Processing of Metal Waste—Sludge from the Galvanizing Plants

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Abstract: This paper deals with the possibility of obtaining zinc from waste galvanic sludge, which is formed during galvanic plating. The aim of the experimental and practical part was to obtain zinc after the leaching of galvanic sludge. Leaching was performed in sulfuric acid, nitric acid and hydrochloric acid at different temperatures and time intervals with the addition of oxidizing agents as hydrogen peroxide or ozone. A separation of the leach and filtrate using filtration followed. The leach was further processed by a precipitation of iron and other metals using various agents. After a further filtration, the electrolysis was performed in order to obtain pure zinc on the cathode at the electrical voltage of approximately 3.5 V. Leaching using a solution of sodium hydroxide or potassium hydroxide was also performed when the prior dissolving of a major part of zinc into the leach occurred, while iron and non-ferrous metals remained in the leaching residue. After the filtration of the leach, the electrolysis with a high zinc yield of a purity of more than 99% followed. This way seems to be an optimal one for building a semi-industrial line for galvanic sludge recycling. All the partial products, i.e., the leach, the leaching residue, the filtrate, the solid precipitate and the separated metal on the cathode were subjected to chemical analyses. The analyses results are presented in tables and graphs.

Keywords: metals; galvanic sludge; leaching; zinc; sodium hydroxide; electrolysis

1. Introduction

Galvanic zinc plating is an electrolytic process during which a zinc coating generated by electrochemical dissolution of a zinc anode deposits on electro-conductive materials, mostly on iron parts (as a cathode). Today zinc plating is typically carried out in a diluted hydrochloric acid with additions of other agents. All automatic bath lines involve technological processes: degreasing, pickling, surface activation, galvanic deposition of zinc layers, passivation of zinc layers and application of sealing paints. Using automated conveyors, parts are gradually dipped into degreasing baths, pickling baths and a bath for the surface activation. After them, the surface of the parts is cleaned, and a new zinc layer has been deposited on it using the electric current. Subsequently, in order to increase the corrosion resistance, the zinc coating passivation is performed, and in case of need, a sealing paint is applied. All the zinc plating process is completed by the air drying of parts and returning back to conveying units. The result of these processes is a high-quality smooth surface with a shiny zinc layer. A standard thickness of the zinc coat ranges between 8 and 12 μm.

Recovering waste materials and recovering metals from various secondary sources is of major importance due to the economic and environmental benefits. Zinc is one of the most popular and versatile metals that finds a wide range of applications including plating, coating and alloying with other metals [1,2]. The high demand for zinc has also

led the industry to exploit secondary sources such as zinc waste, zinc slag and leaching residues as potentially valuable resources [3]. Empirical data collected on the performance of galvanized steel in environments ranging from industrial to marine to suburban and rural suggest that zinc can prevent the corrosion of the underlying steel more than other surface treatments because it corrodes at a rate of about 1/30th that of iron [4].

The galvanic sludge, which contain larger amounts of heavy metals, constitute waste that is suitable for recycling. This sludge is classified as hazardous waste because of the potential release of metals into the environment. Their disposal consists mainly in landfills [5]. In Germany, sludge is treated in an incinerator, if the composition of the sludge permits, or in hazardous waste landfill. Currently, there is a great desire to avoid the negative impacts associated with the landfill of sludge, and different treatment routes are being sought [6–8]. These are generated during the treatment of waste water from the operation of the galvanic plant. It is a mixture of metal oxides or hydroxides mainly with iron, zinc, chromium and others. The sludge is collected in reaction pits and pumped to a sludge lagoon after sedimentation is complete. From there, they are dewatered by a sludge pump in a sludge tank and then are collected in containers. Hydrometallurgical methods are used for sludge treatment. Acid or alkaline leaching is used to convert the metals of interest into a leach liquor. Most of the waste substances do not dissolve in the environment or are converted to a difficult-to-dissolve compound. The leach is then treated by electrolysis to separate the individual metals [6–12].

The technological process generates different kinds of wastes, such as pickling baths that have to be disposed after their saturation with dissolving metals, as they contain a high concentration of hydrochloric acid, zinc and iron. Rinsing water and spent pickle liquor are subsequently treated in four steps in neutralization stations. A resulting product of this treatment is a galvanic sludge that can contain up to 18 wt.% of zinc and up to 8 wt.% of iron. These concentrations are interesting enough for a proposal of an applicable recycling technology. In accordance with the European Waste Catalogue, sludge and filter cakes from neutralization stations belong among hazardous substances. This is sludge of a solid and powdery consistency, with a yellow-green to brown color and a neutral reaction.

With rapidly developing galvanic plating, even increasing attention has been focused on the galvanic sludge. Galvanic sludge features the contents of heavy metals, for example zinc, iron, nickel, manganese, copper, cadmium and chromium. Sludge fall within hazardous waste by reason of the potential releasing of metals to the living environment. Their disposal is carried out mostly by deposition [13,14].

Galvanic waste processing through a vitrification method is described in [15,16]. A lot of studies have been oriented on the re-gaining of different metals from the galvanic sludge, e.g., zinc and iron, nickel and chromium [17] or copper [18]. The main problem is a varied composition and a high content of heavy metals. On the other side, the sludge is a potential secondary source of heavy metals. Zinc sludge can be treated by hydrometallurgical methods [6–10]. Literature data on the hydrometallurgical treatment of wastes mainly considers the leaching method in sulfuric [10], nitric or hydrochloric acids [9].

Kepák [19] presented a technology based on metals' recycling from the galvanic sludge—Figure 1. This is a so-called "MAR-Process", which allows a separation of non-ferrous metals from iron and chromium [20]. In the first step, the ammonium carbonate is a leaching agent, and 80% of non-ferrous metals is solved. An effectiveness of non-ferrous metals dissolution increases to 97–98% due to further leaching by the diluted sulfuric acid, and approximately 98% of iron and chromium remains in the leach liquor that is dumped. Cu, Ni and Zn are selectively separated from the leaching solution by solvent extraction, which is performed in particular steps. Electrolytic copper, nickel sulfate and nickel carbonate are final products.
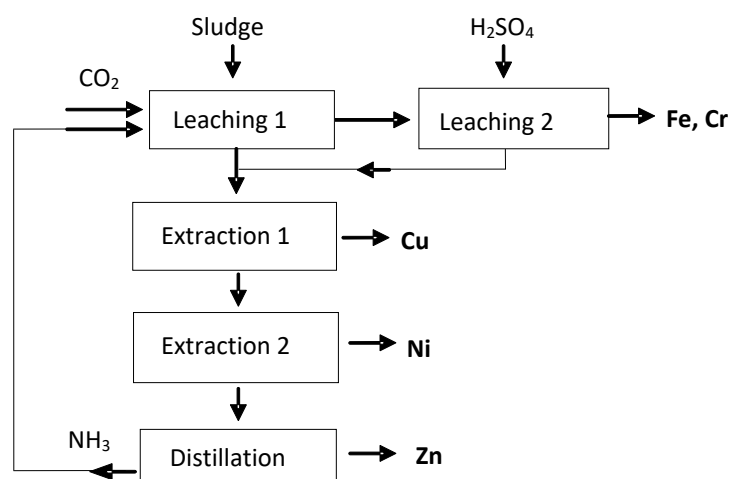
Figure 1. Block diagram of "MAR-Process" technology for galvanic sludge processing [19].

For the hydrometallurgical processing of galvanic sludge, the following procedure can be used:

1. Leaching in an appropriate environment with the aim to transfer utility metals into the leach and to separate indissoluble substances by filtration.
2. Removing iron and other metals from the leach using chemical precipitation.
3. The leach refining with the aim to remove harmful elements and admixtures.
4. Zinc separation by electrolysis on a cathode.
5. Zinc refining by distillation or rectification (as needed).

In the text below, a literary research concerning the given issues is presented.

1.1. Leaching

Jandová, Maixner and Grygar [21] performed experiments of waste galvanic sludge leaching in 0.5 M sulfuric acid at 20 °C temperature with an addition of H_2O_2 oxidation agent. The very leaching was carried out in two different liquid:solid (L:S) ratios, with various pH up to 3.9. The total zinc yield ranged from 63 to 65%. During the subsequent processing of highly acidic leaches the zinc mass yield decreases substantially [21].

Silva, Soares, Paiva, Labrincha and Castro [22] used galvanic sludge that was treated by drying, milling and sieving to particles < 1 mm. The mixing velocity was 700 RPM using a magnetic stirrer. Leaching was carried out in H_2SO_4 at the room temperature under the atmospheric pressure for a period of 24 h. L:S (liquid:solid) = 5:1 ratio appeared to be the most effective condition with the Zn yield of 99.2%. The leaches were analyzed through the AAS method and leaching residues through the X-ray fluorescence spectrometry [22].

Makovskayia and Kostromin [23] leached the sludge samples in 1 M solution of sulfuric acid at pH = 1.5 in 25 °C temperature, for a period of 1 h, with intensive mixing. The obtained leach contained 90% of Zn.

Formánek [24] dealt with the acid leaching of electrode materials from alkaline batteries in 15% H_2SO_4 at L:S = 5:1. He succeeded in transferring 90 up to 98% of Zn into the leach during 60 min independently on the processed fraction composition. Salátová [25] carried out galvanic sludge experimental leaching in 0.5 M H_2SO_4 at pH = 4, L:S = 10:1, 20 °C, for a period of 60 min. The iron was leached only slightly. However, at pH = 1.4, the Fe was transferred into the leach.

Świerk, Bielicka, Bojanowska and Maćkiewicz [26] carried out galvanic sludge leaching in nitric acid at room temperature in 0.02 M HNO_3, 1 M HNO_3 and 8 M HNO_3. The heavy metals contents (Ni, Cu and Cr) were analyzed after different leaching periods. The results have demonstrated that along with the increasing concentration of nitric acid the leached metal amount increases.

Kacinczy et al. [27] performed a leaching of a hot-dip galvanizing plant sludge in 25% NH_4OH in L:S = 7.5:1 ratio at room temperature, for a period of 1 to 2.5 h. The highest zinc mass yield was after 1 h.

A team [28] of Sri Lanka scientists performed experiments with sludge collected from an electro-technical processing plant. The sludge was dried and crushed to a fraction < 1 mm and leached using both organic and inorganic acids. The releasing of metals from the sludge was observed in an environment of three inorganic acids (nitric, sulfuric and phosphoric) and three organic acids (acetic, malic and citric) in concentrations ranging from 0.1 to 2.0 mol/L. Experiments with various L:S ratios were carried out. A key factor for metals is the proper selection of a leaching agent and its ratio to the solid proportion.

A group [29] from Northeast Normal University in China performed a study of galvanic sludge leaching. The sludge was mixed with 3 M HNO_3 and 2 M HCl in the L:S = 1:1 ratio using permanent stirring at 90 RPM and a temperature of 80 °C for a period of 3 h. The leach was collected and analyzed afterwards by the inductively coupled plasma optical emission spectrometer (ICP-OES). The generated acid solution contained Fe, Al and Zn. After hydrothermal processing in the presence of phosphate and glucose more than 99% and 96% of Fe/Al was precipitated effectively. Approximately 98% of Zn remained in the remaining solution which can be neutralized so that Zn can be precipitated as zinc phosphate dihydrate ($Zn_3(PO_4)_2 \cdot 2H_2O$).

Dvořák [30] carried out leaching in the hydrochloric acid at a temperature about 90 °C and also in a solution of 240 g of NaOH/L, for 1.5 to 4 h, at a temperature 95 °C; he reached the Zn yield of 80 to 85%.

A team from the Technical University of Košice [31] dealt with the hydrometallurgical processing of waste galvanic sludge and possibilities of obtaining some metals of interest. On the basis of the experimental results it was confirmed that a maximum extraction of copper and zinc of 90% and 85% can be reached at the room temperature using a sulfuric acid concentration of 0.25 M and L:S = 40:1 ratio just after five minutes. It was revealed that the use of a higher acid concentration is not necessary.

The research concerning the galvanic sludge leaching implies a variety of the used leaching solutions for an effective transfer of zinc, iron and other metals into the leach. In order to separate zinc as a metal of interest from the leach, a further precipitation process needs to be included with the aim to separate zinc from the present metals.

1.2. Precipitation

Aside from the Zn in interest, and/or Mn, acid leaches contain quite a number of impurities that have to be removed during the refining process prior to the final separation of metal Zn or its compounds. These are mainly Fe, Cr, Cu, Cd, Ni, possibly even Mn if a metal of interest is only Zn.

For the Fe removing from the leach, many procedures can be applied: Application of Na_2CO_3 or ZnO neutralization agents at pH = 2.5–3.5 with an addition of 1.5 mL/L H_2O_2 into the leach after acid leaching. Another possibility is the use of KOH or NaOH solutions to achieve pH = 4 to 5, resulting in the precipitation of Fe and some other metals [24]. Bivalent Fe^{2+} has to be converted into Fe^{3+} in the leach, leading to its precipitation in the leaching residue. The following methods have been developed for this purpose: The Goethite process: $2\ FeSO_4 + H_2O_2 + 2\ H_2O = 2\ FeOOH + 2\ H_2SO_4$. The reaction is influenced by a temperature, pH and a slow oxidation of Fe^{2+} ions (optimal pH = 2 to 3.5, a temperature of 70 to 90 °C). ZnO or MgO can be used as a neutralization agent by which 95% of Fe can be removed, and the residual Fe content in the leach is 1 to 0.05 g/L. The Hematite process: $2\ FeSO_4 + \frac{1}{2} O_2 + 2\ H_2O = Fe_2O_3 + 2\ H_2SO_4$. It has a temperature of 170 and up to 220 °C. The initial condition: iron in a form of Fe^{2+}. There is oxidation by oxygen at a pressure of 1.8 MPa up to 3.5 MPa with low pH values. It has good filterability. The H_2SO_4 concentration has to be lower than 50 to 70 g/L, otherwise $Fe(OH)SO_4$ is generated. The Jarosite process: $3\ Fe_2(SO_4)_3 + Na_2SO_4 + 12\ H_2O = 2\ NaFe_3(SO_4)_2(OH)_6 + 6\ H_2SO_4$.

There is good filterability of precipitates, with a pH = 1.5, a temperature of 85 to 100 °C and a need of oxidation of Fe^{2+} ions to Fe^{3+}. It has an effectiveness of 95%.

Lisá [32] carried out the experimental removing of iron from sulfated leaches using the Jarosite precipitation under the following conditions: pH = 1.5 to 2.5, a temperature of 90 °C, and an addition of 100% up to 400% of the stoichiometric amount of Na_2SO_4 with an addition of 20 g/L inoculant. The pH was modified using 25% of NaOH under a simultaneous aeration (formation of Fe^{3+} ions) with an addition of 5 mL of H_2O_2.

The hydrolytic precipitation of Fe in a form of ferric hydroxide can be preferably performed using 50% NaOH at a modification of acid solutions to pH = 4 to 4.5 [25]. However, during this process, Cu, Ni and Co losses occur. Zn and Ni precipitate together at pH = 6 to 8. Al, Cu and Si precipitate at pH = 3 to 7, and Mg and Ca at pH above 8. The optimal pH is 4 to 5 to remove Fe and partly Al and Si.

1.3. Cementation

After Fe precipitation, Cu and Cd can be removed from the leach through cementation using the powder Zn with a 4–5-multiple stoichiometric excess of Zn at pH = 5. The main factors affecting the cementation effectiveness are a cementation agent amount and a temperature. The activated cementation can be performed with an addition of Sb_2O_3. The Ni concentration can be decreased to 1 mg/L through a 10-multiple excess of Zn at 70 °C and pH = 5. Cementation using zinc powder is used in order to remove Cu, Ni, Co and Cd collectively (the reaction catalyst is $CuSO_4 \cdot 5H_2O$), pH = 5. For the galvanic sludge with a high manganese content, the oxidation precipitation using NaClO at pH = 2 can be used [24].

1.4. Electrolysis

Regarding the negative standard zinc potential -0.76 V, the zinc separation by electrolysis needs to be carried out in purified sulfate solutions containing Zn 120–170 g/L. The cathode zinc separation occurs on the cathode by the action of the electric current. For a successful process of the cathode zinc separation with a high current yield, such conditions need to be established, under which the hydrogen development on the cathode does not occur, or its amount is reduced to a minimum. The electrolyte has to be free of all undesirable impurities (see Table 1).

Table 1. Limit contents of elements in solutions for zinc separation by electrolysis [24,33].

Element	As	Sb	Ge	Ni	Co		
Content in leach (wt.%)	0.01–1	0.05–0.1	0.002–0.005	0.05–3.0	0.1–1.0		
Element	**Cu**	**Mn**	**Pb**	**Ni**	**Co**	**Fe**	**Al**
Given range (mg/L)	0.05–0.2	6.5–12	1	0.01–0.5	0.1	0.2–25	10

The recommended parameters for the electrolysis are as follows: 400–700 A/m^2 current density, 2.5 to 3.5 V voltage on electrodes, 35–40 °C temperature of the electrolyte. Cathode current yields range between 90–93%, which mostly depend on the electrolyte purity. For the electrolysis in practice, aluminum cathodes with a thickness of 3 to 4 mm and lead anodes with an addition of Ag 1 wt.% and with a thickness of 5 to 8 mm are used, which reduces corrosion while increasing the anode operating life. The obtained zinc reaches as high as 99.9% Zn purity and does not need to be further refined. The cathode zinc can be further re-melted in furnaces and cast into ingots. In order to achieve higher zinc purity, an additional refining through rectification needs to be performed.

Ubaldini [34] recommends the following conditions for Zn electrolysis: voltage between the cathode and the anode of 3.8 V; current density of 120 A/m^2; pH = 5; the electrolyte temperature of 95 °C, a time period of 8 h, mixing at 200 RPM. Freitas [35] carried out the electrolysis at Zn content in the electrolyte of 9.2 g/L and 49 g of H_2SO_4/L; 150–270 A/m^2; 25 °C temperature; 80% current efficiency.

Formánek [24] used the following electrolysis conditions: voltage of 3.8 to 4.2 V, current density of 120 to 300 A/m^2, pH = 5, a time period of 8 h and mixing at 200 RPM. On the basis of the discovered findings, it was recommended to apply a slightly to strongly acidic electrolyte, a current density of 400–600 A/m^2, a temperature up to 40 °C, an application of electrodes with a smooth surface and a reduction in the presence of impurities in the electrolyte.

The Zn electrolysis from alkaline solutions exhibits a lower sensitivity to a content of impurities, which have a lower consumption of electrical energy. The Zn concentration is 8 up to 25 g/L with a NaOH concentration of 80 up to 320 g/L, and a current density of 50–200 A/m^2 with a temperature of 30 to 40 °C. The separated Zn is of a spongy structure, a current efficiency of 97% at 30 °C and 100 up to 150 A/m^2. For the electrolysis, it is advisable to add approximately 50 mg of glue per 1 liter of the electrolyte for higher quality of the separated zinc without dendrites.

Gürmen and Erme [36] dealt with an influence of a current density, temperature and concentration of impurities on the separated Zn quality. They used the electrolyte with the following composition: 25 g Zn/L, 240 g NaOH/L and voltage about 3 V. There is a cathode of a stainless plate, with the anode of Ni plate. Brown et al. [37] carried out experiments with 75 g of Zn/L, and 25% of NaOH with bubbling air through the electrolyte for the purpose of Mn and Fe oxidation. Cu, Cd and Pb were removed through cementation in the previous step.

In accordance with the legislation of the European Union the goal of the entire project was to find ways for a waste-free economy, a maximum use of secondary raw materials and, if possible, a closed cycle for the processing of galvanic sludge, which belongs to the category of hazardous waste. At the same time, a relatively high zinc content primarily gives a chance for obtaining it from a "rich source".

2. Materials and Methods

Experimental works were carried out within the framework of the project of the Technological Agency of the Czech Republic No. SS01020312, "Innovative technology of the closed loop water circulation in the electro-galvanizing process and processing of metal waste—sludge and filtration cakes from the galvanizing plant". Galvanic sludge samples were obtained from six galvanizing plants that were taken in various campaigns within the years 2020–2022. The results of the analyses of the samples delivered from six companies marked with different letters are given in Table 2. A significant difference in the concentrations of particular elements can be noticed here. Therefore, a design of an optimal procedure for the sludge processing using the hydrometallurgical process will be demanding for obtaining the adequately pure zinc through recycling. An average zinc content in the sludge was about 15 wt.%, which is a value interesting enough for its regaining. Iron concentrations were approximately 6 wt.% in average. From an economical point of view, this is a rather low value for its subsequent obtaining. There has been an extraordinarily high manganese content found out in one company, which relates to the manufacturing technology. In addition, the processing of the sludge with such a high manganese content using hydrometallurgical processes is difficult, and a different recycling technology would have to be developed.

The first step in galvanic sludge processing is the leaching process. An appropriate leaching agent needs to be chosen. Three kinds of acids were selected: sulfuric acid, nitric acid and hydrochloric acid, which were diluted adequately. Further, a temperature, leaching period and L:S ratio needs to be selected. The hydrogen peroxide (30% H_2O_2) or ozone O_3 was occasionally used as an oxidation agent for leaching. The ozone was produced in a concentration of 140 mg/L, and a volume of feed gas was 8 l/min (device Korona L20 SPALAB generator, Narutowicza 94/96 97-300 Piotrków Trybunalski, Poland). Mixing was often problematic due to a consistency of some sludge. In the first phase before leaching, the sludge were dried at a temperature about 105 °C, crushed to finer fractions

and weighed. For separating the leach from the leaching residue, the classical filtration through filter papers or fritted glass was used.

Table 2. Chemical analysis of the sludge delivered from 6 companies—ED-XRF (wt.%).

Firm	Zn	Fe	Cr	Mn	Cu	Ni	Co	Sn	Pb
D20	15.9	12.3	0.08	0.07	0.01	-	-	-	-
D21	11.3	7.1	0.1	0.08	0.1	-	-		-
D22	9.5	0.9	0.51	-	-	-	0.11	-	-
D22A	5.4	4.1	0.1	0.08	0.1	-	-	-	-
H19	23.6	3.9	0.2	-	0.08	0.01	-	-	-
H20	21.7	4.3	0.1	0.04	0.03	0.01	-	-	-
H21	15.8	2.7	0.5	0.03	-	-	0.23	-	-
H22	9.4	11.5	0.18	0.17	-	-	-	-	-
B20	35.5	3.9	0.7	0.08	0.07	0.01	-	-	0.01
B21	19.4	3.1	0.1	0.1	0.1	-	-	-	-
P20	4.5	5.2	0.3	8.4	0.2	0.4	-	0.08	0.01
P21	6.75	4.3	0.2	13.08	0.2	0.6	-	0.1	-
K20	12.6	10.5	2.1	0.2	1.3	1.8	-	0.01	0.3
K21	10.4	7.1	1.8	0.14	0.3	1.7	0.1	-	0.1
O20	28.7	7.5	1	0.07	0.05	0.01	-	-	0.02

Note: The results of the analyzes are only indicative and can be used as comparative analyses.

The leaches were subjected to chemical analyses using AAS (Atomic Absorption Spectroscopy) and ICP-AES (Inductively Coupled Plasma—Optical Emission Spectroscopy). For the analysis of leaching residues and solid samples, ED-XRF (Energy Dispersive X-ray Fluorescence Analysis) was used (Delta X mobile X-ray spectrometer, BAS Rudice s.r.o., 678 01 Blansko, Czech Republic). An X-ray diffraction analysis for a presence of phases in the sludge and leaching residues was applied as well. Everything was documented in photographs.

In order to support a process of precipitating undesirable metals, in particular, of iron, a solution of ammonia NH_4OH, sodium hydroxide or potassium hydroxide and sodium carbonate Na_2CO_3 with the addition of H_2O_2 was applied for a transformation of divalent iron Fe^{2+} in leaches into a precipitate of trivalent iron Fe^{3+}. Considering the fact that the leaching was performed in a highly acidic environment (pH was around zero), the pH of the leach needs to be modified to values around 3, when iron and other elements precipitate.

The electrolysis was performed in laboratory conditions at a 4 V voltage and current at about 1 A at room temperature. The electrolysis time period was chosen according to the very process of the zinc separation on the cathode. The cathode was made of thin plates of various materials in accordance with the electrolyte chemical composition. The same was also applied for the anode. For the electrolysis of the leach obtained after leaching in H_2SO_4, the cathode was made of an Al plate, or possibly an Zn plate. The anode was made of Pb. In a case of the use of HCl acid, the anode and cathode were made of graphite materials that proved themselves in terms of their inertness towards the given electrolyte. The zinc ions contents were fluctuating. All depended on the delivered sludge sample and the used leaching agent.

3. Results

Figure 2 shows galvanic sludge samples after drying before a subsequent leaching. On the left-hand side, you can see the input material—sludge from galvanic plants, on the right-hand side—sludge after drying-up and milling.

Figure 2. Preparation of samples for leaching—on the left: the delivered samples, on the right: sludge after milling and drying-up. Source: own.

An X-ray diffraction analysis of the P20 sample for a presence of various phases was carried out—see Figure 3. The results of the diffraction analysis demonstrate a presence of zincite ZnO, zinc hydrogen sulfate $Zn(HSO_4)_2$, calcite $CaCO_3$, caoxite $Ca(C_2O_4) \cdot H_2O$, and franklinite $ZnFe_2O_4$.
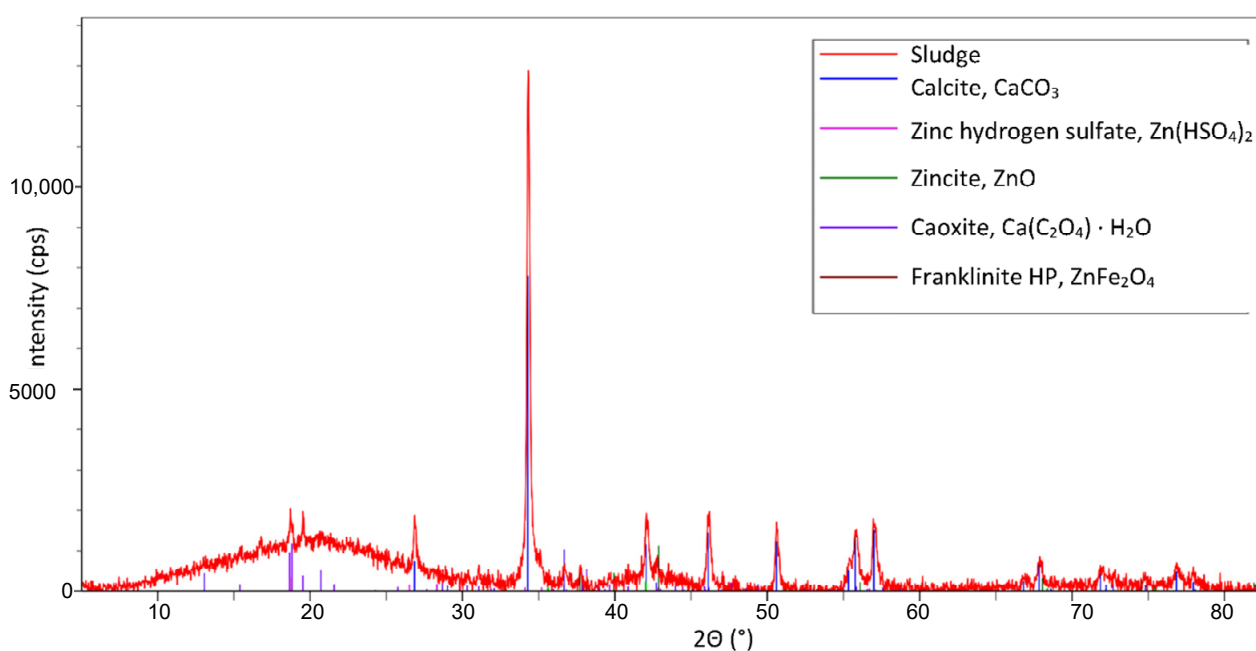
Figure 3. X-ray diffraction analysis for a presence of phases in the sludge sample from P20 supplier.

Leaching solutions were prepared from concentrated acids by dilution. The initial concentration of acids was 93% for sulfuric acid, 65% for nitric acid and 35% for hydrochloric acid. The acids were diluted in accordance with the performed calculations, the sulfuric acid solution to 18% or 20%, the nitric acid solution to 12% and the hydrochloric acid solution to 7% or 15%.

The samples were leached using three methods: leaching without an oxidation agent addition, with the hydrogen peroxide addition or with ozone blowing. Two temperatures of 40 and 60 °C were used for each acid. The weighed amounts and volumes were:

(a)   A total of 50 g of a sample and 200 mL of an acid;

(b)   A total of 50 g of a sample and 200 mL of an acid with an addition of 20 mL of hydrogen peroxide of 29–32% concentration;

(c)   A total of 50 g of a sample and 200 mL of an acid, and ozone was blown into the sample.

In order to compare the effectivity of leaching in the acids, leaching in distilled water was carried out as well.

Leaching parameters were given by a number of revolutions of a mixer, a time period, a leaching agent amount, a temperature and an oxidation agent addition.

For each solution the leaching was performed for a period of 6 h. A total of 5 mL of the leach was taken off every two hours. After the sampling, the pH was always measured and represented one of the leach properties. After the last sampling, the remaining leach was separated from the leaching residue by filtration. After having been dried-up, the leaching residue samples were further subjected to crushing. Their orientation analysis using the X-ray fluorescence spectrometry was carried out. Each sample was analyzed three-times, and the measurement was always performed on a different part of the analyzed sample.

The results of D20 sample leaching are shown—see Figure 4.
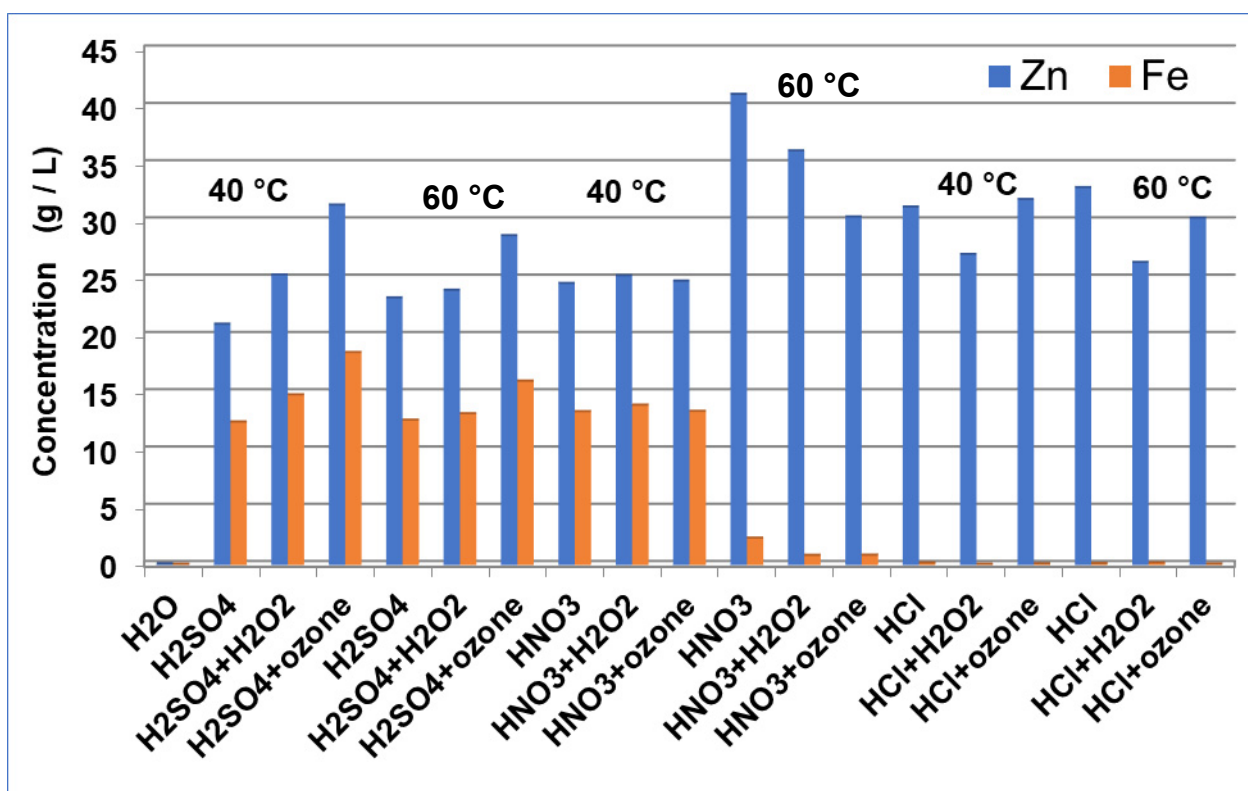
Figure 4. Effectiveness of leaching of Zn and Fe (sludge) D20 depending on the type of leaching agent, additives and temperature (g/L).

By leaching in sulfuric acid, a lower zinc mass yield was reached than in nitric acid, but it had the highest iron yield. The results were similar for higher temperatures.

When using nitric acid as a leaching agent, it was found that better results were achieved at a lower temperature, when both metals were precipitated at a temperature of 40 °C. At a higher temperature, there are noticeable changes only for zinc, and the iron was dissolved only slightly.

When hydrochloric acid was applied, the zinc was obtained in a similar amount as in a case of sulfuric acid. In this case, the iron was not precipitated. The chosen leaching temperatures do not influence the amount of precipitated zinc.

An addition of oxidation agents H_2O_2 and ozone demonstrated a favorable effect only for leaching in H_2SO_4.

On the basis of preliminary results given in Table 2 (chemical composition of input materials) experiments with leaching in H_2SO_4 were carried out with different concentrations of the acid, at temperatures of 40 °C and 60 °C and with the additions of H_2O_2 or O_3. Sampling was always carried out after 2, 4 and 6 h. The results of the analyses of the leaches are documented in Table 3. Prior to the AAS analysis, into the taken-off sample, a certain amount of nitric acid was added in order to stabilize the solution [38].

Table 3. Content of zinc and iron in the leach in dependence of concentration and temperature of H_2SO_4, time of leaching at addition of H_2O_2 or O_3. Sample: H21.

40 °C, 10% H_2SO_4			60 °C, 10% H_2SO_4		
Addition, Time	**Zn (mg/L)**	**Fe (mg/L)**	**Addition, Time**	**Zn (mg/L)**	**Fe (mg/L)**
H_2O_2, 2 h	10,800	0.8	H_2O_2, 2 h	16,400	4.5
H_2O_2, 4 h	11,100	2.8	H_2O_2, 4 h	24,400	15.8
H_2O_2, 6 h	11,400	5	H_2O_2, 6 h	36,100	18.6
O_3, 2 h	18,600	4.7	O_3, 2 h	17,300	344
O_3, 4 h	19,900	76	O_3, 4 h	22,300	820
O_3, 6 h	20,000	2150	O_3, 6 h	23,200	4360
40 °C, 30% H_2SO_4			**60 °C, 30% H_2SO_4**		
Addition, Time	**Zn (mg/L)**	**Fe (mg/L)**	**Addition, Time**	**Zn (mg/L)**	**Fe (mg/L)**
H_2O_2, 2 h	40,200	6980	H_2O_2, 2 h	47,500	8480
H_2O_2, 4 h	31,600	5781	H_2O_2, 4 h	35,400	6890
H_2O_2, 6 h	31,700	6200	H_2O_2, 6 h	43,700	8420
O_3, 2 h	29,700	5140	O_3, 2 h	32,400	7260
O_3, 4 h	19,500	3660	O_3, 4 h	27,920	5200
O_3, 6 h	15,600	4000	O_3, 6 h	13,700	4360

Table 3 shows that a higher concentration of sulfuric acid and a higher temperature causes a more complete dissolution of Zn as well as Fe; however, Zn and Fe concentration decreases in time. Hydrogen peroxide added during the leaching process was more effective in the 30% H_2SO_4 environment than ozone. On the other hand, ozone was more active during leaching in 10% H_2SO_4. In any case, the oxidation agent had positive effect in the leaching process. However, aside from Zn and Fe, other metals also present in the galvanic sludge are transferred into the leach.

Table 4 implies that leaching in 10% H_2SO_4 does not reach a high efficiency for zinc dissolving, and its transfer into the leach and more or less does not depend on the used temperatures. A positive effect of ozone was demonstrated itself for both the concentrations of H_2SO_4 in a case of zinc and iron and also for other found out metals. Some other metals were identified in leaching residues on a level of tens of ppm.

Table 4. Measured values of concentrations of elements in leaching residues for H21 samples (wt.%), ED-XRF method.

	10% H_2SO_4				30% H_2SO_4			
	H_2O_2		O_3		H_2O_2		O_3	
Element	**40 °C**	**60 °C**	**40 °C**	**60 °C**	**40 °C**	**60 °C**	**40 °C**	**60 °C**
Cr	0.54	0.58	0.17	0.18	0.16	0.12	0.07	0.03
Fe	3.25	3.58	2.75	2.39	0.86	0.38	0.26	0.11
Cu	0.04	0.03	-	-	-	-	-	-
Zn	15.21	12.61	2.11	2.08	5.47	2.26	1.76	1.21
S	10.67	12.9	14.92	15.35	20.26	23.42	23.04	23.06
Co	0.13	0.09	-	-	0.09	0.04	-	-

In the next step, all the delivered sludge samples from 2021 were subjected to leaching under the following conditions: 100 g of sludge after crushing and drying-up, leaching in 400 mL of 20% H_2SO_4, a temperature of 50 °C, a total period of leaching 5 h with sampling after 2 and 5 h, and an addition of 40 mL of H_2O_2.

For some samples after leaching in 20% H_2SO_4 (see Figure 5), a lower content of zinc and iron (D21, H21 and B21 samples) was observed after 5 h leaching than after 2 h. It was caused by the evaporation of the sulfuric acid leaching solution. After the 1st sampling after 2 h, the bath was supplemented with 20% of sulfuric acid to the initial volume of 400 mL. The pH was measured after the filtration in all the leaches (at a temperature of 25 °C).
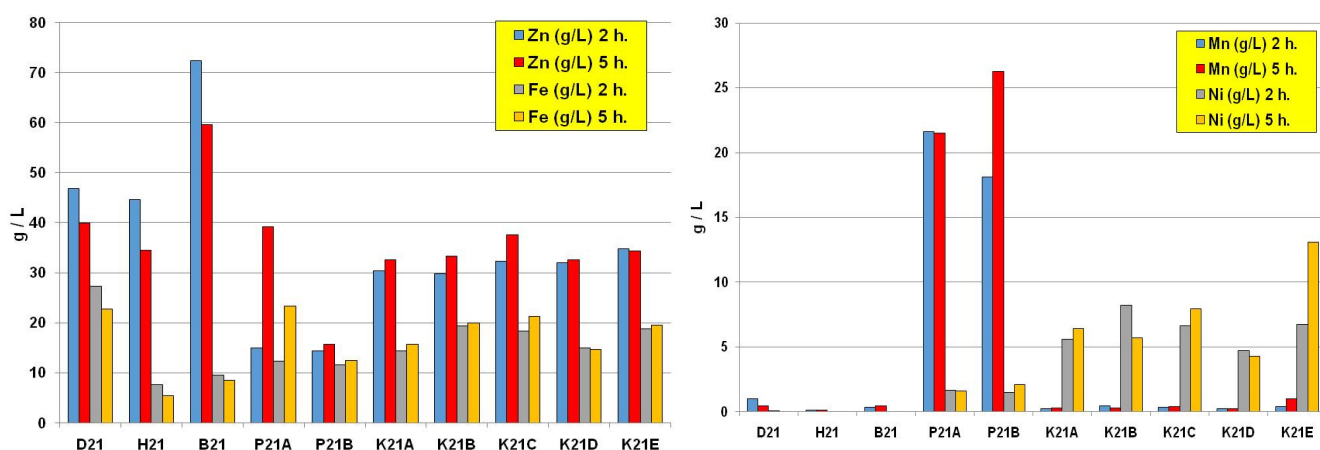
Figure 5. AAS analyses of leaches after sludge leaching in 20% H_2SO_4 after 2 and 5 h.

Table 5 shows that even for leaching residues, there are differences in concentrations of particular metals depending on a supplier and on a time of sampling during the leaching process after 2 h and 5 h. Along with an increasing time of leaching, a content of elements in leaching residues is mostly higher after 5 h than after 2 h thanks to an addition of a fresh acid.

Table 5. ED-XRF results of leaching residues (wt.%) after leaching of various kinds of input sludge (20% of H_2SO_4, 50 °C and an addition of 40 mL of H_2O_2 depending on a time of sampling of 2 or 5 h).

Sample	Time	Zn	Fe	Cr	Mn	Cu	Co	Ni	Sn	Pb
D21	2 h	4.83	3.05		0.04	0.02				
	5 h	5.98	3.67		0.04	0.03				
H21	2 h	2.75	0.53	0.05						
	5 h	3.7	0.66	0.08			0.05			
B21	2 h	7.88	3.35	0.03	0.04					
	5 h	7.02	2.48	0.03	0.03					
P21A	2 h	1.33	1.39	0.02	2.01	0.04		0.11	0.04	
	5 h	2.79	2.26	0.11	3.79	0.07		0.23	0.03	
P21B	2 h	1.58	1.71	0.05	2.56	0.04		0.14	0.04	
	5 h	3.76	3.59	0.21	4.36	0.1		0.39	0.04	
K21A	2 h	2.22	1.24	0.26	0.03	0.11		0.55		0.09
	5 h	3.2	1.64	0.42	0.03	0.13	0.06	0.73		0.1
K21B	2 h	2.31	1.79	0.42	0.03	0.16		0.65		0.43
	5 h	2.96	2.12	0.54	0.04	0.18		0.7		0.45

Table 5. *Cont.*

Sample	Time	Zn	Fe	Cr	Mn	Cu	Co	Ni	Sn	Pb
K21C	2 h	2.22	1.69	0.36	0.03	0.18		0.63		0.48
	5 h	2.71	1.92	0.5	0.03	0.17		0.57		0.45
K21D	2 h	1.94	1.37	0.17		0.1		0.47		0.09
	5 h	2.65	1.37	0.31	0.02	0.09	0.05	0.45		0.07
K21E	2 h	1.83	1.33	0.22	0.02	0.08		0.4		0.45
	5 h	3.94	2.62	0.54	0.06	0.1		0.54		0.34

Based on the results of analyses of the leaching residues given in Table 4 (a condition after 5 h) and analyses of the entry materials a mass yield of Zn and Fe was calculated after leaching [39]—see Table 6.

Table 6. Calculation of zinc and iron mass yield at leaching in 20% H_2SO_4; extractable degree (grey coloring) results in wt.%.

Sample	Zn (%)	Fe (%)	Zn (%)	Fe (%)
D21	52.9	51.7	47.1	48.3
H21	23.4	24.4	76.6	75.6
B21	40.6	95.7	59.4	4.3
P21	41.3	52.6	58.7	47.4
K21-1	35.1	30.9	64.9	69.1
K21-2	27.4	25.9	72.6	74.1
K21-3	29.3	23.1	70.7	76.9
K21-4	28.9	27.4	71.1	72.6
K21-5	29.0	29.8	71.0	70.2

A residue of a metal in the leaching residue was calculated as a ratio of a metal concentration in the leaching residue and its content in the initial sludge sample. During the performed experiments, 59% of Zn and 54% of Fe were transferred into the leach, on average. Therefore, the leach will need to be subjected to a further chemical process with the aim to separate zinc in the leach from other present metals, which were also transferred into the solution, and to increase the zinc mass yield in the leach.

Regarding the fact that the leaches contained a relatively high amount of other metals that could make problems during the electrolysis, the zinc separation from other elements during the process of subsequent processing should be as effective as possible.

After leaching in sulfuric acid the samples were subjected to further refining for the purpose of Zn separation from other admixtures. In the first phase, the precipitation using the ammonia solution was used according to the following scheme:

(a) Leaching of 10 g of sludge from different companies in 100 mL of 20% H_2SO_4 for a period of 4 h.
(b) Separation of the liquid and solid phase through the filtration.
(c) The undissolved fraction was washed by distilled water and dried-up at 110 °C for a period of 4 h.
(d) Afterwards, the filtrate was precipitated in 150 mL of 25% solution of NH_4OH.
(e) The leach was oxidized in 20 mL of H_2O_2 for a period of 3 h and the formed precipitate was subsequently washed and dried-up at 110 °C.
(f) The samples of the particular filtrates were analyzed using the AAS method for zinc and iron content—see Table 7.

Table 7. Zn and Fe contents in the leach (filtrate) after leaching and subsequent precipitation using ammonia (mg/L).

Firm	Zn	Fe	Ni	Cu
O21	3390	220	-	3.0
H21	8770	360	2.1	4.8
B21	11,570	200	2.6	5.2
K21	4230	180	780	260

Table 8 below shows the results of ED-XRF analyses of solid fractions after leaching (leaching residue) and after the precipitation using ammonia.

Table 8. ED-XRF analysis for Zn, Fe and Cr (wt.%) of leaching residues and precipitates after refining using ammonia (an average of three measurements). Other elements (with grey color) are in wt. ppm.

Sample	Zn	Fe	Cr	Mn	Co	Ni	Cu	As	Zr	Mo	Pb
O20-2	0.08	0.41	-	121	-	-	110	126		280	953
O20-4	5.43	19.13	1.17	2673	-	118	113	67	26	634	20
H21-2	0.032	0.22	-	-	-	-	20	-	17	322	12
H21-4	10.03	15.87	2.02	1170	7986	-	212	59	118	460	135
B21-2	0.63	3.67	0.03	64	-	67	50	-	151	161	61
B21-4	20.09	11.43	2.03	1820	-	53	304	94	120	427	28
K21-2	0.05	0.35	-	-	-	177	567	148	20	19	6935
K21-4	5.09	26.79	2.69	3891	-	7564	3438	42	20	318	426

Note: The first letter and two numbers in the left-hand column designates a company brand, number 2 designates the leaching residue and number 4 designates the solid fraction formed after the precipitation using ammonia.

Table 8 clearly shows a high effectiveness of the leach precipitation using ammonia. In the precipitate, there were the more or less concentrated elements of Fe, Cr, Mn, Co, Ni, Cu and Mo, including zinc, which is undesirable in this case because Zn is our metal of interest. A comparison of the concentration of elements in the leaching residue and in the precipitate shows an increase in concentrations by as much as two orders of magnitude for Zn, Fe, Cr and Mn, in most of the cases. Such a result is disadvantageous for the further processing of the leach through the electrolysis by reason of a loss of a high amount of zinc from the leach.

Two electrolysis experiments (H21 company) were carried out as follows: 100 g of the sludge sample were dissolved in a 2000 mL capacity beaker in a 20% (or 10%) H_2SO_4 solution of 1000 mL volume for a period of 4 h. After leaching, the solution was filtered and rinsed by 300 mL of distilled water on a fritted glass with a vacuum filtration. A solid proportion was weighed after having been dried-up to 72.8 g (or 73.21 g). The filtrate was evaporated to 1000 mL volume and after cooling down was precipitated by a 25% solution of NH_4OH (250 mL), when $Fe(OH)_3$ was precipitated in the form of a ferruginous precipitate. To accelerate oxidation, the 30% H_2O_2 in a volume of 5 mL was added for a reaction period of 3 h and the solution was gravitationally filtered afterwards. The rinsed precipitate was dried-up at a temperature of 110 °C for a period of 24 h and weighed: 53.21 g (or 55.12 g). The filtrate was diluted by distilled water to a volume of 3000 mL (or 2000 mL) and subjected to the electrolytic precipitation of zinc. The electrolyte temperature was 30 °C, 3 V voltage and 0.8 A current. The cathode in a form of a plate (5 mm thickness) was made of pure Al, the anode was made of a Pb plate. The precipitated Zn was removed from the cathode, filtrated, rinsed, dried-up, weighed and subsequently chemically analyzed. During the electrolysis, the pH of the solution was 7 (or pH = 8). The second experiment resulted in a higher zinc yield after the electrolysis. The analyses' results of the samples taken off continuously during the experiments are given in Table 9.

Table 9. Results of chemical analyses of solid samples (Zn and Fe in wt.%; other elements marked with grey color in wt. ppm)—an average of three measurements (supplier H21).

Sample	Zn *	Zn	Fe *	Fe	Mn	Ni	Co	Cu	Pb	Cr	Hg
Input	21.7 *	20.7	4.3 *	4.35	536	54	875	128	<20	3300	0.021
After leaching	1.8 *	3.4	2.34 *	2.76	392	77.3	3910	30.7	84.9	920	0.035
After Fe precipitation	6.57 *	6.88	13.5 *	16.9	2270	34.7	2250	35.0	31.4	5870	0.013
After electrolysis	48.6 *	59.3	0.19 *	<0.01	53.8	592	6230	959	614	93	0.08

Methods of the analyses: ICP AES, US EPA apparatus and 6010 method. Mercury was determined by AMA 254 device. ED-XRF X-ray spectrometry—Delta X instrument (analyses marked with *).

Table 9 evidently shows that the leach precipitation using ammonia after leaching resulted in a concentration of more or less all elements including zinc in the precipitate. The cathode zinc of 60% purity was obtained through the electrolysis. However, a presence of Co (0.6 wt.%), Cu (0.1 wt.%), Ni and Pb (à 0.06 wt.%) was identified here as well. Iron was not contained in the cathode zinc.

Conditions of the third electrolysis experiment: Dissolution of 100 g of the sludge (B21 supplier) in 10% solution of H_2SO_4. The solid fraction was weighed after having been dried-up (60 g). The filtrate was precipitated using 25% solution of NH_4OH (250 mL) to $Fe(OH)_3$. After having been dried-up, the precipitate had a weight of 67.4 g. The electrolysis was carried out under the following conditions: a bath temperature of 30 °C, 3 V voltage, 0.8 A current and pH = 8. The precipitated Zn with significant dendritic sections was removed from the aluminum cathode, and its weight was 7.93 g. A photographic image of the product after the electrolysis is shown in Figure 6, below [40].

Figure 6. Photo documentation of the precipitated zinc on the cathode after the electrolysis [40]—sample B21. The appearance of cathode zinc with dendritic formations after the electrolysis has been documented. Conditions at the electrolysis are above in the text. Source: own.

In another experiment, a cathode mass of a chemical composition given in Table 10 was obtained. Zn concentration was almost 50%; however, a high Cr content (3.2 wt.%) was found out. Cu, Cd and Pb were below a level of 1 wt.%. These analyses imply that further refining procedures will need to be brought into focus.

Table 10. ED-XRF analysis of the cathode mass after the electrolysis (input sludge—B21 supplier). (wt.% Zn, Fe, Cr, Co; wt. ppm, Mn, Ni, Cu, As, Zr, Mo, Cd, Sb and Pb— grey color).

Sample	Zn	Fe	Co	Cr	Mn	Ni	Cu	As	Zr	Mo	Cd	Sb	Pb
After electrolysis	48.6	0.19	3.64	3.17	249	1621	8533	741	487	1650	5850	1225	9631

Within the experiments mentioned above, the aim was to find optimal conditions for the leaching of the galvanic sludge with a high Zn and Fe content obtained from six different galvanizing plants. Sulfuric acid was applied at different temperatures and time periods of leaching, possibly with an addition of H_2O_2 or ozone. For the separation of Zn and Fe ammonia was used, and also when iron precipitation in a form of $Fe(OH)_2$ occurred, or $Fe(OH)_3$ after adding H_2O_2. The results unambiguously confirmed the Zn separation from Fe in the filtrate—see Table 11. During the subsequent electrolysis, different conditions were tested. An optimal electrolyte temperature seems to be 30 °C, with a voltage of 3 V, a current of 0.8 A and pH = 8. The obtained product on the cathode contained 58 wt.% of Zn, and the Fe content was neglectable. In this phase the experiments were carried out in the laboratory scale.

Table 11. Chemical composition of the electrolyte before and after the electrolysis process—AAS analysis (mL/L); input sludge—B21 supplier.

Sample	Zn	Fe	Pb	Cu	Ni	Mn	Cr	Cd
Before electrolysis	4060	0.54	8.9	0.89	1	0.43	0.52	3
After electrolysis	1750	0.26	3.3	0.15	-	0.38	<0.1	0.25

During further experiments after leaching in H_2SO_4 and the following precipitation using further agents, such as KOH, NaOH, Na_2CO_3, in the best case the cathode zinc purity was achieved on a level of 79 wt.%. The precipitation process is highly sensitive to the gradual adding of a precipitating agent. During the very leaching in the acidic environment, the pH ranges between 0 to 1.6, whereas during the precipitation pH needs to be achieved higher than 3, i.e., the sphere of Fe^{3+} separation from the leach in a form of a precipitate. The liquid phase separation from the solid one is highly complicated by reason of the precipitate consistency, which is often in a gelled form. The same also applies for the leaching of some galvanic sludge from suppliers. Moreover, a noticeable foam formation occurs particularly after an addition of hydrogen peroxide. The Jarosite precipitation method was also used (see the research); nevertheless, a modification of pH is considerably sensitive when the pH increase occurs in a jump after achieving the neutralization state. However, a complete precipitation of iron and other metals present in the sludge, which influences the very electrolysis process negatively, is not guaranteed. At a higher iron content in the electrolyte, the process of zinc separation on the cathode is substantially limited and the zinc yield is low.

Based on the above-mentioned findings, the experiments with pure metals were carried out afterwards—cathode zinc (99.5%) and iron (c. 99%), which were dissolved in diluted H_2SO_4 and HCl acids for the purpose of the optimization of leaching and subsequent electrolysis. Zinc weighed amounts were about 2.5 g. Dissolving of the pure electrolytic (cathode) iron in H_2SO_4 failed, however, in the HCl acid, the results were positive. For Zn dissolving in HCl acid and the subsequent electrolysis, graphite electrodes were used as a cathode as well as an anode. For the electrolysis of Zn solution in H_2SO_4, an Al plate was used as a cathode (a smooth surface was necessary, and the presence of an Al_2O_3 layer was appreciated). The anode (pure lead) in the strongly acidic environment was corrosively attacked—tiny Pb grains were found on the beaker bottom after finishing the electrolysis process. For analyses, these methods were used: AAS (for solutions) and ED XRD (for solid phases). After the electrolysis, the cathode zinc mass yield was over 87% for both the acids, when pH was about 0.5—see Table 12. The obtained zinc purity was between 99% in the

case of leaching in HCl acid and 87% for H_2SO_4, when sulfur was also identified in the product (over 10%). In all three cases, the zinc was segregated on the cathode in the form of dark small grains—see Figure 7 on the left. On the right-side the cathode Zn in the flask before ED-XRF analysis is documented.

Table 12. AAS analysis results—a condition after dissolving in acids and after the electrolysis.

Sample	Zn (g)	Solution	Zn before (mg/L)	Zn after (mg/L)	pH before Electrolysis	pH after Electrolysis	Zn Cathode (g)	Recovery Ratio (%)
M	2.28	100 mL 20% HCl	23,400	357	−0.01	1.81	1.98	86.8
O	2.71	100 mL 20% H_2SO_4	29,700	915	0.54	0.45	2.36	87
P	2.47	100 mL 20% H_2SO_4	27,400	973	0.63	0.52	2.26	91.5
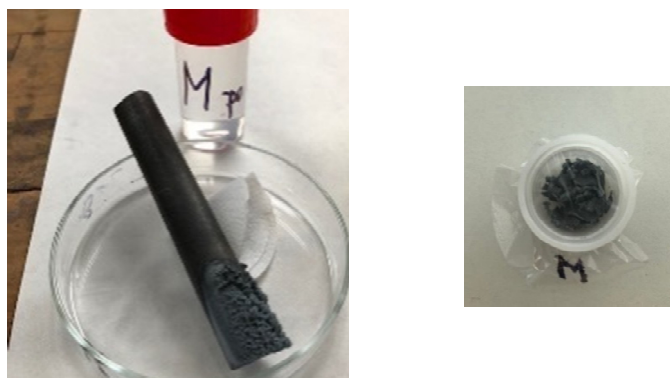
Figure 7. Segregated zinc on the graphite cathode (the electrolyte: HCl solution) on the left side—sample M (see Table 12). Cathode zinc in the flask for ED-XRF analysis. Source: own.

Other "pure" experiments were performed using chemically pure compounds containing zinc and iron. A total of 24.9 g of oxide zinc ZnO, which corresponds to 20 g of zinc content, were dissolved in 200 mL of a solution of 20% H_2SO_4 at room temperature. Dissolving was easy and relatively fast. The process had to simulate the dissolving of galvanic sludge, in which zinc occurred in a form of chemical compounds, mostly Zn oxides. Further, the $ZnSO_4.7H_2O$ compound was used of a weight of 41.5 g, which corresponds to 10 g of pure zinc for leaching in 20% H_2SO_4 (100 mL). In order to create a solution with iron 25 g of $Fe_2(SO_4)_3 \cdot 9H_2O$ was applied, which corresponds to 5 g of elementary iron, also in 100 mL of 20% H_2SO_4. In both the cases, dissolving was slow. Both the solutions were mixed.

The solutions prepared this way were subjected to the electrolysis under the following conditions: the electrolyte volume of 140 mL, pH = 0.5 (Zn solution) and pH = 0.11 (Zn + Fe solution), 4 V voltage, 1 A current, the cathode of Al plate, the anode of Pb plate and a time period of the electrolysis—5 h. In the case of the electrolyte with Zn, 5.5 g of zinc of 95.6% purity (the rest was sulfur) was obtained on the cathode. At the electrolysis of the Zn + Fe solution with Zn:Fe = 2:1, ratio only 0.15 g of Zn was segregated on the cathode. This proves a harmful effect of the Fe presence in the electrolyte upon a resulting product and the process efficiency. As stated in the theoretical part, Fe concentrations in the electrolyte are strictly limited. Even the Jarosite method of iron precipitation with the application of 140 mL of $(NH_4)_2SO_4$ solution did not result in positive results. The pH increased to a 0.69 value and after an addition of 10 mL of H_2O_2, the solution became brown; thus a part of Fe became precipitated.

At acidic leaching, the metal components in the sludge are dissolved and transferred into the leach, including high contents of Fe that have to be eliminated prior to the very electrolysis through complicated and slow processes. This considerably extends the time for sludge processing and deteriorates the zinc mass yield at the electrolysis. Moreover, in

the precipitation, a part of zinc transfers from the leach into the solid fraction and thus it is irrecoverably lost.

In the next step, the leaching of galvanic sludge from two suppliers, D21 and H21 (see Table 2), in various environments was tested, i.e., in a HCl solution (25 °C), H_2SO_4 (40 °C) and NaOH (60 °C) for a period of 4 h under the conditions given in Table 13. The results of the AAS analyses of the leaches are also demonstrated here; these results imply higher Zn concentrations in the leach for H21 supplier, which is related to a higher zinc concentration in the used galvanic sludge. However, a fact has been proven again that in the acidic leaching, the high iron content transfers into the leach, and the other metals Cr, Mn, Cu and Ni have been identified here as well. In the case of leaching in NaOH, only a negligible amount of Fe is present in the leach, and the other metals were below a measurability limit. An environment with high pH considerably hampers the dissolving of most metals except zinc, which is a desirable intermediate product for further processing. The leaches were subsequently separated from the leaching residues by a filtration. The results of analyses of the leaching residues using ED-XRF are given in Table 14, which implies that approximately 2 to 3 wt.% of zinc remained unleached in the sludge. The most effective leaching with regard to Zn and Fe was carried out in the H_2SO_4 solution.

Table 13. The pH values and the results of AAS analyses of the leaches (mg/L) after leaching in HCl, H_2SO_4 and NaOH.

Sample	pH	Volume	Sludge	Zn	Fe	Cr	Mn	Cu	Ni
D21—15% HCl	0.39	1000 mL	250 g	11,500	7990	243	116	21.9	6
H21—15% HCl	0.59	1000 mL	250 g	31,500	5970	1150	60	41.2	13
D21—20% H_2SO_4	0.96	1000 mL	250 g	12,500	8860	318	155	27.1	8
H21—20% H_2SO_4	1.28	1000 mL	250 g	36,100	6780	1100	70	45.9	13.7
D21—25% NaOH	13.69	1000 mL	250 g	13,200	12	-	-	12	6
H21—25% NaOH	13.81	1000 mL	250 g	38,800	5	-	-	-	-

Table 14. The analyses results of the leaching residues—ED-XRF (wt.%).

Sample	Zn	Fe	Mn	Cr	Al	Co
D21—15% HCl, 25 °C	3.48	3.31	0.03	0.05	-	-
H21—15% HCl, 25 °C	3.77	0.83	-	0.08	-	-
D21—20% H_2SO_4, 40 °C	1.80	1.1	-	-	-	-
H21—20% H_2SO_4, 40 °C	2.42	0.52	-	0.02	-	-
D21—25% NaOH, 60 °C	2.45	5.92	0.09	0.15	0.17	-
H21—25% NaOH, 60 °C	2.42	1.80	-	0.16	-	0.05

Table 15 shows the analyses results of the electrolytes after finishing the electrolysis. A comparison of the contents of particular metals in the electrolyte and the leach implies that in the case of leaching in acids, a significant part of ions of zinc, iron and other non-ferrous metals, such as Cr, Ni, Mn and Cu, remains in the electrolyte. As a matter of fact, zinc on the cathode was not obtained in the subsequent electrolysis of acidic solutions. A cause is a considerable iron content hampering a proper separation of zinc. It is evident that without iron elimination in the electrolyte the zinc mass yield on a required level cannot be ensured. Even the iron precipitation in the leach with HCl using $NH_4OH + H_2O_2$ did not result in improving the situation. The pH modification at least to a value of 3, when Fe^{2+} in the solution transfers to Fe^{3+}, is complicated as to the technical and hygienic aspects.

A more favorable situation was for the leaching of sludge samples in a NaOH solution (pH = 13), when actually all zinc transferred into the leach and a segregation of other metals was neglectable (contents on a ppm level). When comparing Tables 13 and 15, a noticeable zinc decrease in the electrolyte after the electrolysis, by as much as one order is apparent. This is important knowledge for following electrolysis because a problem with a precipitation of harmful elements (in particular, of iron) would be eliminated; for the

electrolysis the level has to be below 20 mg/L, which is problematic in the case of acid leaching, as shown in Table 13. Therefore, a further study was oriented towards galvanic sludge leaching in a hydroxide environment.

Table 15. The result of AAS analyses of the electrolytes after the electrolysis (mg/L).

Sample	Zn	Fe	Cr	Cu	Ni	Mn
D21 HCl	11,400	8280	184	23.9	<10	123
H21 HCl	33,400	6420	712	39.2	12.9	65.6
D21 H$_2$SO$_4$	13,050	9440	233	27.5	<10	161
D21A H$_2$SO$_4$	7150	5130	122	<10	<10	77.3
H21 H$_2$SO$_4$	35,500	9280	1050	18.4	17.9	102
H21A H$_2$SO$_4$	8910	3600	363	<10	<10	39
D21 NaOH	578	<1	-	-	-	-
D21A NaOH	595	<1	-	-	-	-
H21 NaOH	2410	<1	-	-	-	-
H21A NaOH	1960	<1	-	-	-	-

Note: The samples marked as A were diluted 1:1; other samples were used directly from the leach solutions.

In the first phase of the experiments galvanic, sludge from D21, H21 and B21 companies of a weight of 125 g were used. Leaching was carried out in 20% NaOH of 500 mL volume, at temperatures of 40 °C and 60 °C under continuous mechanical mixing. Sampling was always performed after two hours. The total leaching time was 8 h. During leaching, a foam was not generated. A filtration and sampling of leaching residues followed.

Figure 8 shows changes in the zinc concentrations in the leach during the leaching process of galvanic sludge from three suppliers in 20% NaOH solution.
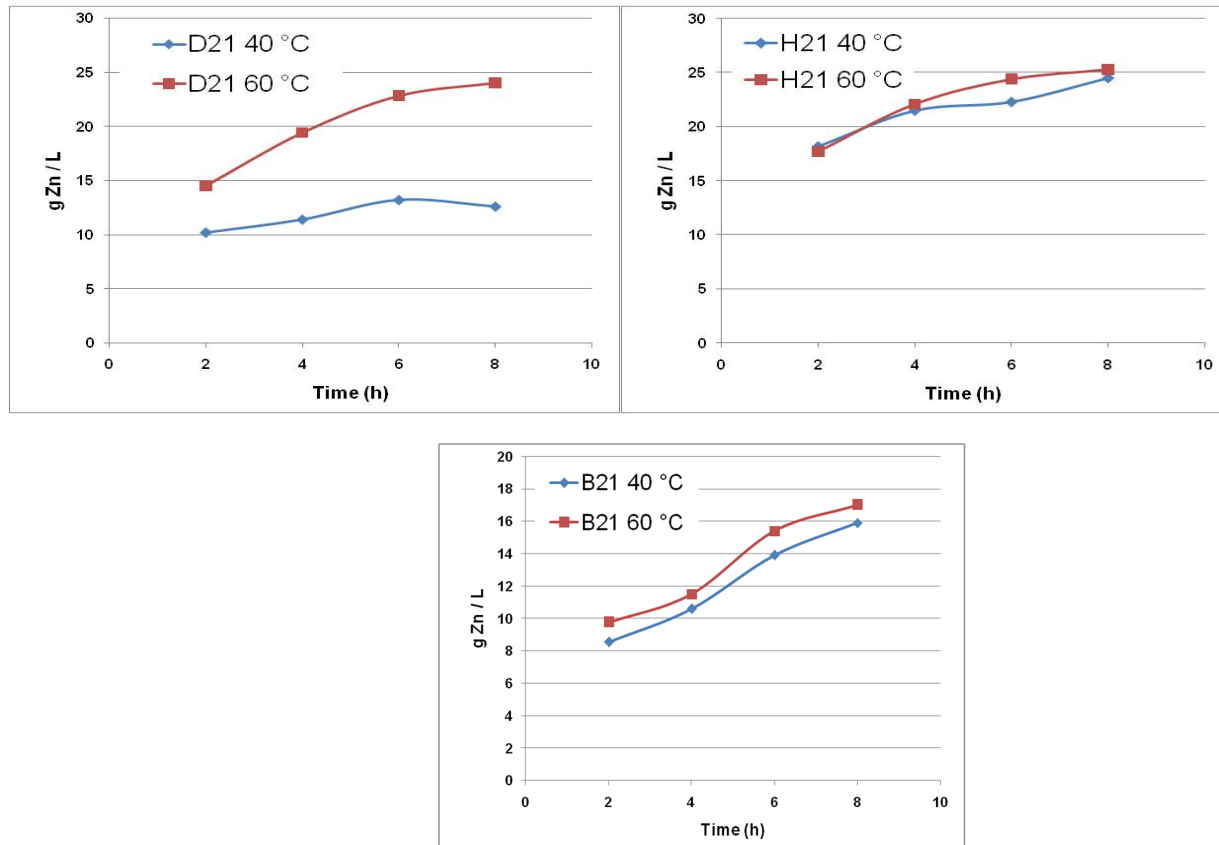
Figure 8. The temperature dependence of zinc content in leaches during leaching in 500 mL of 20% NaOH solution (a sludge weighed amount was always 125 g).

Figure 8 implies a positive influence of a temperature upon the zinc dissolving process in NaOH solution, and an adequate time period for leaching is 8 h, when Zn content in the leach reached more or less a stable value. After the filtration, the leaches were directly subjected to the electrolysis under the following conditions: a voltage of 5 V, current of 2 A, cathode as well as an anode—graphite, and time period of the electrolysis—4 h, at room temperature. The electrolyte volume for D21 sample was 260 mL, and 4.62 g of 95.86 wt.% Zn purity was segregated on the cathode. For the H21 sample, the electrolyte volume was 200 mL and 4.16 g of 95.65 wt.% Zn purity was segregated on the cathode. The conditions of another electrolysis experiment have been summarized in Table 16. There was a high zinc yield found for the B21 sample.

Table 16. The conditions for the electrolysis of the leaches from three suppliers, the cathode—a stainless plate; the anode—a nickel plate.

Sample	Solution, Volume	Electrolysis Conditions	pH	Time (h)	Δm Zn (g)
D21 60 °C NaOH	Leach, 85 mL	4 V, 1 A	13.82	2	+5.87
H21 60 °C NaOH	Leach, 120 mL	4 V, 1 A to 5 A	13.79	2	+4.13
B21 40 °C NaOH	Leach, 170 mL	4 V, 1 A	13.95	2.5	+20.42
B21 60 °C NaOH	Leach, 140 mL	4 V to 3 V, 1 A	13.59	2.5	+19.42

In the following phase of the experiments, the conditions for leaching, filtration and electrolysis of sludge samples from three companies, which were delivered in 2021 and 2022, were optimized. In Table 17, the analyses results have been summarized as to the particular sampling. One can observe that in many cases the zinc transition from the sludge into the leach was not successful, which has been proven by high zinc concentrations in the leaching residues. Nevertheless, the resulting product—the cathode zinc—was of a purity of 99.7% at a minimum, which can be considered a success.

Table 17. The results of ED-XRF analyses of the input galvanic sludge, leaching residues and cathode zinc after the electrolysis. (Note: average values of three measurements over 300 ppm) (wt.%).

No.	Sample	State	Zn	Fe	Mn	Cu	Cr	Al	Co	Ni
D21	Input	Sludge	13.3	9	0.17	0.03	0.11	1.6	-	-
D21	40 °C NaOH 8 h.	Leaching residue	10.6	11.2	0.15	-	0.1	0.2	-	-
D21	60 °C NaOH 8 h.	Leaching residue	10.5	10.81	0.2	0.03	0.2	0.22	-	-
D22	Input	Sludge	9.49	0.87	-	-	0.51	-	0.11	-
D22	60 °C NaOH 8 h.	Leaching residue	2.85	8.92	0.16	-	0.12	0.12	-	-
H21	Input	Sludge	12.4	2.71	-	0.03	0.20	-	-	-
H21	40 °C NaOH 8 h.	Leaching residue	13.4	3.23	0.04	-	0.44	-	-	-
H21	60 °C NaOH 8 h.	Leaching residue	16.1	3.61	0.05	0.03	0.66	-	0.1	-
H21	60 °C NaOH	Cathode	99.9	0.04	-	0.07	-	-	-	-
H22	Input	Sludge	9.4	11.5	0.17	-	0.18	0.07	-	-
H22	60 °C KOH 8 h.	Leaching residue	8.03	1.82	0.03	-	0.77	-	0.18	-
B21	Input	Sludge	14.57	2.6	0.07	-	0.06	0.3	-	-
B21	40 °C NaOH	Cathode	99.7	0.04	-	0.09	0.05	-	-	0.01
B21	60 °C NaOH	Cathode	99.9	0.04	-	0.08	0.04	-	-	0.01

Further, the leaching of the D22 and H22 samples in potassium hydroxide and sodium hydroxide was carried out. The leaching was performed under the following conditions: 125 g of the sludge, 620 mL of 20% KOH or 20% NaOH, a temperature of 60 °C, mechanical mixing, sampling of leaches after 4 h and after 8 h. A filtration for a separation of the leach from the leaching residue followed. The obtained leach was subjected to the electrolysis.

Table 18 implies that a time of 8 h of galvanic sludge leaching is adequate for the zinc transition into the leach and that there are no significant differences between leaching in KOH and NaOH. In all the cases in the following electrolysis, the zinc consumption in the electrolyte occurred and, here, the residual Zn content was below 100 mg/L. The electrolysis conditions have been summarized in Table 19, below.

Table 18. The results of AAS analyses of the leaches (1st sampling after 4 h, 2nd sampling after 8 h of leaching) and of the electrolytes after finishing.

Sample	Zn (mg/L)	Fe (mg/L)
Leach D22 NaOH, 1st collection	5140	1–10
Leach D22 NaOH 2nd collection	7480	1–10
Electrolyte D22 NaOH	78.2	0.95
Leach D22 KOH 1st collection	5350	1–10
Leach D22 KOH 2nd collection	7270	1–10
Electrolyte D22 KOH	47.2	1.22
Leach H22 NaOH 1st collection	14,900	1–10
Leach H22 NaOH 2nd collection	21,100	1–10
Electrolyte H22 NaOH	97.6	1–10
Leach H22 KOH 1st collection	11,700	1–10
Leach H22 KOH 2nd collection	12,200	1–10
Electrolyte H22 KOH	38.3	1–10

Table 19. The conditions and results of the electrolysis of the leaches obtained from leaching in NaOH and KOH solutions.

Sample	Solution	Electrolysis	Cathode	Anode	Time (h)	Δm Zn (g)
D22 60 °C NaOH	Leach, 300 mL	4 V, 3 A	Stainless steel	Ni	4	+14.39
D22 60 °C KOH	Leach, 230 mL	4 V, 3,5 A	Stainless steel	Ni	4	+7.23
H22 60 °C NaOH	Leach, 260 mL	4 V, 2,5 A	Stainless steel	Ni	4	+28.05
H22 60 °C KOH	Leach, 340 mL	4 V, 2,5 A	Stainless steel	Ni	4	+16.76

In Figure 9 is the photo of the cathode zinc on the stainless plates after electrolysis in NaOH solution.

Figure 9. A photo documentation of the zinc product segregated on a stainless plate after electrolysis—sample H22. Condition at the electrolysis: cathode—stainless plate, anode—nickel plate, electrolyte—20% solution of NaOH, voltage 4 V, current 2.5 A, time 4 h and temperature 23 °C.

The results of the size distribution of the Zn particles obtained after electrolysis are presented for sludge D22 in Table 20 and Figure 10. The condition at the electrolysis was cathode—stainless plate, anode—nickel plate, 130 mL electrolyte 20% solution of NaOH, voltage 4.5 V, current 1 A, time 2 h, temperature 21 °C.

Table 20. Condition at the laser diffraction analysis of Zn powder.

Analysis			
Particle name	Zinc	Particle refractive index	2.008
Dispersant name	Water	Dispersant refractive index	1.330
Particle absorption index	0.100	Laser obscuration	1.87%
Weighted residual	0.44%	Scattering model	Mie
Analysis model	General purpose	Analysis sensitivity	Normal
Results			
Concentration	0.0037%	Span	1.752
Uniformity	1.265	Result units	Volume
Specific surface area	340 m^2/kg	Dv (10)	14.7 μm
D [3;2]	17.6 μm	Dv (50)	40.9 μm
D [4;3]	76.2 μm	Dv (90)	86.3 μm
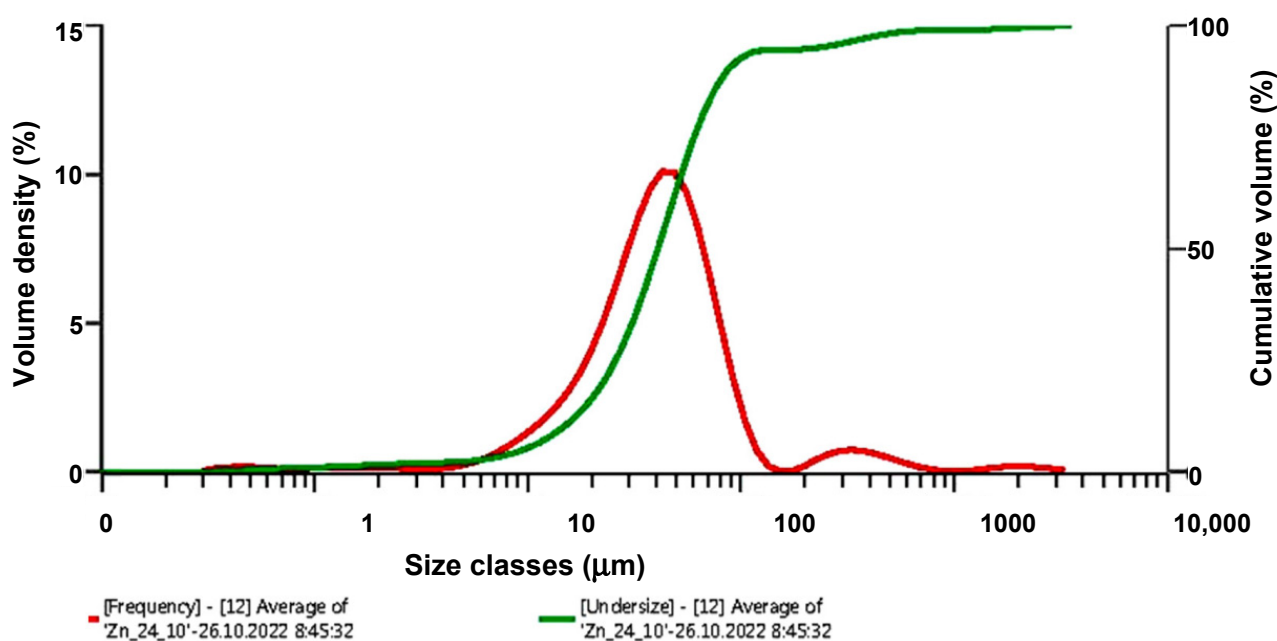
Figure 10. Results of laser diffraction analysis (device Mastersizer 3000—producer: firm Malvern) for Zn powder obtained at the electrolysis process. Radionuclide Co was used. Conditions are described in Table 20 above. Time of ultrasonic mixing: 60 min at 3000 rpm. Dv(50) = 40.9 μm.

It can be seen from Figure 10 that the mean size of Zn particles after electrolysis is about 41 μm. Morphology of Zn particles was studied on scanning electron microscopy type JEOL JEM-2100F, Japan at various enlargements—see Figure 11.

At follow-up, an influence of the voltage on the electrodes during the electrolysis was observed. A leach obtained in the leaching of the D22 galvanic sludge sample under the following conditions was used: 250 g of a sludge, 1000 mL of 20% NaOH, a temperature of 60 °C and time period of 7 h with a pH of 13.9. The electrolyte always had a volume of 200 mL, the cathode: a stainless plate, the anode: a nickel plate and a temperature at the electrolysis—the room temperature (in some cases, when the electrolysis was finishing, a slight temperature increase occurred to 40 °C at a maximum). The electrolyte samples were taken in time intervals of 30 min. The total time period of the electrolysis did not exceed 150 min. The zinc mass yields on the cathode have been documented in Figure 12, which implies that the voltage on the electrodes is optimal between 3 to 4 V, and at the starting current around 1 A; an active anode surface area was 5 × 5 cm. At higher voltages of 5 and 6 V, the direct-current source was extremely electrically stressed and the process had to be terminated before time. Figure 12 also shows an experiment, when the electrolyte

was re-used after the previous electrolysis for the leaching of the same D22 sludge sample and the leach was subjected to the electrolysis for the second time. Approximately 5.5 g of pure zinc on the cathode was obtained at 3.9 V of voltage. This result is significant for the finding that a fresh hydroxide solution is not always needed for leaching but it can be supplemented by a relatively pure electrolyte, which is ecologically highly important from the point of view of the closed recycling cycle.
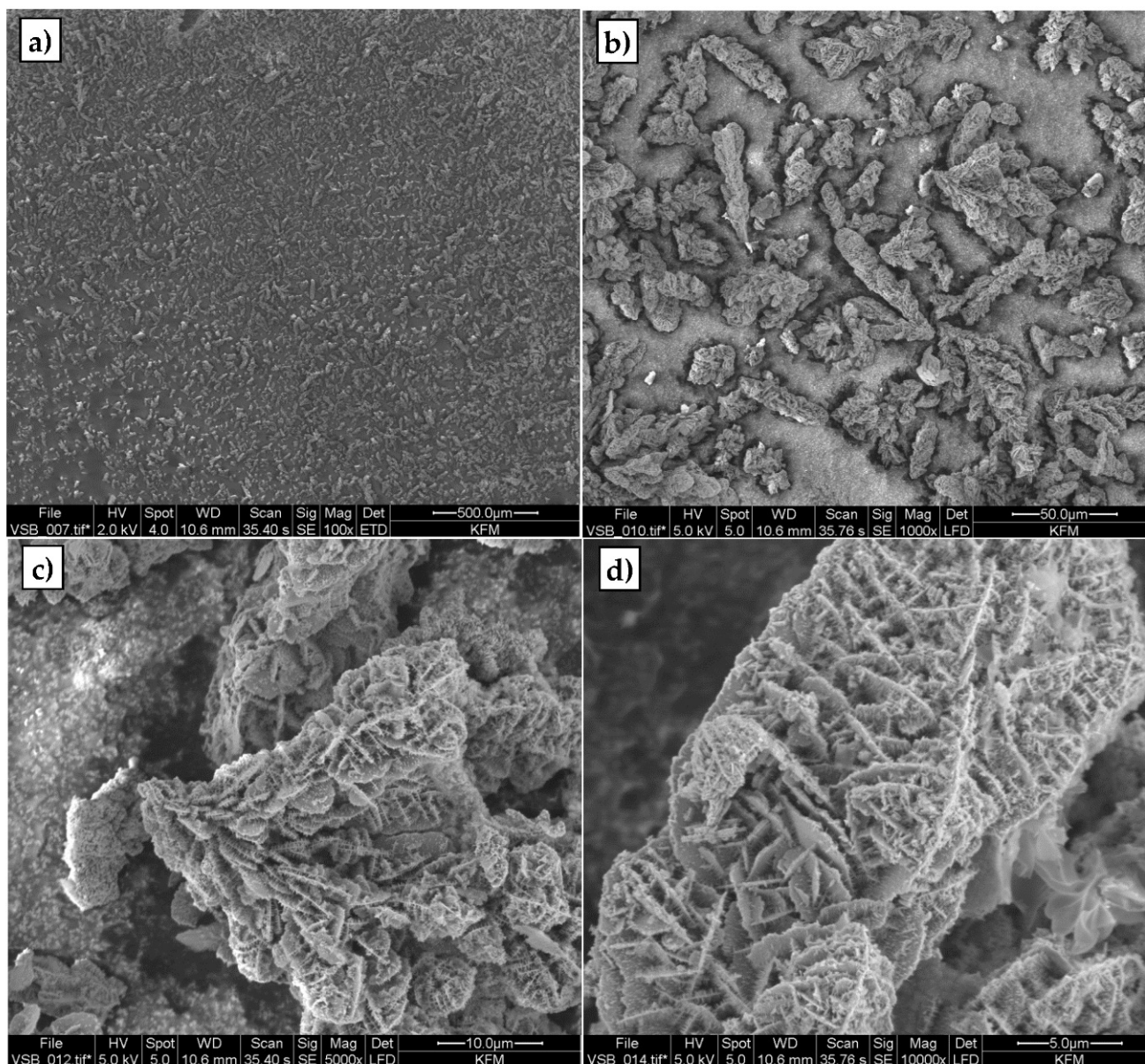
Figure 11. Microstructure of Zn powder (SEM analysis) after electrolysis process at various enlargement—sample D22. (**a**) Zinc particles at low magnification. (**b**) Dendritic structure of the sample at higher magnification. (**c**) Small whiskers are visible on the surface of the zinc particles. The thickness of the lamellae is about 10 nm. (**d**) The zinc particles are very thin. The surface was indented, and the arrangement resembles a fine dendritic structure.
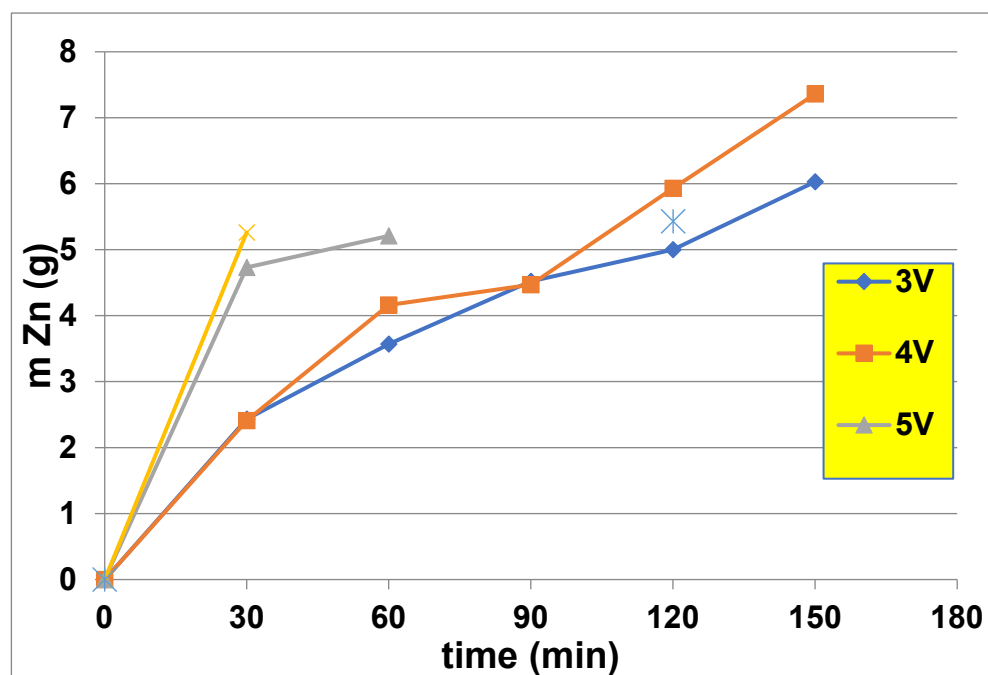
Figure 12. An influence of the electric voltage of the electrolytic cell upon the efficiency of the cathode zinc obtaining.

4. Discussion

Within the presented work, the aim was to propose an optimal technology for a zinc separation, perhaps even iron, from galvanic sludge delivered from six selected galvanizing plants within the years of 2020 to 2022. Table 2 shows that zinc and iron contents differ markedly in the particular delivered samples, which depend on an actual production campaign of a galvanizing plant, a time of sludge sampling, etc. For one company, there was even an abnormally high manganese content found; for another company an increased chromium and nickel content was found.

Based on the former experiments carried out at the University of Chemistry and Technology in Prague within the framework of four dissertations and other technical literature (see the research part), the sludge samples were subjected on the basis of positive laboratory results and recommendations to leaching in the acidic environment of solutions of H_2SO_4, HNO_3 and HCl acids with a possible addition of hydrogen peroxide or ozone. Based on our own experiments, it was found out that leaching in the acidic environment (pH = 0 to 1) ensures a transition of the metal elements' majority into the leach with a relatively high efficiency. However, for a following electrolysis, the zinc from the leach needs to be separated from other metals, in particular from iron. There are plenty of schemes in the literature on how to precipitate iron as well as other metals through a change in pH to a value of 3 to 4. In our experiments a solution of NH_4OH with an addition of an oxidizing agent in the form of H_2O_2 was applied first. A precipitation of Fe and other metals was carried out through a change in pH of the leach aiming to transform the divalent iron to a trivalent that forms a precipitate, and this can be separated by a filtration. The recommended pH values for the Fe precipitation are between 2 to 4. During the precipitation experiments we have found out that the additions of precipitating agents are a highly sensitive matter as to dosing. Even with an addition of, e.g., 5 mL of a precipitating agent, a jump change of pH to values as high as around pH = 8 to 9 often occurred, and many times a turbidity was formed that was difficult to filter out. The formed precipitate was difficult to filter and, moreover, even zinc from the leach transferred into it. Even the application of other precipitating agents such as sodium hydroxide, potassium hydroxide, sodium carbonate or the use of the recommended Jarosite process have not led to positive

results. In addition, the precipitation processes are highly time-demanding with a high consumption of other chemicals, which were not applicable in practice.

The following electrolysis of filtered leaches has confirmed a very low yield of cathode Zn in the case of a high Fe concentration in the electrolyte. This concerned the acid leaching. The Fe presence in the electrolyte limits the zinc separation on the cathode. Thus, if a leach with a low Fe ions level cannot be ensured, the electrolysis will not be successful.

Therefore, the other part of the experiments was oriented to hydroxide leaching, when actually only zinc transfers into the leach and other metals remain in the leaching residue. The electrolysis results in the case of leaching using NaOH appear to be promising because a relatively high zinc proportion was obtained in the cathode mass in this case. Graphite electrodes were used, and later a cathode of a stainless plate and an anode of a thin nickel plate proved themselves useful. The hydroxide leaching in 20% NaOH and/or in 20% KOH came out slightly in favor of the NaOH application. The recommended voltage on the electrodes at the electrolysis is 3.5 to 4 V, with a time period of the electrolysis 150 to 180 min at room temperature and a current density of c. 300 A/m^2.

An issue that remains to be solved is processing of zinc segregated on the cathode after the electrolysis in a strongly alkaline electrolyte. The cathode zinc in a form of dark small grains even after rinsing in distilled water is subject to a very rapid surface oxidation on air at an oxide zinc generator. The processing of such a material is rather complicated because a reduction using carbon (coke) needs to be performed at temperatures above 1200 °C, when zinc releases in the form of vapors (the boiling temperature of pure zinc is about 906 °C), and these need to be collected in a condenser. All of this makes the pure zinc obtaining process complicated and leads to extra financial costs. Therefore we solve the issue on how to preserve the zinc immediately after the electrolysis and after its separation from the stainless plate in a metal form for its use for the remelting and subsequent casting into appropriate molds, or it can possibly be refined to a purity of 99.95% through distillation or rectification in distillation columns and subsequently returned to galvanizing plants for the galvanic zinc plating of metal components.

A possibility of iron obtaining from galvanic sludge appears to be economically disadvantageous, although an average Fe content in the sludge from six galvanizing plants is about 6 wt.%. In leaching in the hydroxide environment, iron and other non-ferrous metals predominantly remain in the leaching residue and could be transferred into the leach only in the HCl acid solution, where other non-ferrous metals could be leached as well, and a selective precipitation would be complicated and economically disadvantageous.

In our experiments, of course, tests were carried out to obtain Fe. The results were diverse, as Fe separation is sensitive to precipitation conditions and, at the same time, other metals are separated at the selected pH, which would lead to further refining processes and thus to an increase in the consumption of chemicals. Economic reasons prevent us from dealing with this issue. In the future, we are considering the use of leaching residues containing Fe and other compounds in the field of civil engineering.

At present, on the basis of the obtained positive results from the galvanic sludge processing with the aim of pure zinc obtained through recycling a line has been built with the purpose of verifying the technology on a semi-industrial scale. The equipment will be assembled of three plastic reservoirs with a capacity of c. 100 l each. In the first reservoir a leaching process will take place in a solution of sodium hydroxide or potassium hydroxide for a period of approximately 8 h at a temperature of 60 to 70 °C. After finishing the leaching and the leaching residue settles down, the leach will be drawn off into the second container intended for a filtration. The liquid phase will be subsequently drawn over into the third container intended for the electrolysis.

Nowadays, we also seek for possibilities of processing and utilization of residual products—leaching residues after the leaching process, possibly after the filtration, in, for example, civil engineering. This way, a complete utilization of galvanic sludge would be ensured; at present, it is stored in the sludge dump as hazardous waste that is costly for galvanizing plants.

5. Conclusions

This work concerns a design and experimental verification of the applicable hydrometallurgical processing of sludge from galvanizing plants. The first experiments of leaching in the acidic environment ensured a high level of the transition of zinc, iron and other metals into the solution. The following precipitation process using various chemicals with the aim of a precipitation of iron and other metals contained in the leach at a higher pH value is rather time-demanding and sensitive to a proper dosing of agents and oxidizing agents (hydrogen peroxide). The electrolysis was successful only when the iron content in the electrolyte decreased below the limit value. At the follow-up, on the basis of these findings the hydroxide leaching process started to be performed. Surprisingly, the results were very positive. Leaching in NaOH or KOH solutions ensured the dissolving of a substantial part of zinc in the leach, while iron and other metals practically were not leached in the environment with a very high pH. This way, a quite complicated precipitation process is eliminated, and after the filtration, the hydroxide leach can be directly subjected to the electrolysis.

The recommended procedure for galvanic sludge processing is as follows:

1. Leaching in 20 to 25% NaOH or KOH, with an optimal ratio L:S = 4:1, a temperature of 60 to 70 °C and a time period of 8 h at minimum.
2. A filtration for a separation of a liquid fraction from a leaching residue using a fritted glass or under pressure using a water-jet air-pump.
3. A total of 3.5 to 4 V for the electrolysis, with 300 to 400 A/m^2 current density, a cathode—a stainless plate, an anode—a nickel plate, 25 °C temperature and a time period of the electrolysis of 5 to 8 h.
4. The cathode zinc needs to be protected against a consequential oxidation and subjected to immediate remelting in a reduction or inert atmosphere, or possibly a distillation or rectification should be carried out with the aim to obtain the compact metal zinc re-usable in galvanizing plants again.

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