

## POSSIBILITIES OF ZINC EXTRACTION FROM GALVANIC SLUDGES BY MEANS OF ELECTROLYSIS

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### Abstract

The aim of the work is a proposal of innovative technology of metal waste processing – sludges 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 an acid environment was optimized in the laboratory, resulting in separation of iron and organic components from sludge. The obtained leach was processed by means of the electrolysis in order to get pure zinc. Results of chemical analyses of individual products at the hydrometallurgical processes are presented in the article.

**Keywords:** Galvanic sludge, zinc, leaching, electrolysis, chemical analysis

### 1. INTRODUCTION

Galvanic zinc plating is an electrolytic process during which a zinc coating generated by electrochemical dissolution of a zinc anode deposits on electroconductive materials, mostly on iron parts (a cathode). For the galvanic process the alkaline or acidic coating can be chosen. Today zinc plating is typically carried out in a diluted hydrochloric acid with additions of other agents. According to shapes and sizes, zinc plated parts are either hung on hooks on a galvanic rack (larger parts) or they are placed into a drum (small parts). 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 the surface of parts was cleaned, a new zinc layer has been deposited on it using electric current. Subsequently, in order to increase the corrosion resistance the zinc coating passivation is performed, in case of need a sealing paint is applied. All the zinc plating process is completed by 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 – 12  $\mu\text{m}$ .

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.

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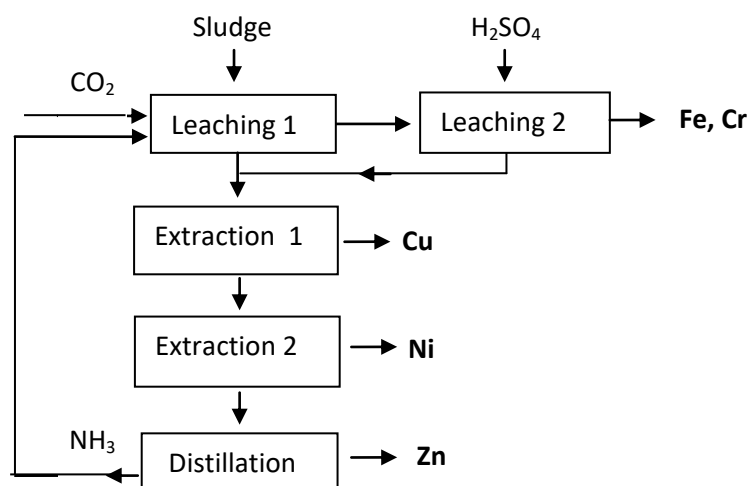
process and processing of metal waste – sludges and filtration cakes from the galvanizing plant“. One of aims of this project is the proposal of technology of the waste sludge processing and obtaining of elemental metals as secondary raw material.

With rapidly developing galvanic plating, ever increasing attention has been focused on the galvanic sludge. Galvanic sludges feature a content of heavy metals, for example zinc, nickel, copper, cadmium and chromium. These sludges fall within hazardous waste by reason of potential releasing of metals to the living environment. Their disposal is carried out mostly by deposition [1,2]. In Germany sludge is disposed in incineration plants, if allowed by the sludge composition, or on hazardous waste dumps. One of often used possibilities of hazardous waste storage is its use for a protection and stabilization of abandoned parts of potash and salt mines [3, 4]. At present every endeavor is made to avoid a negative impact related to sludge dumping and therefore various ways of processing are looked for.

In India the research is oriented on the solidification stabilization and the following use of sludge as a structural material [5]. A manufacture of clay bricks with an addition of galvanic sludge, where immobilization of heavy metals can be improved by adding waste glass, is described in [6]. The modern technologies development in Ukraine includes above all the use of the galvanic sludge as an inert filler in structural materials [7]. The sludge utilization as a sub-base material stabilized by cement and fly ash is solved in [8]. At the Northeast Normal University, China, the galvanic sludge re-use for a preparation of new adsorbents for waste water treatment has been brought into focus [9].

Galvanic waste processing through a vitrification method is described in [10,11]. A lot of researches have been oriented on re-gaining of different metals from the galvanic sludge, e.g. zinc and iron [2], nickel and chromium [12] or copper [13]. 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.

In accordance with the European Waste Catalogue sludges and filter cakes from neutralization stations belong among hazardous substances (cat. no. 11 01 09). These are sludges of a solid and powdery consistency, yellow-green to brown color and a neutral reaction. Several hazardous properties were identified in them (H5, H13, H14) [14]. Galvanizing plant OEZ s.r.o. Letohrad contractually hands over wastes of 11 01 09 group to World Resources Company, Wurzen, for recycling. Heavy metals (nickel, copper, zinc) can be recovered from galvanic sludges. These non-ferrous metal concentrates are delivered to metallurgical works as a free commercial product, where it is used as a raw material or a supplement for the production of primary metals or metal salts.



**Figure 1** Block diagram of “MAR-Process” technology for galvanic sludge processing [16]

František Kepák has presented a technology based on metals recycling from the galvanic sludge – **Figure 1** [15]. This is a so-called “MAR-Process”, which allows a separation of non-ferrous metals from iron and chromium [16]. In the first step the ammonium carbonate is a leaching agent, 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 leaching solution by solvent extraction performed in particular steps.

Electrolytic copper, nickel sulfate and nickel carbonate are final products.

The aim of this work is a proposal of an applicable procedure of leaching of galvanic sludge samples obtained from various galvanizing plants using a suitable leaching technology, separation of iron and zinc and subsequent obtaining of metal zinc through electrolysis.

## 2. EXPERIMENTS

Galvanic sludge samples were obtained from 6 different galvanizing plants in Olomouc Region and Moravian-Silesian region. Results of X-ray analyses determined zinc content ranging between 5 to 35 wt%, 4 - 12 wt% of iron and up to 2 wt% of Cr. In one case a high content of manganese about 8 wt% was found out, too.

Galvanic sludges from different galvanizing plants were processed in following ways: At first damp samples of waste sludge were treated by drying at approximately 100 °C and then homogenized by hand milling to an appropriate size of particles. The following solutions were used for the leaching process: 18% sulfuric acid, 12% nitric acid or 7% hydrochloric acid. Leaching was performed at temperatures of 40 °C or 60 °C, with an addition of hydrogen peroxide or ozone blowing. The aim of these experiments was to optimize the leaching process and to achieve the maximum dissolution of metals of interest from sludges. Partial results have been presented in [17]. It was found out that when sulphuric acid was used for leaching, a noticeable transition of metal elements to the leach occurs.

A content of zinc, iron, nickel and other metals in solutions was determined by a method of atomic absorption spectrometry (AAS) with the atomization process in a flame. Varian AA 280Z spectrometer was used, including the integrated diluter system. The highest standards for a calibration curve were 2.5 mg/l for zinc and 5 mg/l for iron and nickel. The samples were stabilized by nitric acid.

In order to separate zinc from other metals, precipitation of the leach after acidic leaching through NH<sub>4</sub>OH was used. 10 g of the sludge sample was always dissolved in 100 ml of the acid (see **Table 1**). The solution was diluted to 200 ml and while slowly adding concentrated NH<sub>4</sub>OH, Fe(OH)<sub>2</sub> precipitate occurred. By adding 2 ml of H<sub>2</sub>O<sub>2</sub> hydrogen peroxide, ferruginous consistent precipitate Fe(OH)<sub>3</sub> was formed. A filtration followed, then rinsing in 100 ml of distilled water and in the end the precipitate was dried up. The results of X-ray analyses (DELTA X Professional handheld x-ray spectrometer, ED-XRF method, SDD for radiation detection) for the particular samples after the above mentioned processing are shown in **Table 1**.

**Table 1** Results of X-ray chemical analyses of precipitates (wt% or wt. ppm) – an average of three measurements

Leaching	Zn	Fe	Mn	Ni	Cu	As	Zr	Mo	Cd	Sn	Pb	Cr	Hg
65% HNO <sub>3</sub>	4.4	14.5	1690	70	90	20	20	10	---	50	100	5940	---
20% H <sub>2</sub> SO <sub>4</sub> *	0.2	29.0	730	50	450	60	10	80	---	---	---	550	---
20% H <sub>2</sub> SO <sub>4</sub> **	4.7	14.2	1010	20	70	20	20	10	40	---	30	340	---
20% HCl	20.2	17.2	2320	210	410	80	100	10	110	100	80	7370	140

\* - the solution heated to 80 °C for a period of 30 min after H<sub>2</sub>O<sub>2</sub> addition; \*\* - temperature 21 °C after H<sub>2</sub>O<sub>2</sub> addition.

After dissolving in 20% H<sub>2</sub>SO<sub>4</sub>\*\*, the leach contained 4240 mg/l of Zn and 0.17 mg/l of Fe (AAS analysis).

After dissolving in 20% HCl, the leach contained 4160 mg/l of Zn and 0.13 mg/l of Fe (AAS analysis).

The results imply that the leach contained zinc, the Fe content was at minimum. So after leaching in sulphuric acid and subsequent precipitation using NH<sub>4</sub>OH, a significant separation of zinc from iron occurred.

The sludge with weight of 10 g from different suppliers was dissolved in 100 ml of 20% H<sub>2</sub>SO<sub>4</sub> for a period of 4 hours. A filtration of undissolved solids followed, where the solid undissolved proportion was washed by distilled water and dried at 110 °C for a period of 24 h. The filtrate was then precipitated using 25% solution of NH<sub>4</sub>OH. The formed precipitate was oxidized using 20 ml of H<sub>2</sub>O<sub>2</sub> for a period of 3 hours; afterwards the precipitate was washed and dried at 110 °C. The samples of the particular filtrates were analyzed for zinc, iron, nickel and copper content - see **Table 2**.

**Table 2** Chemical analyses of filtrates (AAS) – weights and contents of elements in solids after dissolving in H<sub>2</sub>SO<sub>4</sub> and after the precipitation of iron using ammonia. A composition of the delivered sludge after having been dried-up is given as well (X-ray analysis)

Supplier	After leaching in 20% H <sub>2</sub> SO <sub>4</sub> (g)	After coagulation in NH <sub>4</sub> OH (g)	Zn (mg/l)	Fe (mg/l)	Ni (mg/l)	Cu (mg/l)	Zn* (wt%)	Fe* (wt%)	Ni* (wt%)	Cu* (wt%)
D	1.0	1.69	3394	0.223	---	3.01	15.9	12.3	---	---
H	5.74	3.62	8768	0.357	2.09	4.83	21.7	4.3	0.01	0.03
B	1.24	2.18	11575	0.203	2.57	5.22	35.5	3.9	0.01	0.07
K	2.47	3.62	4229	0.178	784	260	12.6	10.5	1.8	1.3

Note: \*The delivered galvanic sludge state (wt%)

Zinc can be separated from aqueous solutions by electrolysis despite a significantly negative electrode potential -0.763 V. The electrolyte cleanliness, a condition of electrode surfaces and a current density are necessary for the proper electrolysis process. A presence of impurities in the electrolyte is a crucial issue for Zn separation by electrolysis. Impurities can be divided into three groups: Impurities more electronegative than Zn (e.g. Al, Mg, Mn) do not affect the Zn separation process directly, nevertheless their high concentration in the electrolyte increases the viscosity, thus restraining diffusion processes in the layer adjacent to electrodes. Impurities (e.g. Pb, Cd and Sn) the electrode potential of which ranges between Zn<sup>+</sup> and H<sup>+</sup> can be separated along with Zn, contaminating the resulting product. However, some admixtures can be dissolved back (e.g. Fe, Co, Ni), thus reducing the cathode current yield. More electropositive impurities than Zn (e.g. Cu, As, Sb, Ge etc.) have a harmful effect on the separated zinc. They form local cells on a cathode, resulting in dissolving of the separated Zn, thus reducing the current yield [18].

Recommend parameters for the zinc electrolysis are as follows: 400 – 600 A m<sup>-2</sup> current density, 2.5 - 3.5 V voltage on electrodes, 35 – 40 °C electrolyte temperature. A cathode is usually made of aluminum plates of min. 99.5 % purity, a material for an anode is usually a Pb plate with a small addition of Ag (0.5 – 0.85 wt%) for mechanical strength increasing. Cathode current yields range between 90 – 93 % depending on the electrolyte cleanliness [18].

The first two experiments of electrolysis (H supplier) were carried out as follows: 100 g of the sludge sample were dissolved in a 2000 ml capacity beaker, in 1000 ml of 20 % (or 10 %) H<sub>2</sub>SO<sub>4</sub> solution, for a period of 4 hours. After dissolving, the solution was filtered and rinsed by 300 ml of distilled water on a fritted glass with a vacuum filtration. A proportion of solids was weighed after having been dried-up - 72.8 g (or 73.21 g). The filtrate was evaporated to 1000 ml volume. Further, after cooling-down the filtrate was precipitated using NH<sub>4</sub>OH solution (250 ml), where Fe(OH)<sub>3</sub> was precipitated in the form of a ferruginous precipitate. In order to accelerate oxidation, 5 ml of concentrated hydroperoxide was added for a reaction period of 3 hours and subsequently the solution was gravitationally filtered. The rinsed precipitate was dried at 110 °C temperature for a period of 24 h and weighed - 53.21 g (or 55.12 g). The filtrate was diluted by distilled water to 3000 ml (or 2000 ml) and subjected to electrolytic precipitation for zinc. The bath temperature of 30 °C, 3 V voltage and 0.8 A current.

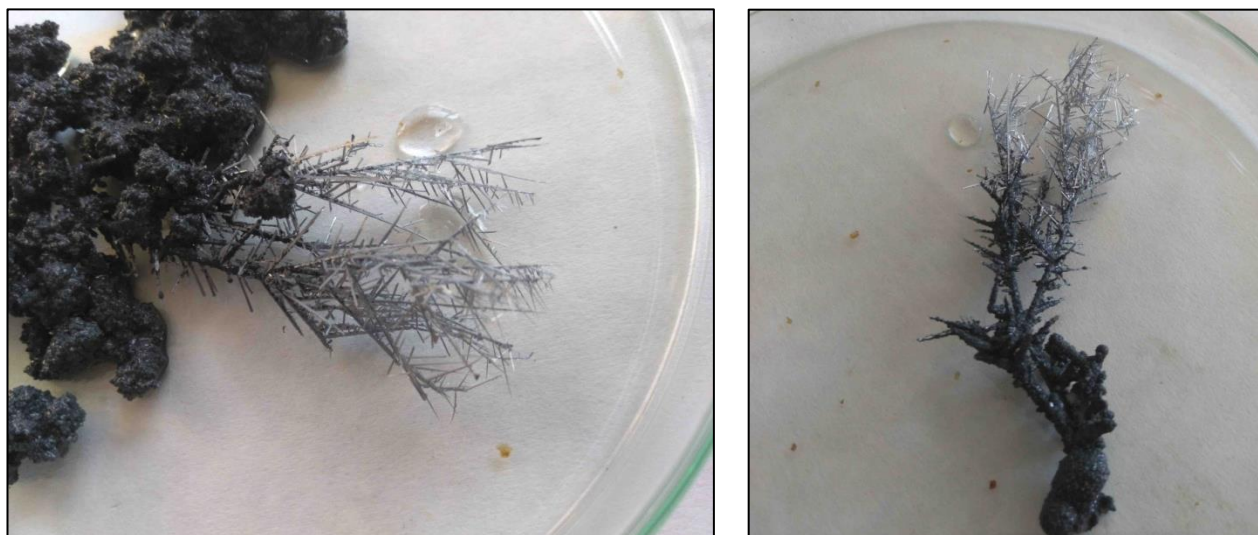
The cathode was made of pure Al, the anode was a Pb plate. Precipitated Zn was removed from the cathode, filtrated, rinsed, dried-up, weighed - 0.53 g (or 3.35 g) and chemically analyzed afterwards. During the electrolysis the solution had pH = 7 (or pH = 8). The above mentioned results imply that the 2<sup>nd</sup> experiment resulted in a higher zinc yield after the electrolysis - see **Table 3**.

**Table 3** Results of chemical analyses of solid proportions (wt% or mg/kg) – an average of three measurements (supplier H)

Sample	Zn*	Zn	Fe*	Fe	Mn	Ni	Co	Cu	Pb	Cr	Hg
Delivered state	21.7*		4.3*		400*	100*		300*		1000*	
After leaching	1.8*	3.4	2.34*	2.76	392	77.3	3910	30.7	84.9	920	0.035
After coagulation of Fe	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, 6010 method. Mercury was determined by AMA 254 device. X-ray spectrometry – Delta X instrument (analyses marked \*)

Conditions of the 3<sup>rd</sup> electrolysis experiment: Dissolution of 100 g of the sludge (B supplier) in 10% solution of H<sub>2</sub>SO<sub>4</sub>. A proportion of solids was weighed after having been dried-up (60 g). The filtrate was precipitated using 25% solution of NH<sub>4</sub>OH (250 ml) for Fe(OH)<sub>3</sub>. After having been dried-up, the precipitate had a weight of 67.4 g. The electrolysis was performed under the following conditions: the bath temperature of 30 °C, 3 V voltage, 0.8 A current, pH = 8. The precipitated Zn removed from the aluminum cathode had a weight of 7.93 g, which was more than in foregoing experiments. A photographic image of the product after the electrolysis is shown in **Figure 2**. Chemical analyses have not yet been carried out.



**Figure 2** Photo of the separated zinc on the cathode after the electrolysis (the 3<sup>rd</sup> experiment)

### 3. DISCUSSION

Within the experiments mentioned above, the aim was to find optimal conditions for leaching of the galvanic sludge with a high Zn and Fe content obtained from six different galvanizing plants. HNO<sub>3</sub>, H<sub>2</sub>SO<sub>4</sub> and HCl acids were applied at different temperatures and periods of leaching, possibly with an addition of H<sub>2</sub>O<sub>2</sub> or ozone [17]. H<sub>2</sub>SO<sub>4</sub> acid worked best. For separation of Zn and Fe the ammonia was used, when iron



precipitation in the form of  $\text{Fe}(\text{OH})_2$  occurred, or  $\text{Fe}(\text{OH})_3$  after adding  $\text{H}_2\text{O}_2$ . The results confirmed unambiguously the Zn separation from Fe in the filtrate - see **Table 2**. During the subsequent electrolysis different conditions were tested. The electrolyte temperature of 30 °C, 3 V voltage, 0.8 A current and pH = 8 seem to be optimal. The obtained product on the cathode contained 58 wt% of Zn, the Fe content was neglectable – see **Table 3**. In this phase there were laboratory-scale experiments.

#### 4. CONCLUSION

In this work, experiments of galvanic sludge leaching, iron precipitation using  $\text{NH}_4\text{OH}$  and following electrolysis with the aim to obtain metals of interest were performed. The conditions and results of these experiments are described in the text and shown in the relevant tables. In the follow-up phase we will focus on optimization of particular processes parameters, so that we can obtain zinc as pure as possible, suitable for further application in galvanizing plants. A further step will be a transition from the laboratory scale to a pilot plant process.

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