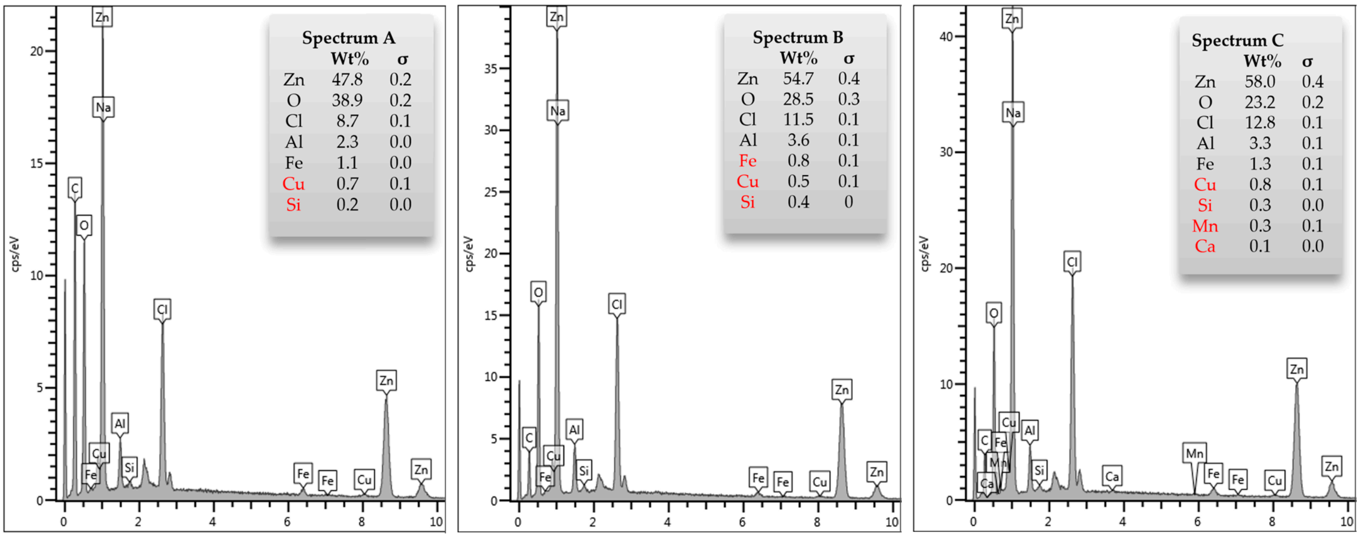


Figure 1. Morphology of GFD residue.



Spectrum A

	Wt%	σ
Zn	47.8	0.2
O	38.9	0.2
Cl	8.7	0.1
Al	2.3	0.0
Fe	1.1	0.0
Cu	0.7	0.1
Si	0.2	0.0

Spectrum B

	Wt%	σ
Zn	54.7	0.4
O	28.5	0.3
Cl	11.5	0.1
Al	3.6	0.1
Fe	0.8	0.1
Cu	0.5	0.1
Si	0.4	0

Spectrum C

	Wt%	σ
Zn	58.0	0.4
O	23.2	0.2
Cl	12.8	0.1
Al	3.3	0.1
Fe	1.3	0.1
Cu	0.8	0.1
Si	0.3	0.0
Mn	0.3	0.1
Ca	0.1	0.0

Figure 2. Multi-elemental semi-quantitative energy dispersive spectrometry (EDS) analysis of three spectrum areas, A, B, and C, are marked in Figure 1. The red color indicates elements with a lower probability of their presence.

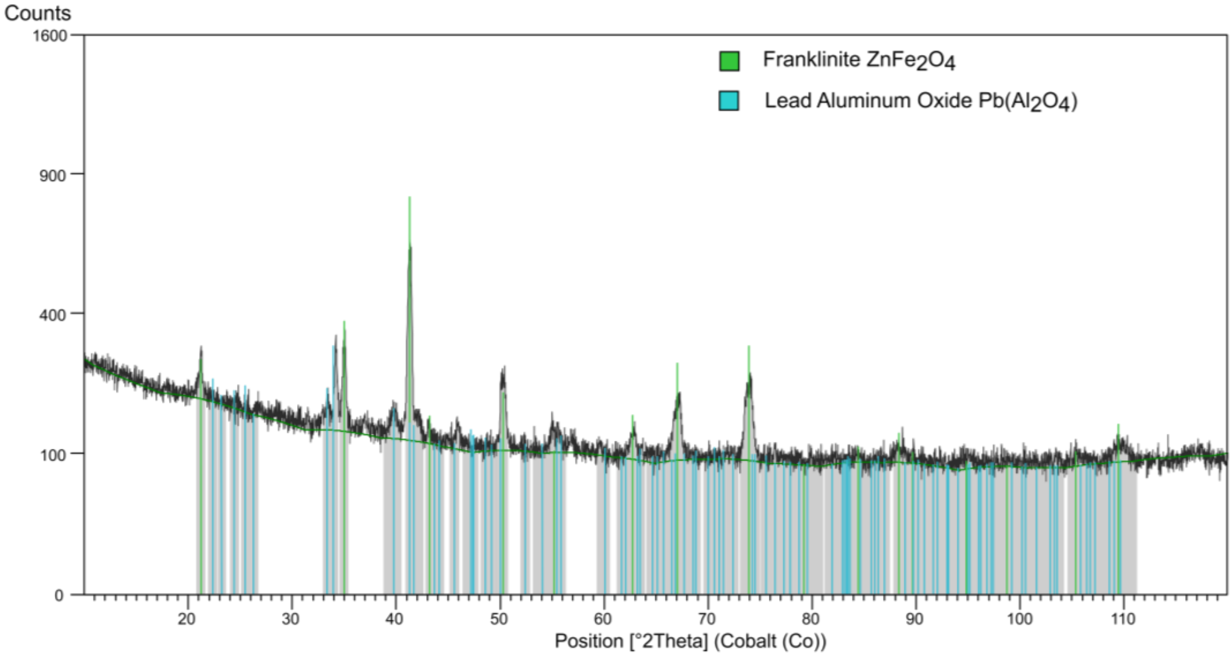


Figure 3. X-ray diffractogram of the GFD residue.

Table 2. Estimated value of the elements in the GFD residue, data from [32–34].

Element	Content (%)	Marketable Products	Price of Marketable Product [1] ($/t)	Estimated Value of Marketable Product in 1 t of GFD Residue ($/t)
Zn	42.46	Zn	2425.50	1029.87
Al	2.51	Al	2236.00	56.12
Pb	0.2	Pb	2245.00	5.78
Fe	1.17	$FeO_{(Fe = 77.73\%)}$	40	0.60
Mn	0.07	Mn	1500	1.05
Ca	0.03	$CaSO_{4\ (Ca = 29.43\%)}$	300	0.31
Si	0.25	-	-	-

[1] Prices of marketable products from 31 October 2023.

3.2. Thermodynamic Study

Previous analyses of the GFD residue indicate the presence of zinc mainly in the form of oxides and franklinite, and due to the character of the waste generation and the presence of chlorine, it is possible to assume the presence of easily soluble $ZnCl_2$. Possible leaching reactions in sulfuric acid and hydrochloric acid were determined for the phases present. In general, most chlorides are well soluble in water, and therefore, it is not necessary to conduct a thermodynamic study of chloride leaching. The individual leaching reactions of the non-chloride phases in sulfuric and hydrochloric acid are shown in Equations (3)–(13) with the corresponding values of the standard Gibbs free energy change.

$$ZnO_{(s)} + H_2SO_{4(aq)} = ZnSO_{4(aq)} + H_2O_{(l)} \qquad \Delta G^\circ_{293.15} = -121.589\ KJ \tag{3}$$

$$ZnCl_{2(s)} + H_2SO_{4(aq)} = ZnSO_{4(aq)} + 2HCl_{(l)} \qquad \Delta G^\circ_{293.15} = -95.008\ KJ \tag{4}$$

$$ZnFe_2O_{4(s)} + 4H_2SO_{4(aq)} = ZnSO_{4(aq)} + Fe_2(SO_4)_{3(ia)} + 4H_2O_{(l)} \qquad \Delta G^\circ_{293.15} = -247.052\ KJ \tag{5}$$

$$Al_2O_{3(s)} + 3H_2SO_{4(aq)} = Al_2(SO_4)_{3(aq)} + 3H_2O_{(l)} \qquad \Delta G^\circ_{293.15} = -183.626\ KJ \tag{6}$$

$$PbO_{(s)} + H_2SO_{4(aq)} = PbSO_{4(s)} + H_2O_{(l)} \qquad \Delta G^\circ_{293.15} = -171.653\ KJ \tag{7}$$

$$ZnO_{(s)} + 2HCl_{(aq)} = ZnCl_{2(aq)} + H_2O_{(l)} \qquad \Delta G^\circ_{293.15} = -181.716\ KJ \tag{8}$$

$$ZnFe_2O_{4(s)} + 8HCl_{(aq)} = ZnCl_{2(aq)} + 2FeCl_{3(aq)} + 4H_2O_{(l)} \qquad \Delta G^\circ_{293.15} = -438.607\ KJ \tag{9}$$

$$Al_2O_{3(s)} + 6HCl_{(aq)} = 2AlCl_{3(aq)} + 3H_2O_{(l)} \qquad \Delta G^\circ_{293.15} = -441.870\ KJ \tag{10}$$

$$PbO_{(s)} + 2HCl_{(aq)} = PbCl_{2(aq)} + H_2O_{(l)} \qquad \Delta G^\circ_{293.15} = -196.411\ KJ \tag{11}$$

$$Fe_2O_{3(s)} + 6HCl_{(aq)} = 2FeCl_{3(aq)} + 3H_2O_{(l)} \qquad \Delta G^\circ_{293.15} = -319.925\ KJ \tag{12}$$

$$FeO_{(s)} + 2HCl_{(aq)} = FeCl_{2(aq)} + H_2O_{(l)} \qquad \Delta G^\circ_{293.15} = -145.194\ KJ \tag{13}$$

The negative values of ΔG° for each reaction confirm the possibility of GFD leaching in both studied leaching solutions. If sulfuric acid is used, it is possible to reduce the leachability of lead in the leaching step, which can affect the purity of the obtained zinc in the zinc recovery step, and compared to hydrochloric acid, this acid evaporates at a lower rate, and the vapors are less dangerous.

Theoretical molarity and theoretical concentrations of specific elements at different L/S ratios needed for thermodynamic calculations (Table 3) were calculated according to Equations (14) and (15). Figure 4 shows Eh-pH diagrams of Zn, Fe, and Al from GFD residue in H_2SO_4 and HCl leaching systems with corresponding molarities.

$$\text{Theoretical Concentration} = \frac{m_{Me}}{V_{L/S}} = \frac{m_{L/S} \cdot w_{Me}}{V_{L/S}} \left(g\,/\,dm^3\right) \tag{14}$$

$$\text{Theoretical Molarity} = \frac{n_{Me}}{V_{L/S}} = \frac{\frac{m_{L/S} \cdot w_{Me}}{M_{Me}}}{V_{L/S}} \left(mol/dm^3\right) \tag{15}$$

where m_{Me} is the weight of the specific element, $m_{L/S}$ is the weight of the sample at a specific L/S ratio, w_{Me} is the weight percent of the element, n_{Me} is the mole of the element, M_{Me} is the molar mass of the element, and $V_{L/S}$ is the volume at a specific L/S ratio.

Table 3. Theoretical molarity and concentration for leaching system at different L/S.

Element	Content (%)	L/S = 10		L/S = 5		L/S = 3	
		Molarity (M)	Concentration (g/L)	Molarity (M)	Concentration (g/L)	Molarity (M)	Concentration (g/L)
Zn	42.56	0.651	42.56	1.302	85.12	2.17	141.867
Fe	1.17	0.021	1.17	0.042	2.34	0.07	3.9
Al	2.51	0.093	2.51	0.186	5.02	0.31	8.367
Pb	0.20	0.001	0.20	0.002	0.40	0.003	0.667

The Eh-pH diagram shows that zinc leaching can take place in both studied leaching media below pH 4, even at ambient temperature, which corresponds to the results of previous experiments with similar types of zinc-containing waste [27]. In addition to zinc, there is also a small amount of iron and aluminum in the GFD residue. For iron in the pH range from 1 to 4, it is possible to observe the slightly soluble FeO×OH phase; in the case of aluminum, the Na_2AlCl_6 phase is found in the area of water stability in an acidic environment. The exact solubility of the mentioned phase cannot be reliably and accurately determined, and therefore, the effectiveness of leaching must be verified experimentally. Based on a thermodynamic study and previous results with similar waste, the leaching of the GFD residue in relatively strong leaching agents (4 M) at laboratory temperature was first investigated.

3.3. Leaching

In the first series of experiments, the leaching efficiency of the GFD residue in H_2SO_4 (Figure 5) and HCl (Figure 6) was investigated depending on the change in the L/S ratio at laboratory temperature, 400 rpm with sampling times of 1, 3, 5, 10, and 30 min. The aim of reducing the L/S ratio was to identify the highest possible concentration while maintaining a sufficiently high leaching efficiency.

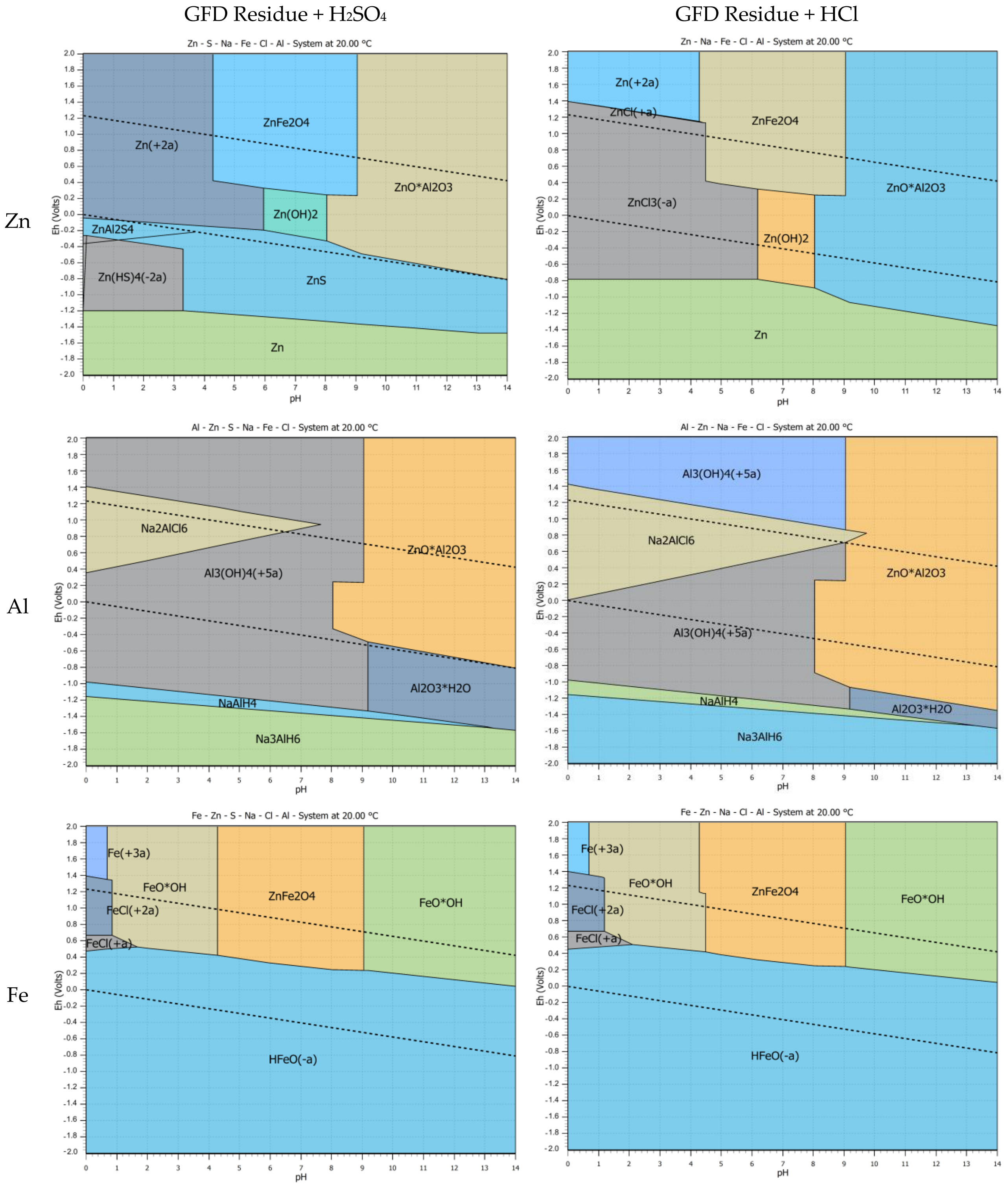


Figure 4. Eh-pH diagrams for GFD residue leaching systems in H_2SO_4 (**left**) and HCl (**right**) for Zn, Al, and Fe. Molarity: Zn = 0.651 M, Al = 0.093 M, Fe = 0.021 M.

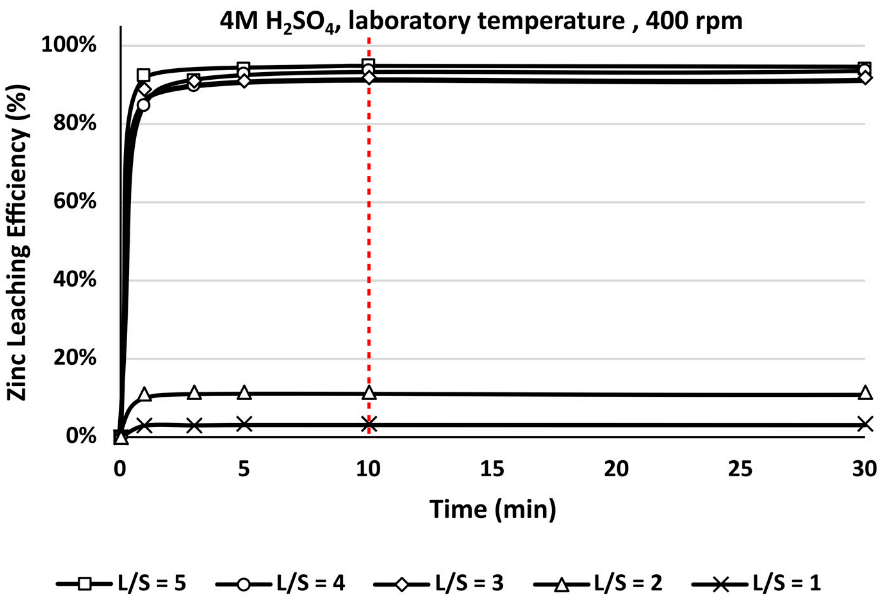


Figure 5. Zinc leaching efficiency of the GFD residue in 4 M H_2SO_4 over time at laboratory temperature, 400 rpm, and L/S ratios 1 to 5. The average standard deviations at L/S ratios 1 to 5 are 0.073%, 0.210%, 1.894%, 2.831% and 2.589% respectively. The red line represents data from 10 min of leaching, which were used to create Figure 7.

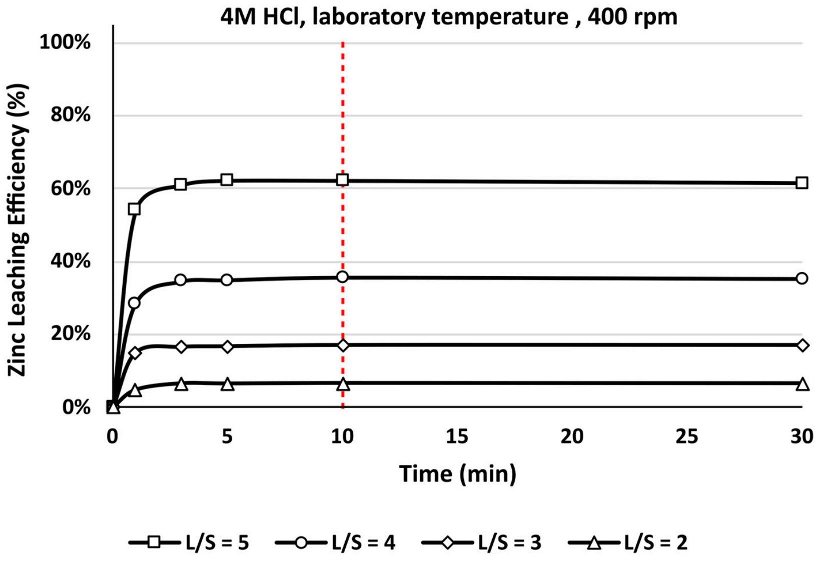


Figure 6. Zinc leaching efficiency of the GFD residue in 4 M HCl over time at laboratory temperature, 400 rpm, and L/S ratios 2 to 5. The average standard deviations at L/S ratios 2 to 5 are 2.589%, 2.831%, 1.894%, 0.210%, and 0.073%, respectively. The red line represents data from 10 min of leaching, which were used to create Figure 7.

The numerical values in Figure 7 show the leaching efficiencies at individual L/S ratios in the 10th minute of leaching, while the *Y* axis shows the maximum theoretical concentrations of zinc in the solution. Obtaining a leachate with a high zinc concentration is necessary for further electrolytic recovery of zinc from the leach solution. The efficiency of following electrolytic recovery of metallic zinc decreases with decreasing zinc concentration due to reduced conductivity, and thus, electrical losses occur [35,36].

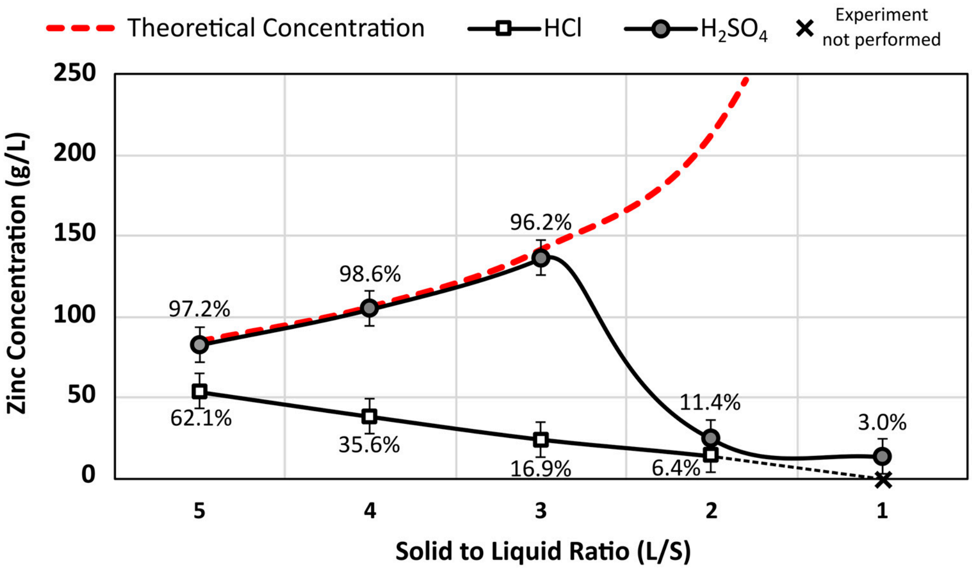
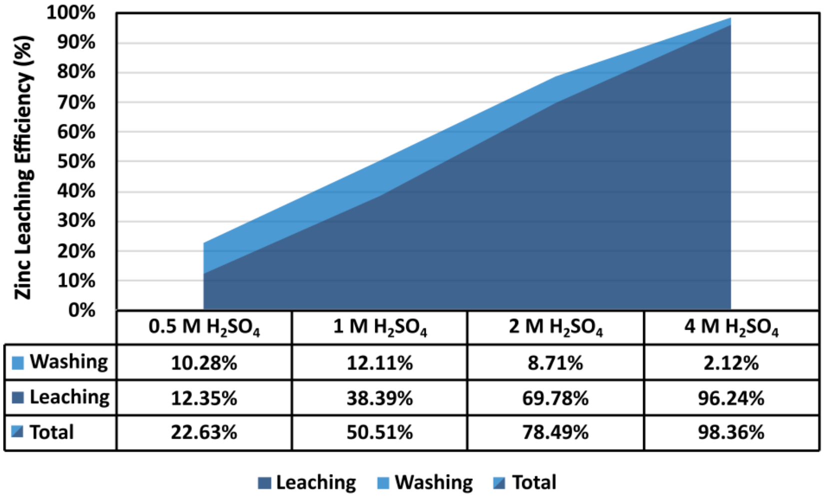


Figure 7. Theoretical zinc concentration at different L/S ratios (red line) compared to concentrations after leaching in 4 M HCl and 4 M H_2SO_4 after 10 min with corresponding leaching efficiency.

The results (Figures 5 and 6) indicate that the leaching process occurs relatively quickly, with maximum leaching efficiency being achieved within the first few minutes of the experiments. The leaching efficiency in HCl gradually decreased from 62.1% at L/S = 5 to 6.4% at L/S = 2. Low leaching efficiencies may be attributed to the reduced ability of HCl to dissolve the solid input material, which causes adsorption on the surface of the filtered material. In the case of the experiment at L/S = 1 with the use of HCl, it was not possible to take a liquid sample due to the high viscosity of the slurry. Leaching efficiencies in H_2SO_4 reached 97.2%, 98.6%, and 96.2% at L/S ratios of 5, 4, and 3, respectively. Leaching at L/S ratios of 2 and 1 led to a decrease in the leaching efficiency due to the high amount of undissolved residues and the associated adsorption. An L/S ratio of 3 using 4 M H_2SO_4 proved to be optimal, in which the solution obtained contains 136.532 g/L of zinc, which represents 96.24% leaching efficiency of the GFD residue. In the subsequent experiment, the concentration of H_2SO_4 was gradually reduced from 4 M to 2, 1, and 0.5 M, and the solid residues were washed with a constant volume of distilled water. The results of zinc leaching efficiencies and solid residue washing efficiencies at different molarities are shown in Figure 8.

The results confirm that by reducing the molarity at L/S = 3, the leaching efficiency decreases from the original 96.24% at 4 M H_2SO_4 to 69.78%, 38.39%, and 12.35% at 2, 1 and 0.5 M H_2SO_4, respectively. The remaining 2.12% can be washed from the solid residue with distilled water after leaching in 4 M H_2SO_4 with total efficiency for obtaining zinc from the GFD residue of 98.36%. The washing solutions can be utilized to prepare 4 M H_2SO_4 solutions, and subsequently, for leaching of the next batch of the GFD residue. The concentration of elements in GFD leach solution analyzed by AAS method is shown in Table 4.

The results show that there is a relatively small concentration of impurities in the solution, which may or may not affect the purity of the obtained zinc in further operations. The low leaching efficiency of aluminum (11.22%) and iron (5.97%) partially corresponds to the thermodynamic study and Eh-pH diagrams (Figure 4), in which the formation of poorly soluble phases was predicted. According to a thermodynamic study, lead in H_2SO_4 reacts to form an insoluble $PbSO_4$ phase, which was also confirmed with a leaching efficiency of 0.53% and a concentration 3.56 mg/L. In further research, it will be important to investigate the influence of impurities on the electrolytic extraction of zinc and, if necessary, also include the process of refining the solution (Figure 9). Alternatively, a second approach involves extraction of the zinc from the solution through carbonate precipitation, followed by calcination.



	0.5 M H_2SO_4	1 M H_2SO_4	2 M H_2SO_4	4 M H_2SO_4
■ Washing	10.28%	12.11%	8.71%	2.12%
■ Leaching	12.35%	38.39%	69.78%	96.24%
■ Total	22.63%	50.51%	78.49%	98.36%

Figure 8. Zinc leaching efficiency dependence on the molarity of H_2SO_4 and washing efficiency of the solid residue at L/S = 3, 10 min, laboratory temperature, and 400 rpm.

Table 4. Concentration of elements and leaching efficiency in the solution obtained by leaching in 4 M H_2SO_4 at L/S ratio 3, 400 rpm, and laboratory temperature for the duration of 10 min.

Analyte	Zn	Fe	Al	Pb
Concentration (g/L)	136.532	0.233	0.938	0.004
Leaching efficiency (%)	96.24	5.97	11.22	0.53

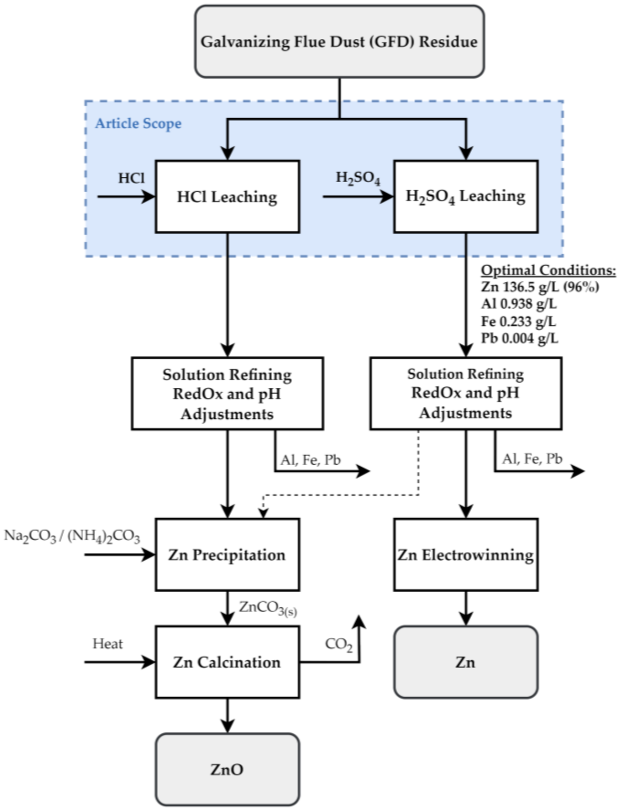


Figure 9. Proposed galvanizing flue dust residue recycling with the aim of obtaining metallic zinc.

4. Conclusions

GFD residue is a solid waste that remains after the initial hydrometallurgical processing of galvanizing flue dust. The analysis confirmed a high zinc content (42.46%). In addition to zinc, the GFD residue also contains Al (2.51%, Fe (1.17%), and other elements such as Si, Pb, Mn, and Ca with concentrations below 0.25%. XRD failed to identify the exact phase representation of zinc, but SEM–EDS analysis confirmed the presence of oxygen (23.2–38.9%) and chlorine (8.7–12.8%), from which it is possible to assume the presence of oxides and chlorides in the GFD residue. The price of 1 ton of GFD residue waste in the value of zinc presently is $1029 (€962), while the value of landfilling hazardous waste in Slovakia is currently approximately €500, depending on the cost of transportation. The results show the following:

- A thermodynamic study confirmed the leachability of the GFD residue in both investigated reagents, H_2SO_4, and HCl, at ambient temperatures.
- The goal of the first GFD residue leaching experiments was to achieve a high concentration of zinc in the leachate while simultaneously maintaining a high leaching efficiency, which was investigated using 4 M H_2SO_4 and 4 M HCl at ambient temperature by changing the L/S ratio.
- The next series of experiments investigated the possibility of reducing the concentration of H_2SO_4, which, however, resulted in a significant reduction in the leaching efficiency.
- The ratio L/S = 3 using 4 M H_2SO_4 proved to be optimal, in which the solution obtained contains 136.532 g/L of zinc, which represents 96.24% leaching efficiency of GFD residue.
- The possibility of using leachate for the purposes of electrolytic extraction of metallic zinc is investigated. In addition to the electrolysis itself, the effect of the decrease in zinc concentration on the current efficiency of the electrolysis and the effect of impurities on the purity of the obtained zinc deposit is investigated in detail.

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