

POSSIBILITIES OF INDUSTRIAL WASTE RECYCLING BY LEACHING IN ORDER TO OBTAIN ZINC

¹Hana RIGOULET, ¹Jaromír DRÁPALA, ¹Silvie BROŽOVÁ, ¹Šárka LANGOVÁ,
¹Jiřina VONTOROVÁ, ²Jaroslav KUBÁČ, ³Dominik JANÁČEK

¹VSB - Technical University of Ostrava, Ostrava, Czech Republic, EU, hana.rigoulet@vsb.cz

²GALVA s.r.o. Držovice, Czech Republic, EU, kubac@galva.cz

³WANZL spol. s r.o., Hněvotín, Czech Republic, EU, Dominik.Janacek@wanzl.cz

<https://doi.org/10.37904/metal.2022.4517>

Abstract

The paper deals with the possibility of obtaining zinc from waste galvanic sludge, which arises during galvanic plating. Galvanic sludges, which contain significant amounts of heavy metals, form waste suitable for hydrometallurgical recycling. This method has already been proven as a suitable way of treating this type of industrial waste. The aim of the experiments is to obtain zinc by leaching several types of waste samples in different acids and hydroxide, at selected temperatures and time intervals. The leaching process will be followed by electrolysis of the leachate and recovery of the product as a secondary raw material. The practical part also includes chemical and material analyses of leaching products.

Keywords: Galvanic sludge, zinc, leaching, chemical analyses

1. INTRODUCTION

Politics and legislation aim at a more sustainable society. The EU Waste Hierarchy sets the priorities for different waste treatment approaches needed to reach these goals: material recycling and energy recovery are preferred over final disposal [1].

Zinc recycling from waste materials is very important from ecological and economical point of view. Zinc is one of the most versatile metals, which is used for many applications, including plating and coating. The use of secondary resources, such as zinc waste, is a consequence of the high demand for zinc. Electroplating sludge is one of the rich sources of zinc [2-4]. At present, these sludges are now transported to the landfill, then disposed of and not used in any way. Galvanic sludge is considered to be one of the most highly toxic types of waste and stored mainly in sludge pits. Such practice has not any economic or environmental advantages [5].

Recycling of hot-dip galvanizing by-products allows zinc to be recovered as a metal or other compounds and returned to the production cycle, thereby reducing the input of primary metal and improving environmental protection [2]. Zinc sludge can be treated by both pyrometallurgical and hydrometallurgical methods [7,8].

The latter are efficient, economical, relatively clean and can be adapted on a small or medium industrial scale. Literature data on hydrometallurgical treatment of wastes mainly consider the leaching method in sulphuric or hydrochloric acid [7,9].

This article presents the results of preliminary studies of hydrometallurgical treatment of sludge from electroplating produced by industrial sources [10]. At present, this waste is disposed of domestically by zinc producers or sold to foreign recycling companies. The aim of the research was to find out the influence of sulfuric acid, hydrochloric acid and sodium hydroxide on the amount of leached metal, with intensive stirring

and selected temperatures. From the obtained results, it is possible to design a process for recycling zinc from this type of waste and its use as a secondary raw material [11-13].

The aim of the work is to obtain zinc from leaching of waste galvanic sludge. A partial goal is a theoretical analysis of hydrometallurgical processes. The practical part is focused on the treatment of samples, subsequent leaching of galvanic sludge in sulfuric acid, hydrochloric acid and sodium oxide, under predetermined conditions. The work ends with the evaluation of the conditions under which the highest zinc recovery is achieved after leaching of galvanic sludge. This phase is followed by further processing.

2. HYDROMETALLURGICAL TREATMENT OF GALVANIC SLUDGE WASTE

Waste residues can be treated mainly in two ways, pyrometallurgically and hydrometallurgically. At present, the hydrometallurgical method is the most common method of zinc extraction and involves leaching, purification and electrolysis [11-16].

Hydrometallurgical processes are based on the leaching of pretreated enriched ore, in order to obtain sulphates which are highly soluble in suitable leaching agents. The resulting products are two phases, a solid residue and an extract containing the metal of interest. We then obtain the metal of interest from the leachate through a number of processes. With a relatively rich feedstock, a number of other metals will still be present in the leachate, which can be further leached with leaching agents to obtain leachate and depleted leachate.

Sludges from electroplating processes, which contain large amounts of heavy metals, are waste suitable for recycling. They arise during the treatment of wastewater from the operation of electroplating plants. It is a mixture of metal hydroxides or oxides, mainly iron, zinc, chromium and other metals. The sludge is sedimented in the reaction wells. After the sedimentation it is completed and pumped into the sludge lagoon. From there, they are drained by a sludge pump in a sludge tank. The dewatered sludge is then collected in containers. Hydrometallurgical methods are commonly used for sludge treatment. Acid or alkaline leaching is used to convert the metals of interest into leaches. Most waste materials do not dissolve in the environment or turn into a sparingly soluble compound. The leach is then treated by electrolysis to separate the individual metals [11-20].

3. EXPERIMENTS

The aim of the experimental part was to verify the leaching conditions for the amount of metal of interest obtained. Waste sludge samples from the electroplating process were processed by drying and crushing to the appropriate particle size. This was followed by a leaching process, where sulfuric acid, hydrochloric acid and sodium hydroxide were chosen as the leaching agent for the various dilutions.

The main part of the experimental work was to determine the most suitable conditions for obtaining the maximum recovery of zinc from the electroplating sludge. The samples were analysed for the content of zinc and other metals in the laboratories of the Faculty of Materials Technology. The input chemical analysis of the samples is given in **Table 1**. The analysis was performed on two types of samples.

Table 1 Zinc, iron and other metals content of the input samples, measured by ED-XRF (wt%)

Sample	Zn	Fe	Mn	Cu	Cr	S	Al
D	13.3	9	0.17	0.03	0.11	0.56	1.60
H	12.4	2.71	0.02	0.03	0.20	0.08	-

Waste sludge samples were pretreated by drying under normal conditions and size homogenization by grinding (**Figure 1**).

20% sulfuric acid, 15% hydrochloric acid and 25% sodium hydroxide were chosen for the hydrometallurgical leaching method. The choice of leaching agents should be made on the basis of knowledge from literature sources that deal with the leaching of waste materials. We wanted to compare the amount of metal obtained by changing the conditions of the leaching solution. Leaching solutions were prepared from concentrated acids and hydroxide by diluting to the desired solutions. The leaching was performed with sulfuric acid at 40 °C, hydrochloric acid at 25 °C and sodium hydroxide at 60 °C. Intensive mixing was ensured for all of them throughout the leaching process. Another condition in the experiments was the addition of an oxidizing agent in the form of H₂O₂ after four hours. The total leaching and subsequent collection time was 5 hours for acids and 4 hours for hydroxide.



Figure 1 Galvanic sludge samples for leaching

4. RESULTS AND DISCUSSION

Beakers with prepared samples of 1000 ml of solution together with 250 g of weighed sample of waste galvanic sludge for acids, 250 g of sample for hydroxide were placed on electromagnetic stirrers. The required temperatures were set individually on each electromagnetic stirrer. After the specified time, the leaching process was completed and the leachate substance and leachate were separated by filtration. Leach was subjected to AAS analyses (**Table 2, Figure 2**). pH was measured at all leachate substance.

Table 2 The final zinc, iron and other metals content of the leaching substance measured by AAS (mg/l)

Sample	pH	Zn	Fe	Cr	Mn	Cu	Ni
D HCl	0.39	11500	7990	243	116	21.9	6
H HCl	0.59	31500	5970	1150	60	41.2	13
D H ₂ SO ₄	0.96	12500	8860	318	155	27.1	8
H H ₂ SO ₄	1.28	36100	6780	1100	70	45.9	13.7
D NaOH	13.69	13200	12.2	0	0	12	6
H NaOH	13.81	38800	5.2	-	-	-	-

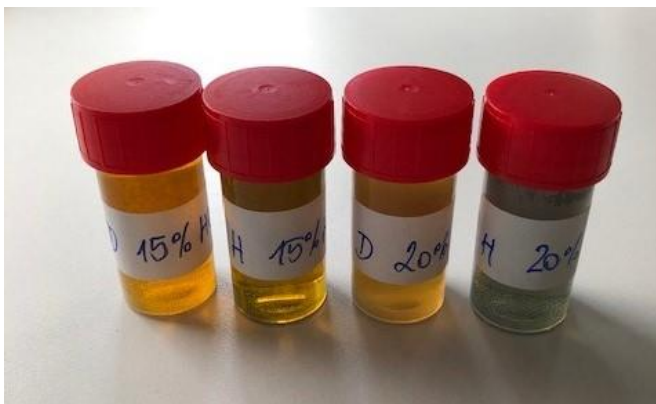


Figure 2 Leachate substance after the filtration process

Leaching residue was subjected to ED-XRF analyses (**Table 3, Figure 3**). The task was analyse the amount of zinc and iron in leach, primarily.

Table 3 The resulting content of zinc and iron in the leaching product measured by ED-XRF (wt%)

Sample	Zn	Fe
D HCl	3.48	3.31
H HCl	3.77	0.83
D H ₂ SO ₄	1.8	1.13
H H ₂ SO ₄	2.42	0.52
D NaOH	2.45	5.92
H NaOH	2.42	1.8

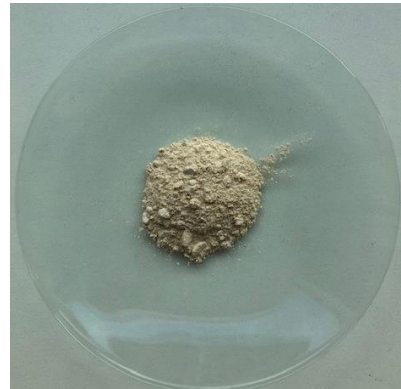
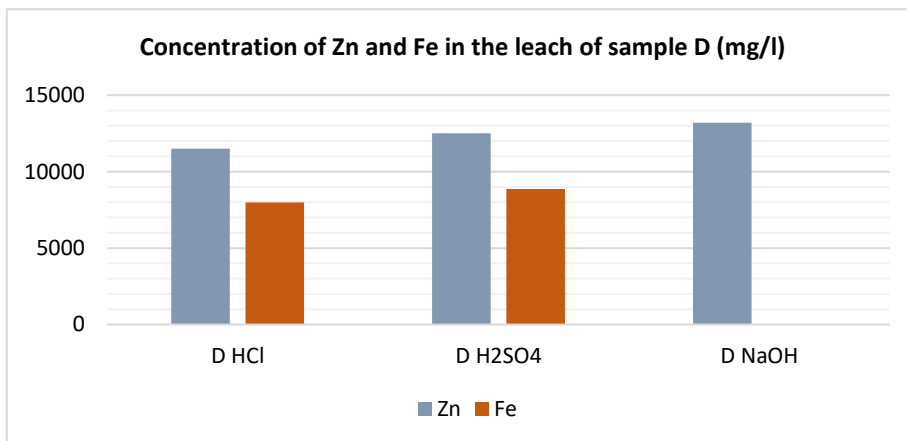
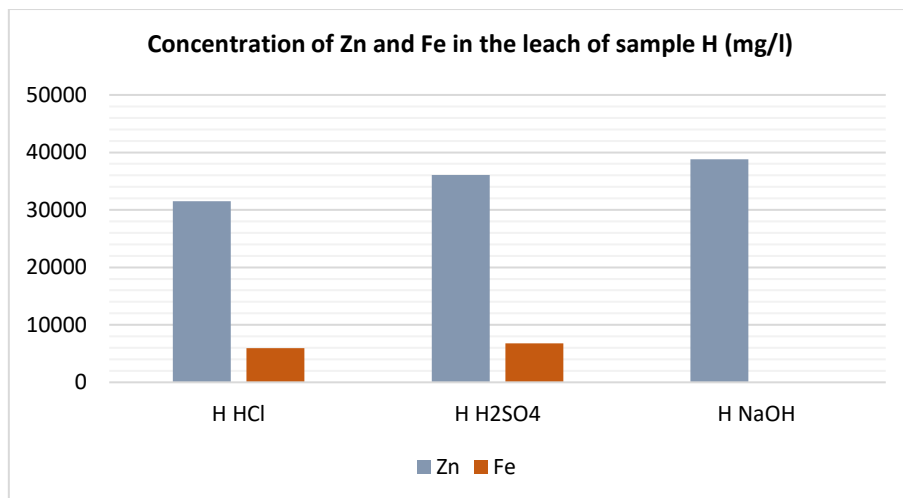


Figure 3 Leaching product after the filtration process (sample H)

Due to the fact that during leaching in individual solutions, iron is also leached into the leachate, which causes difficulties during further processing, **Graph 1** and **Graph 2** show the amount of iron in the leachate, to compare the efficiency of leaching solutions.



Graph 1 Concentration of Zn and Fe in the leach substance of sample D



Graph 2 Concentration of Zn and Fe in the leach substance of sample H

The experiments show that the use of hydrochloric acid is the least suitable and the use of sodium hydroxide as a leaching agent is the most suitable. When using it, most of the zinc passed into the leach, while the iron remained in the leach, as shown in **Graph 1** and **Graph 2**. When using acids, both zinc and iron passed into the leach, which complicates the subsequent electrolysis process.

5. CONCLUSION

The aim of this work was to obtain zinc by hydrometallurgical method from waste galvanic sludge and find optimum conditions for leaching of waste galvanic sludge with high Zn and Fe content. The waste sludge samples were treated and leached in sulfuric, hydrochloric acid solutions and sodium hydroxide under the given conditions. The outputs of the leaching process product was analysed by ED-XRF and AAS. It is clear from the experiments that zinc is leached in both types of acids and hydroxides. However, the use of hydroxide as a leaching agent is most suitable for further experiments, as the presence of iron in the leachate makes further processing of the electrolysis difficult.

ACKNOWLEDGEMENTS

This work was solved in the frame of the project of Technological Agency of Czech Republic No. SS01020312 „Innovative technology of the closed loop water circulation in the electro-galvanizing process and processing of metal waste – sludges and filtration cakes from the galvanizing plant“, and projects of SP2022/68 and SP2022/15.

REFERENCES

- [1] LINDBERG, D., MOLIN, C., HUPA, M. Thermal treatment of solid residues from WtE units: A review. In *Waste Management*. 2015, vol. 37, pp. 82-94.
- [2] DVOŘÁK, P., JANDOVÁ, J. Hydrometallurgical recovery of zinc from hot dip galvanizing ash. *Hydrometallurgy*. 2005, vol. 77, pp. 29-33. Available from: <https://doi.org/10.1016/j.hydromet.2004.10.007>.
- [3] GORDON, R.B., GRAEDEL, T.E., BERTRAM, M., FUSE, K., LIFSET, R., RECHBERGER, H., SPATARI S. The characterization of technological zinc cycles. *Resources, Conservation and Recycling*. 2003, vol. 39, pp. 107-135. Available from: [https://doi.org/10.1016/S0921-3449\(02\)00166-0](https://doi.org/10.1016/S0921-3449(02)00166-0)
- [4] BARAKAT, M.A., MAHMOUD, M.H.M., SHEHATA, H. Hydrometallurgical recovery of zinc from fine blend of galvanization processes. *Separation Science and Technology*. 2007, vol. 41, pp. 1757-1772. Available from: <https://doi.org/10.1080/01496390600588747>
- [5] TWIDWELL, L.G., DAHNKE, D.R. Treatment of metal finishing sludge for detoxification and metal value. *The European Journal of Mineral Processing and Environmental Protection*. 2001, vol. 1, no. 2, pp. 76–88.
- [6] ØDEGAARD, H., PAULSRUD, B., KARLSSON, I. Wastewater sludge as a resource: Sludge disposal strategies and corresponding treatment technologies aimed at sustainable handling of wastewater sludge. *Water Science & Technology*. 2002, vol. 46, no. 10, pp. 295–303.
- [7] BROŽOVÁ, S.; LISIŇSKA, M.; SATERNUS, M.; GAJDA, B.; SIMHA MARTYNKOVÁ, G.; SLÍVA, A. Hydrometallurgical recycling process for mobile phone printed circuit boards using ozone. *Metals*. 2021, vol. 11, p. 820. Available from: <https://doi.org/10.3390/met11050820>.
- [8] BROŽOV, S., DRÁPALA, J., MICZKOVÁ, J., HAVRÁNEK, J. Possibilities of obtaining zinc and iron after leaching of galvanic sludges. In: *METAL 2020. Proceedings 29th International Conference on Metallurgy and Materials*. ISBN 978-80-87294-97-0. Available from: <https://doi.org/10.37904/metal.2020.3629>.
- [9] Liquid waste treatment in galvanizing and zinc electroplating. Industrial wastewater & air treatment. Available from: <https://condorchem.com/en/blog/treatment-waste-electroplating-industry-zinc-coatings/>.
- [10] MAKOSKAYA, O.Y., KOSTROMIN, K.S., BRYANTSEVA, N.I. Hydrometallurgical technology for processing of galvanic sludges. IOP Conf. Series: *Materials Science and Engineering*. 2020, p. 969.

- [11] GUPTA, C. K. *Chemical Metallurgy Principles and Practice*. 2003. Available from: <https://doi.org/10.1002/anie.200385071>.
- [12] AGACAYAK, T., ARAS, A., AYDOGAN, S., ERDEMOGLU, M. Leaching of chalcopyrite concentrate in hydrogen peroxide solution. *Physicochemical Problems in Mineral Processing*. 2014, vol. 50, pp. 657-666. Available from: [10.5277/ppmp140219](https://doi.org/10.5277/ppmp140219)
- [13] HAVLIK, T., ORAC, D., PETRANIKOVA, M., MISKUFOVA, A. Hydrometallurgical treatment of used printed circuit boards after thermal treatment. *Waste Manag.* 2011, vol. 31, pp. 1542–1546. Available from: <https://doi.org/10.1016/j.wasman.2011.02.012>
- [14] FORMÁNEK, J. *Study of hydrometallurgical recycling processes Zn/MnO₂ battery*. Dissertation. VŠChT Prague, 2016, 186 p.
- [15] Galvanizing – GALVA, [online], [cit. 23.05.2022]. Available from: <https://www.galva.cz/zinkovani/>.
- [16] SAFARI, V., ARZEPEYMA, G., RASHCHI, F., MOSTOUFI, N. A shrinking particle-shrinking core model for leaching of a zinc ore containing silicon. *Int. J. Miner. Process.* 2009, vol. 93, pp. 79–83.
- [17] TAKÁCOVÁ, Z., HLUCHÁNOVÁ, B., TRPČEVSKÁ, J., Leaching of zinc from zinc ash originating from hot dip galvanizing. *Metall.* 2010, vol. 64, no. 12, pp. 517–519.
- [18] BRIGHT, M.A., DEEM, N.J., FRYATT, J. The advantages of recycling metallic zinc from the processing wastes of industrial molten zinc applications. *Light Metals*, 2007. Orlando, USA: TMS Annual Meeting & Exhibition.
- [19] ŚWIERK, K., BIELICKA, A., BOJANOWSKA, I., MAĆKIEWICZ, Z. Investigation of heavy metals leaching from industrial wastewater sludge. *Polish Journal of Environmental Studies*. 2006, pp. 447-451.
- [20] SILVA, J.E., SOARES, D., PAIVA, A.P., LABRINCHA, J.A., CASTRO, F., Leaching behaviour of a galvanic sludge in sulphuric acid and ammoniacal media. *J. Hazard. Mater.* 2005, vol. B121, p. 195.