

POSSIBILITIES OF ZINC EXTRACTION FROM GALVANIC SLUDGE BY MEANS OF LEACHING IN SODIUM HYDROXIDE AND FOLLOWING ELECTROLYSIS

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Abstract

The aim of this work is a proposal of innovative technology of metal waste processing - sludge and filtration cakes from galvanizing plants. The paper deals with possibilities of zinc obtaining from waste of galvanic sludge, which arises during galvanic plating. A leaching process in a sodium hydroxide environment was optimized in the laboratory conditions, resulting in separation of zinc from iron and other organic and inorganic components from sludge. The obtained leach was processed by means of the electrolysis in order to get pure zinc. The stainless plate was used as a cathode, nickel plate as an anode. Results of chemical analyses of individual intermediate and final products at the hydrometallurgical processes are presented in this paper.

Keywords: Galvanic sludge, zinc, leaching, chemical analyses

1. INTRODUCTION

Zinc sludge can be treated by hydrometallurgical methods. Literature data on hydrometallurgical treatment of wastes mainly consider the leaching method in sulfuric, hydrochloric acid or hydroxides. This paper reports the results of studies on the hydrometallurgical treatment of galvanic sludge produced by industrial sources. Currently, this waste is managed domestically by zinc producers or sold to foreign recyclers. 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.

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.

For 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).

Galvanic waste processing through a vitrification method is described in [3,4]. A lot of researches have been oriented on re-gaining of different metals from the galvanic sludge, e.g. zinc and iron, nickel and chromium [5] or copper [6]. 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 [7-10]. Literature data on hydrometallurgical treatment of wastes mainly consider the leaching method in sulfuric, nitric or hydrochloric acid [7]. Previous results of the leaching of galvanic waste were published in [11-12].

Zinc can be separated from aqueous solutions despite a significantly negative standard electrode potential - 0.76 V. This is determined by the hydrogen overvoltage presence. Its value is influenced by the electrolyte purity, a cathode surface condition and a current density. Recommend parameters for the electrolysis are as follows: 400 - 700 A/m² 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 depends on the electrolyte purity [13-15]. For the electrolysis in practice are used aluminum cathodes with a thickness of 3 to 4 mm and lead anodes with a thickness of 5 to 8 mm with an addition of Ag 1%, 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, additional refining through rectification needs to be performed.

Zn electrolysis from alkaline solutions exhibits a lower sensitivity to a content of impurities, a lower consumption of electrical energy. Zn concentration of 8 up to 25 g/l, NaOH concentration of 80 up to 320 g/l, a current density of 50 - 200 A/m², 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/m². For the electrolysis it is advisable to add approximately 50 mg of glueper 1 l of the electrolyte for higher quality of the separated zinc without dendrites.

Gürmen and Erme [16] dealt with an influence of a current density, a temperature and a 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. The cathode of a stainless plate, the anode of Ni plate. Brown et al. [17] carried out experiments with 75 g of Zn/l, 25 % 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.

The aim of this work is to obtain zinc from leaching of galvanic sludge. The practical part aims at sample treatment, subsequent leaching of waste sludge in sodium hydroxide. This work concludes with an evaluation of the conditions under which the highest yield of zinc is obtained after leaching of galvanic sludge and after the electrolysis.

2. EXPERIMENT AND RESULTS

The main part of the experimental work was to determine the most suitable conditions for obtaining the maximum recovery of zinc from the galvanic sludge. The samples were analysed for the content of zinc and other metals in the laboratories of the Faculty of Materials Technology. Galvanic sludge samples were obtained from six galvanizing plants that were taken in various campaigns within years 2020 - 2022. The results of analyses of the samples delivered from three companies marked with different letters are given in **Table 1**. A significant difference in 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 is about 18 wt%, which is a value interesting enough for its regaining. Iron concentrations were approximately 5 wt% in average. From an economical point of view this is a rather low value for its subsequent obtaining.

Table 1 Chemical analysis of the sludge delivered from three companies - ED-XRF (wt%)

Firm	Zn	Fe	Cr	Mn	Cu	Ni	Co	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	0.87	0.51	-	-	-	0.11	-
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	-	-	-
Average	18.0	5.5	0.3	0.08	0.07	0.01	0.17	0.01

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, a leaching period and L:S ratio needs to be selected. Hydrogen peroxide H₂O₂ or ozone O₃ (Ozontech - the ozone generator) was occasionally used as an oxidation agent for leaching. 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 [12].

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. X-ray diffraction analysis for a presence of phases in 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 iron, in leaches, a solution of ammonia NH₄OH, sodium hydroxide or potassium hydroxide and sodium carbonate Na₂CO₃ with addition of H₂O₂ was applied for a transformation of divalent iron Fe²⁺ in leaches into a precipitate of trivalent iron Fe³⁺. Considering the fact that leaching was performed in a highly acidic environment (pH was around zero), pH of the leach needed to be modified to values around 3, when iron and other elements precipitate.

The electrolysis was performed in laboratory conditions at 3-4 V voltage and currents about 1 A at the room temperature. The electrolysis time period was chosen according to the very process of zinc separation on the cathode. The cathode was made of thin plates of various materials in accordance with the electrolyte chemical composition. The same also applied for the anode. For the electrolysis of the leach obtained after leaching in H₂SO₄ the cathode was made of Al plate, possibly 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 term 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 [11,12].

X-ray diffraction analysis of D20 sample for a presence of various phases was carried out - see **Figure 1**. The results of the diffraction analysis show a presence of Zn, then also ZnO zincite, Fe₂O₃ iron oxide, FeO(OH) goethite and CaCO₃ calcium carbonate.

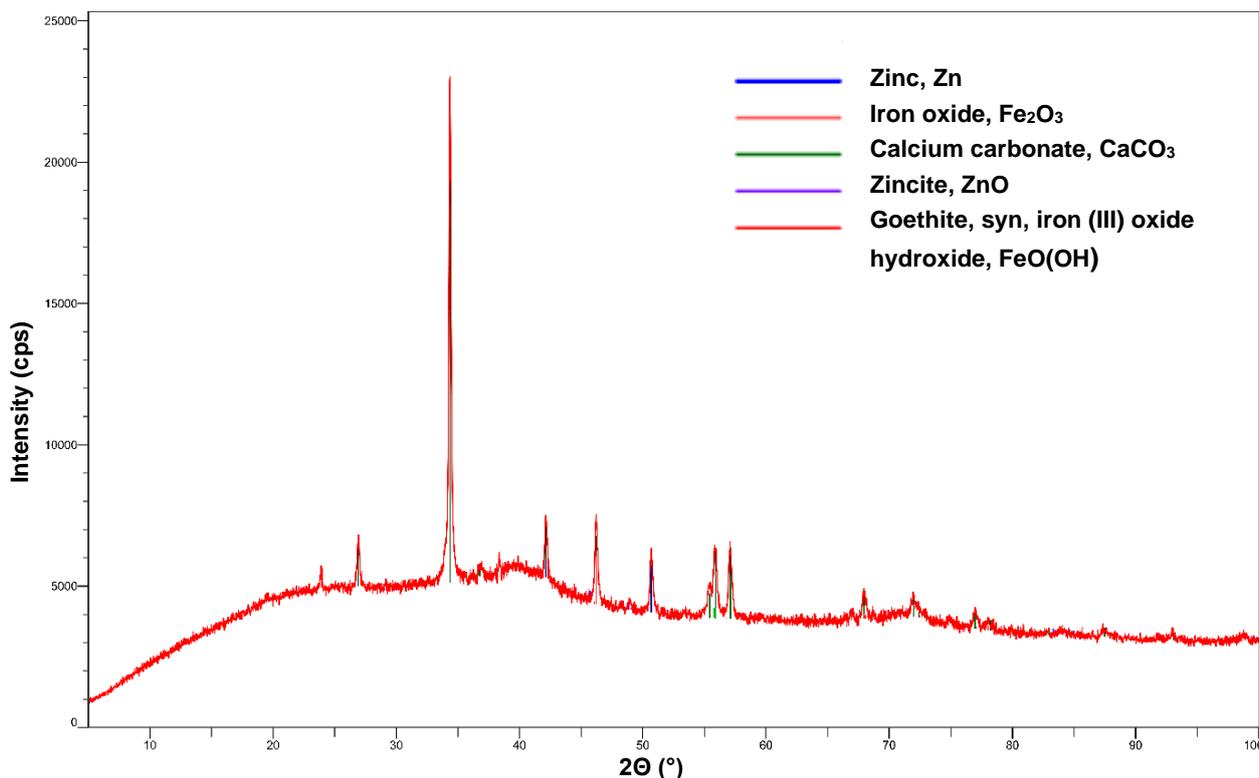


Figure 1 X-ray diffraction analysis for a presence of phases in the sludge sample (supplier D20)

The leaching of galvanic sludge from two suppliers D21 and H21 (see **Table 1**) in various environments was tested, i.e. in HCl solution (25 °C), H₂SO₄ (40 °C) and NaOH (60 °C) for a period of 4 hours under the conditions given in **Table 2**. Results of AAS analyses of the leaches are also shown here; these results imply higher Zn concentrations in the leach for H21 supplier, which relates to a higher zinc concentration in the used galvanic sludge. However, a fact has been proven again that in acidic leaching the high iron content transfers into the leach and 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 other metals were below a measurability limit. An environment with high pH considerably hampers dissolving of most of 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 3** 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 H₂SO₄ solution.

Table 2 Results of AAS analyses of the leaches (mg/l) after leaching in HCl, H₂SO₄ and NaOH (sludge: 250 g, volume of the solution: 1000 ml)

Sample	pH	Zn	Fe	Cr	Mn	Cu	Ni
D21 - 15 % HCl	0.39	11500	7990	243	116	21.9	6
H21 - 15 % HCl	0.59	31500	5970	1150	60	41.2	13
D21 - 20 % H ₂ SO ₄	0.96	12500	8860	318	155	27.1	8
H21 - 20 % H ₂ SO ₄	1.28	36100	6780	1100	70	45.9	13.7
D21 - 25 % NaOH	13.69	13200	12.2	-	-	12	6
H21 - 25 % NaOH	13.81	38800	5.2	-	-	-	-

Table 3 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 ₂ SO ₄ , 40 °C	1.80	1.1	-	-	-	-
H21 - 20 % H ₂ SO 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

The favourable situation was for leaching of sludge samples in 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). This is an important knowledge for a following electrolysis because a problem with a precipitation of harmful elements (in particular 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 2**. Therefore a further research was oriented towards galvanic sludge leaching in a hydroxide environment.

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 hours. During leaching a foam was not generated. A filtration and sampling of leaching residues followed.

Figure 2 shows changes in zinc concentrations in the leach during the leaching process of galvanic sludge from three suppliers in 20% NaOH solution.

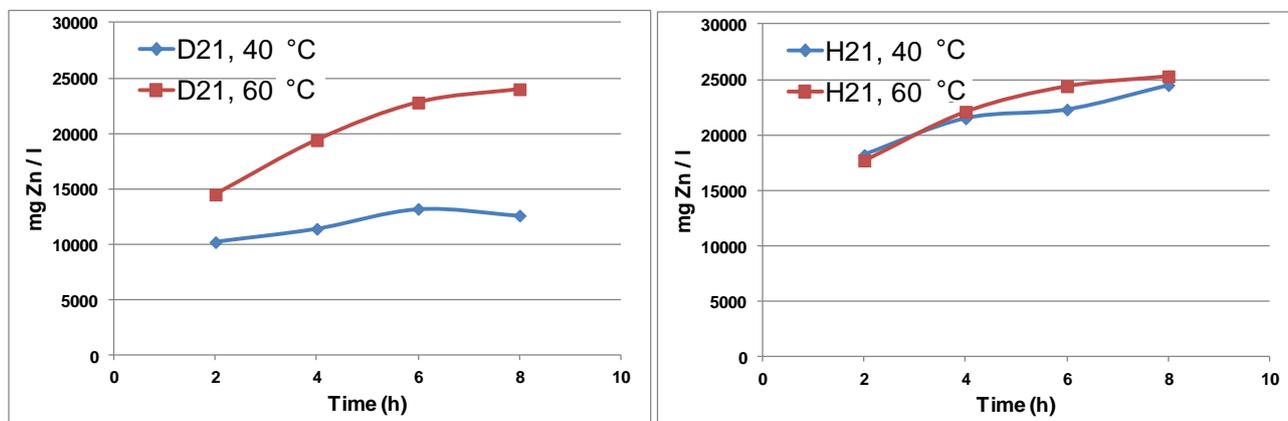


Figure 2 The temperature dependence of a zinc content in leaches during leaching in 500 ml of 20% NaOH solution (a sludge weighed amount was always 125 g)

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

Further, leaching of 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 hours and after 8 hours. A filtration for a separation of the leach from the leaching residue followed. The obtained leach was subjected to the electrolysis.

Table 4 implies that a time of 8 hours 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 the residual Zn content was below 100 mg/l here. The electrolysis conditions have been summarized in **Table 5** below.

Table 4 The results of AAS analyses of the leaches (1st sampling after 4 hours, 2nd sampling after 8 hours 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	14900	1-10
Leach H22 NaOH 2nd collection	21100	1-10
Electrolyte H22 NaOH	97.6	1-10
Leach H22 KOH 1st collection	11700	1-10
Leach H22 KOH 2nd collection	12200	1-10
Electrolyte H22 KOH	38.3	1-10

Table 5 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	4V, 3A	Stainless steel	Ni	4	+14.39
D22 60 °C KOH	Leach, 230 ml	4V, 3,5A	Stainless steel	Ni	4	+7.23
H22 60 °C NaOH	Leach, 260 ml	4V, 2,5A	Stainless steel	Ni	4	+28.05
H22 60 °C KOH	Leach, 340 ml	4V, 2,5A	Stainless steel	Ni	4	+16.76

Follow-up, an influence of the voltage on the electrodes during the electrolysis was observed. A leach obtained in leaching of 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, a time period of 7 h, pH 13.9. The electrolyte had always a volume of 200 ml, the cathode: a stainless plate, the anode: a nickel plate, 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 minutes. The total time period of the electrolysis did not exceed 150 minutes. The zinc mass yields on the cathode have been documented in **Figure 3**, which implies that the voltage on the electrodes is optimal between 3 to 4 V, at the starting current around 1 A, an active anode surface area was 5 x 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 3** shows also an experiment (points for 3.9 V), when the electrolyte was re-used after the previous electrolysis for

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 voltage 3.9 V. 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.

In **Figure 4** is visible zinc product on the cathode after electrolysis with zinc layer (sample H22).

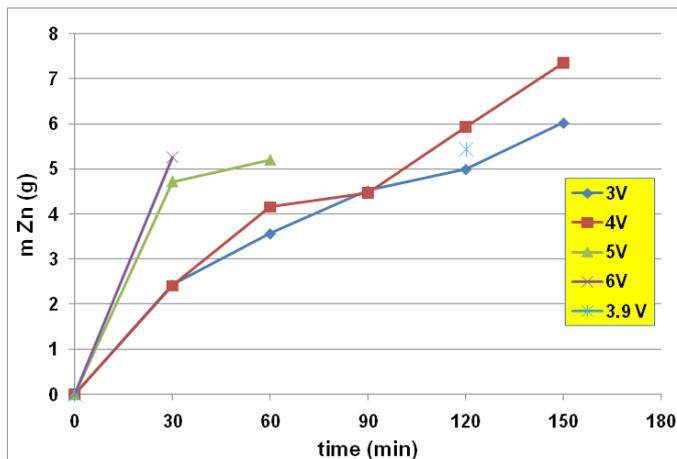


Figure 3 An influence of the electric voltage of the electrolytic cell upon the efficiency of the cathode zinc obtaining (sample D22)



Figure 4 A photo of the zinc product segregated on a stainless plate (sample H22)

3. 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 selected galvanizing plants. **Table 1** shows that zinc and iron contents differ markedly in the particular delivered samples, which depends on an actual production campaign of a galvanizing plant, a time of sludge sampling etc..

Based on our own experiments it was found out that leaching in the acidic environment (pH = 0 to 1) ensures a transition of metal elements majority into the leach with a relatively high efficiency. However, for a following electrolysis zinc from the leach needs to be separated from other metals, in particular from iron. There are plenty of schemes in the literature 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 a 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 trivalent that forms a precipitate and this can be separated by a filtration. During the precipitation experiments we have found out that additions of precipitating agents are a highly sensitive matter as to dosing. Just 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, 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 lead to positive results. In addition, the precipitation processes are highly time-demanding with a high consumption of other chemicals, which could not be 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. So, if a leach with a low Fe ions level cannot be ensured, the electrolysis will not be successful.

Therefore 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, later a cathode of a stainless plate and an anode of a thin nickel plate that proved themselves useful. The hydroxide leaching in 20% NaOH and/or in 20% KOH came out slightly in favour of NaOH application. The recommended voltage on the electrodes at the electrolysis is 3.5 to 4 V, a time period of the electrolysis 150 to 180 minutes at the room temperature, the current density c. 300 A/m².

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 it could be transferred into the leach only in the HCl acid solution, where other non-ferrous metals could be leached, too, and a selective precipitation would be complicated and economically disadvantageous.

At present, on the basis of the obtained positive results from the galvanic sludge processing with the aim of pure zinc obtaining through recycling a line has been built with a purpose to verify 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 hours at a temperature of 60 to 70 °C. After finishing the leaching and the leaching residue settling-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.

4. CONCLUSION

This work concerns a design and experimental verification of applicable hydrometallurgical processing of sludge from galvanizing plants. The first experiments of leaching in the acidic environment ensured a high level of 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. 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 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, an optimal ratio L:S = 4:1, a temperature of 60 to 70 °C, a time period of 8 hours at minimum. Can be used an addition of H₂O₂.
- 2) A filtration for a separation of a liquid fraction from a leaching residue using a fritted glass, or under pressure using water-jet air-pump.
- 3) 3.5 to 4 V for the electrolysis, 300 to 400 A/m² current density, a cathode - a stainless plate, an anode - a nickel plate, 25 °C temperature, a time period of the electrolysis: 3 to 4 hours.
- 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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