THE INFLUENCE OF HYDROCHLORIC ACID ON THE ZINC EXTRACTION FROM FLUX SKIMMING

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Abstract

This paper presents experimental results obtained by agitation leaching of hazardous waste sample – flux skimming. Such flux is formed by $Zn(OH)Cl$ and NH_4Cl phases. Distilled water and water solutions of hydrochloric acid were selected as a leaching media.
The aim of this study was to determine optimal conditions of zinc extraction into the solution. The apparent order of reaction with regard to the initial HCl concentration in the leaching solution is n=0.18 in the concentration range from 0.01 $mol.dm^{-3}$ to 0.25 $mol.dm^{-3}$. The obtained results also indicate that the temperature does not significantly affect zinc extraction. The value of apparent activation energy was estimated to E_a=3.985 $kJ.mol^{-1}$. Optimal liquid to solid ratio L:S=80 for both used leaching media was also determined experimentally as well as the stirring rate at 200 rpm.

Keywords: flux skimming, zinc, hydrochloric acid, apparent activation energy

1   Introduction

In the field of surface treatment the technology of zinc hot-dip galvanizing is wide-spread method of anticorrosion protection of steel products. It is a metallurgical process where the formation of regular zinc coating takes place at the temperature between 450 and 470°C by interaction between the melted zinc and steel part [1 - 6].Zinc hot-dip galvanizing can be divided according to the used technology to continuous and batch. Batch zinc hot-dip galvanizing can be divided to a dry or wet depending on the way of fluxing agent application on the steel what is a part of its preliminary treatment.
During the wet batch hot-dip galvanizing the steel parts proceed to zinc dipping still wet from the process of pickling.

1.1 Specific waste formation

During the wet zinc hot-dip galvanizing process a foam like fluxing agent occurs on the surface of separated part of the zinc bath. The main purpose of fluxing agent is to dissolve surface oxides forming on the surface of steel after the pickling and to activate the surface of steel for the reaction with melted zinc [7, 8].Formation of wastes of liquid, gaseous and solid character

takes place during the process of hot-dip galvanizing. Solid wastes such as bottom dross and zinc ash belong to a group of wastes with a significant amount of zinc [9 - 12].

Specific waste forming only during the wet hot-dip galvanization is flux skimming. It is a spent and inactive fluxing agent which forms on the surface of zinc bath in the separated part of the bath. NH_4Cl is lost by evaporation as well as reaction between zinc, zinc oxide and iron during the hot-dip galvanizing process [13 - 15].

According to authors Kunhalmi [16], Krištofová [6], flux skimming is formed by ammonium chloride, oxides, sulfides, etc. Except original salts such as NH_4Cl, $ZnCl_2$, and $ZnCl_2.2NH_4Cl$, flux skimming also contains 18 – 22 % of Zn in metallic form, 30 – 35 % of ZnO and impurities, mainly Fe_2O_3.

Sjoukes [17] states that the chemical composition of flux skimming is formed by 48.1 % of $ZnCl_2$, 5.6 % of Zn in metallic form, 27.4 % of ZnO, 3.1 % of aluminum chlorides and other chlorides, aluminum, iron and cadmium oxides. According to literature [18], the overall amount of zinc in flux skimming is approximately 40 %.

According to The Europen Waste Catalogue & Hazardous Waste List – Valid from 1 january 2002, flux skimming is placed in the category „ *hazardous waste – 11 05 04"* [19].

2   Experimantal part
2.1 Material and methods of experiment

For experimental purposes a flux skimming sample was supplied by Slovak company. Supplied flux skimming sample had an irregular shape and heterogeneous composition, therefore it was necessary to homogenize it. The treatment of the sample consisted of drying-up, crushing and grinding. After the homogenization, the sample was quartationed with the aim of obtaining representative sample. Afterwards a representative sample was dissolved in 65% HNO_3 and analyzed by atomic absorption spectrometry (AAS). For the determination of chloride content in the samples, the titration method was used (0.1 M $AgNO_3$ with the addition of 5% K_2CrO_4). **Table 1** summarizes the chemical composition of the sample in weight percentage (wt. %).

Table 1   Chemical analyses of the flux skimming sample

Element	Zn	Fe	Al	Cl⁻
Weight [wt.%]	**46.8**	**0.03**	**0.12**	**22.7**

The phase analysis of the investigated samples was carried out by X-ray diffraction method using SEIFERT XRD 3003/PTS (Germany) under following conditions: Co 35 kV, 40 mA radiation, scan step 0.02 2theta. The range of measurements: from 10 to 130° 2θ.

The weights of the sample were 5 g, what represents L:S=80 ratio.The mixing of the sample in the leaching solution of 400 ml volume was supplied by glass stirrer with the constant stirring speed in the range of 200 rpm. Leaching experiments of zinc extraction into the solution were carried out in a solution of HCl with different concentrations (0.01M, 0.05M and 0.25M HCl). The leaching tests were carried out at the following temperatures 293, 313, 333, 353 K. The constant temperature was maintained in each experiment by water thermostat. At fixed time intervals (1, 5, 10, 15, 20 min.), liquid samples were taken in the volume of 5 ml. These samples were analyzed for zinc determination by AAS. The maximum duration of leaching test was 20 minutes.

3   Results and discussion
3.1 Material characterization
The qualitative phase analysis of the investigated sample of waste revealed that the sample contained two phases, i.e. NH_4Cl and $Zn(OH)Cl$. Other zinc-containing phases were not identified. The x-ray diffraction pattern is plotted in **Fig. 1**.

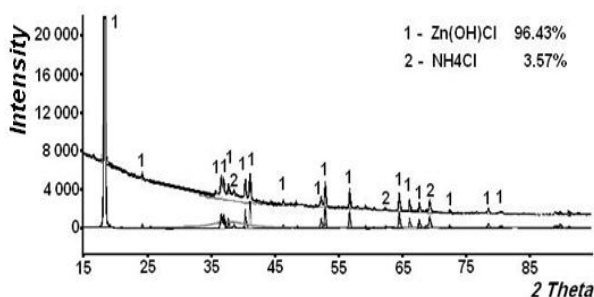**Fig. 1**   Results of x-ray diffraction analysis of flux skimming

The content of identified phases: 96.43 wt. % of $Zn(OH)Cl$ and 3.57 wt. % of NH_4Cl was estimated by quantitative x-ray diffraction phase analysis (**Fig.1**).

3.2 Leaching results
- #### Influence of HCl concentration
The influence of HCl solution concentration on the zinc extraction at the following conditions was investigated in this experimental part:
- leaching temperature – 293 K,
- stirring rate – 200 rpm,
- L:S ratio – 80:1.

The assumed reaction during the leaching of the studied sample in HCl [20] is:

$$Zn(OH)Cl_{(s)} + HCl_{(l)} = ZnCl_{2(ai)} + H2O_{(l)} \qquad \Delta G°_{293} = - 265,056 \text{ kJ/mol}^{-1}$$

Used HCl concentration were 0.01, 0.05 and 0.25 M. The results of leaching experiments in the time interval of 0 to 20 minutes are given in **Fig. 2**.
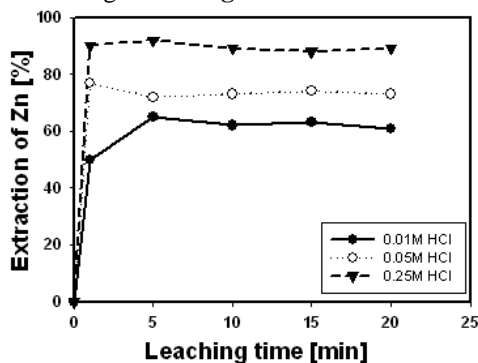

Fig. 2 The influence of concentration of HCl leaching solution on the Zn extraction in the dependence on leaching time

Favorable influence of increasing concentration of the hydrochloric acid solutions on the zinc extraction was observed from the curve position in **Fig. 2** for all leaching time intervals. Maximum Zn extraction (92 %) was observed after 5 minutes of sample leaching in the hydrochloric acid of 0.25 mol.dm^{-3}concentration. Subsequent prolongation of the leaching time did not cause an increase in the zinc extraction.

- **Influence of the temperature on the zinc extraction in 0.01 and 0.25 M HCl**

The following experiments were carried out at two selected HCl concentrations, i.e. 0.01M and 0.25 M. The aim of the experiments was the determination of the temperature influence on the zinc extraction into a solution. The following conditions remained constant during the investigation of the temperature influence:

- leaching solution – 0.01 and 0.25 M HCl
- L:S ratio – 80:1
- stirring rate – 200 rpm
- leaching time – 5 minutes.

Selected leaching temperatures were 295, 313, 333 and 353 K. The results of leaching experiments are given in **Fig. 3**. An increase of the temperature in the range of 295 – 353 K caused insignificant influence on the increase of zinc extraction at both HCl concentrations. Higher extraction was observed for the 0.25 M HCl solution.
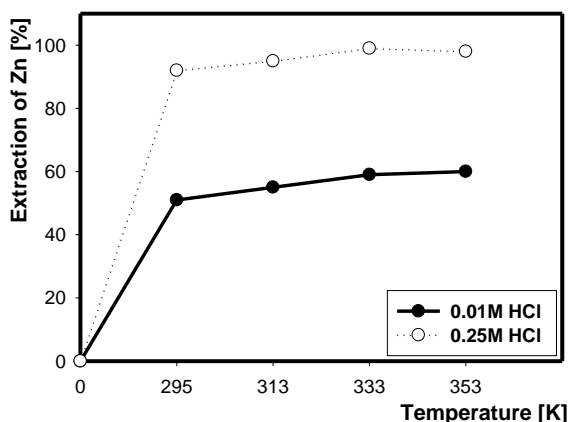

Fig. 3   Influence of the temperature on zinc extraction into a solution for 0.01 and 0.25MHCl

These concentrations of HCl (0.05, 0.01, 0.25M HCl) were chosen on the base of the previous experiments. Leaching at higher concentrations of hydrochloric acid (0.5, 1 and 2 M) were already published [21, 22].

After the 5 minutes of leaching at 295 K in 0.25 M HCl the observed extraction of Zn into a solution was at 92 % and 50 % for the 0.01 M HCl (**Fig.3**).

From **Fig. 3** it follows that the 0.01 M HCl is not sufficient for the maximum extraction of zinc in solution.

- **Apparent activation energy E$_a$**

The value of apparent activation energy E$_a$ was calculated from the initial values of zinc extraction rates according to the author Zelikman [20] in the time interval of 0 – 60 seconds.

Table 2 shows the values of zinc extraction rates experimentally obtained at the following conditions:

- c(HCl) = 0.01 M,
- ratio L:S = 80:1,
- stirring rate = 200 rpm.

Table 2   Dependence of X_{Zn} on the leaching time at temperatures of 293, 313 and 353 K

Leaching time [s]	Fraction of dissolved Zn			
	293 [K]	**313 [K]**	**333 [K]**	**353 [K]**
60	**0.502**	**0.564**	**0.611**	**0.555**
180	**0.504**	**0.567**	**0.612**	**0.578**
300	**0.544**	**0.569**	**0.613**	**0.599**
600	**0.602**	**0.628**	**0.623**	**0.589**

The values of leaching rate, given in **Table 2**, shows that an increase of temperature above 313 K did not significantly affect zinc leaching rate. At temperature of 353 K the value of zinc leaching rate decreased for all time intervals comparing to the temperature of 333 K.
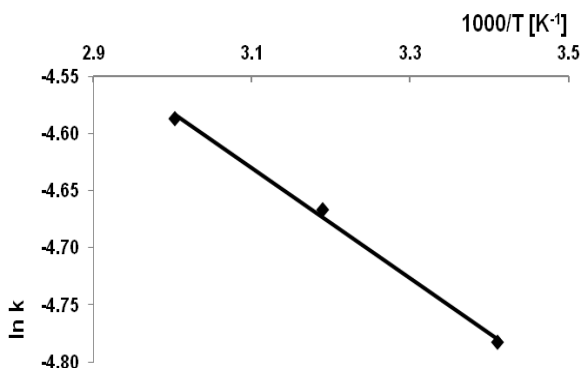

Fig. 4 Arrhenius dependence of temperature influence on rate constant of leaching the Zn containing sample, correlation index r = - 0.9976.

Using the logarithmic Arrhenius equation:

$$\ln K = \ln A - \frac{E_a}{RT} \tag{1.}$$

where **k** is rate constant, **A** is frequency factor and **R** is gas constant (8.314 J K^{-1}mol^{-1}), the values of apparent activation energy in the temperature interval of 293 – 333 K (E_a = 3.985 KJ.mol^{-1}) and frequency factor (A = 0.0431 s^{-1}) were calculated using the method of linear regression. Calculated value of E_a indicates that the rate of waste sample dissolving with the content of Zn(OH)Cl in the investigated temperature range is determined by diffusion speed, what is in accordance with the author Habashi [23], who states that if the E_a lies in the interval of 4.18 – 12.54 kJ.mol^{-1} then the leaching is controlled by diffusion. The behavior of ln k dependence on 1000/T illustrated in **Fig. 4** also indicates that the mechanism of sample leaching is constant in the investigated temperature interval of 293 – 333 K.

- **Determination of apparent order of reaction „n"**

The apparent order of reaction, **n** was determined with regard to the initial concentration of HCl in the leaching solution based on the following equation:

$$v = k.cHCl^n \tag{2.}$$

or as a logarithmic equation

$$\ln K = \ln K + n.\ln cHCl^n \tag{3.}$$

where **n** represents slope of a linear dependence $\ln v = f(\ln c_{HCl})$ which is given in **Fig. 5** and reaches the value of n = 0.18; ln k = -3.944.
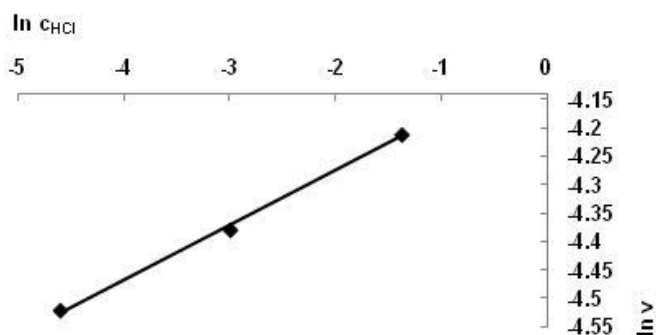

Fig. 5 An example of logarithmic $\ln v$ vs. $\ln c_{HCl}$ at295 K; correlation coefficient r = 0.9927

For the rate of dissolving the sample of waste containing Zn(OH)Cl at the temperature of 295 K it is possible to write an equation:

$$v=0.0193.c_{HCl}^{0.18} \tag{4.}$$

or as a logarithmic equation

$$\ln v = -3.944 + 0.18 \ln c_{HCl} \tag{5.}$$

The apparent order of reaction with regard to the initial HCl concentration in the leaching solution is n = 0.18 in the concentration range from 0.01 mol dm^{-3} to 0.25 mol dm^{-3}.

4 Conclusions

Experiments showed favorable effect of an increasing concentration of hydrochloric acid in the interval of 0.01 to 0.25 M HCl on the zinc extraction, where after 5 minutes of leaching in 0.01 M HCl the zinc extraction was at 51 % and in 0.25 M HCl 92%. It has been determined that leaching of zinc in HCl solution is more efficient than in distilled water.

Obtained results confirmed that the temperature did not significantly affect zinc extraction into the solution. An example can be seen for raising the temperature from 295 to 313 K when leaching in 0.25 M HCl, where the zinc extraction changed from 92 % to 95 % after 5 minutes of leaching.

The values of kinetic parameters such as apparent activation energy E_a = 3.985 kJ/mol and apparent order of reaction with regard to initial concentration of HCl n = 0.18 were also experimentally determined. From the calculated value of the apparent activation energy E_a it may be concluded that the rate of waste leaching in the HCl solution at the given temperature range is determined by the diffusion rate.

References
[1] T. Kuffa: *Non-Ferrous Metals,*first ed., VŠT Košice, Košice, 1982, (in Slovak)
[2] P. Mass, P. Peissker: *Handbuch Feuerverzinken,* third ed., WILEY-VCH, Germany, 2008, (in German)
[3] L. Hubová: MM Industrial range, Vol. 4, 2005, p. 78, (in Slovak)
[4] J. Trpčevská, J. Pirošková, B. Hoľková, M. Laubertová: *The role of aluminium and dross generation in hot dip galvanizing*, 20th Hot Dip Galvanizing Conference, Praha, AČSZ, 2014, p. 136-140
[5] G. Timmers: *Galvalution – Environmental friendly galvanizing*, 16th Hot Dip Galvanizing Conference, Plzeň, AČSZ, 2010, p.115-119
[6] D. Krištofová: *Recycling Non-Ferrous Metals*, USB-Toustrava, Ostrava, 2003, (in Czech)
[7] M. A. Barakat: Acta Metallurgica Slovaca, Vol.9, 2003, No.4, p. 259-269
[8] P. Dvořák, J. Jandová: Hydrometallurgy, Vol. 77, 2005, SI. 1–2, p. 29–33, doi:10.1016/j.hydromet.2004.10.007
[9] P. Bicao, W. Jianhua, S. Xuping, L. Zhi, Y. Fucheng: Surface and Coatings Technology, Vol. 202, SI. 9, 2008, p. 1785–1788, doi:10.1016/j.surfcoat.2007.07.044
[10] J. Pirošková, B. Hlucháňová, J. Trpčevská: *Leaching of solid wastes generateg during batch hot-dip galvanizing process*, 6th Kammel´s Quo vadis Hydrometallurgy, Polygrafia Gutenberg, Herľany, 2012, p. 171-176
[11] J. Trpčevská, J. Briančin, Ľ. Medvecký,A. Bobáková: Treatment of wastes from galvanizing, Vol. 1, 2008, p. 100-103, (in Slovak)
[12] M. K. Jha, V. Kumar, R. J. Singh: Resources Conservation and Recycling, Vol. 33, 2001, p. 1-22, doi:10.1016/S0921-3449(00)00095-1
[13] K. Mec: *Flux regeneration in hot dip galvanizing process,* 17th Hot Dip galvanizing Conference, Ostrava, AČSZ, 2011, p. 94-98
[14] A. R. Marder: Progress in Materials Science, Vol. 45, 2000, No. 3, p. 191-271, DOI:10.1016/S0079-6425(98)00006-1
[15] M. A. Rabah, A. S. El-Sayed: Hydrometallurgy, Vol. 37, 1995, SI. 1, p. 23-32, DOI:10.1016/0304-386X(94)00015-U
[16] G. Kunhalmi: *Metallurgy of secondary raw materials,* VST, Kosice, 1984, (in Slovak)
[17] F. Sjoukes: Anti-Corrosion Methods and Materials, Vol. 37, 1990, SI. 4, p. 12-13, doi: /10.1108/eb007267
[18] [11. 08. 2013], http://www.zaclon.com/pdf/zaclon_galvanizing_handbook.pdf
[19] According to The Europen Waste Catalogue & Hazardous Waste List – Valid from 1 january 2002

[20] A. H. Zelikman, G. M. Voľdman, L. V. Beljajevskaja: *Teoria gidrometallurgičeskich processov,* Moskva, Metallurgija, 1983, (in Russian)

[21] J. Pirošková, J. Trpčevská, M. Laubertová B. Hoľková, E. Sminčáková: Metall, Vol. 68, No. 7-8, p. 302 − 306

[22] J. Pirošková, J. Trpčevská, B. Hlucháňová, M. Laubertová: Acta Metallurgica Slovaca, Vol. 18, 2012, No. 1, p. 34-39

[23] F. Habashi*: Principles of Extractive Metallurgy,* Vol. 1, Gordon and Breach, New York, 1970