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Kinetic Aspects of Leaching Zinc from Waste Galvanizing Zinc by Using Hydrochloric Acid Solutions

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In this work, the results of acid leaching of flux skimmings coming from two plants are presented. Sample A contained two phases, $Zn(OH)Cl$ and NH_4Cl. In sample B, the presence of three phases, $Zn_5(OH)_8Cl_2 \cdot H_2O$, $(NH_4)_2(ZnCl_4)$ and $ZnCl_2(NH_3)_2$, was proved. The aqueous solution of hydrochloric acid and distilled water was used as the leaching medium. The effects of the leaching time, temperature and concentration of the leaching medium on the zinc extraction were investigated. The apparent activation energy, $E_a = 4.61$ kJ mol^{-1}, and apparent reaction order $n = 0.18$ for sample A, and the values $E_a = 6.28$ kJ mol^{-1} and $n = 0.33$ for sample B were experimentally determined. Zinc leaching in acid medium is a diffusion-controlled process.

INTRODUCTION

The increasing demand for zinc in the world has required intensive efforts in terms of its extraction from different sources. Wastes are very important sources of many metals, including zinc, copper, nickel, lead, cobalt and others. The recovery and extraction of zinc from wastes is necessary and important both from the economic point of view and because of the increased requirements for environmental protection. Zinc is primarily used as a coating on steel to protect it against corrosion. Hot dip galvanizing is the most common coating method. During the hot dip galvanizing process, several solid wastes are formed, e.g., in the so called "wet" batch hot dip galvanizing process, spent flux skimmings are created. The recovery of zinc from this waste is of great importance because of its high metal content. There is a lack of research information on the hydrometallurgical processing of this kind of waste.

The hydrometallurgical processes are often superior to the pyrometallurical processes in the extraction of non-ferrous metals and the treatment of secondary materials. Studying the kinetic aspects of the leaching process is one of the key elements before establishing the flowsheet for the hydrometallurgical method of processing zinc-bearing ores, minerals and secondary materials.

The rate of zinc leaching, which is present in various phases in the flux skimmings as $Zn(OH)Cl$ and NH_4Cl or as $Zn_5(OH)_8Cl_2 \cdot H_2O$, $(NH_4)_2(ZnCl_4)$ and $ZnCl_2(NH_3)_2$, respectively, may be affected by selecting the appropriate leaching solution. According to the literature,[1,2] thermodynamics study of the leaching process of zinc indicates that it is possible to use both acid and alkaline media for leaching. The most commonly used acid solutions are H_2SO_4 and HCl.[3–7]

The chemical reaction formula of $Zn(OH)Cl$ and hydrochloric acid is as follows:[8]

$$Zn(OH)Cl_{(s)} + HCl_{(aq)} = ZnCl_2 + H_2O$$
$$\Delta G^0_{298} = -42.701 \text{ kJ} \tag{1}$$
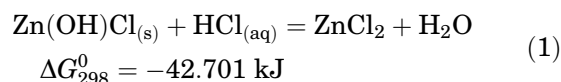
A negative value of standard Gibbs energy indicates that this reaction is thermodynamically feasible and spontaneous.

According to Sithole, it can be assumed that the chemical reaction of $Zn_5(OH)_8$ $Cl_2 \cdot H_2O$ (the main component of the waste sample B) with hydrochloric acid is as follows:[8]

$$\left(Zn_5(OH)_8Cl_2 \cdot H_2O\right)_{(s)} + 8HCl_{(aq)} = 5ZnCl_{2(aq)} + 9H_2O \tag{2}$$
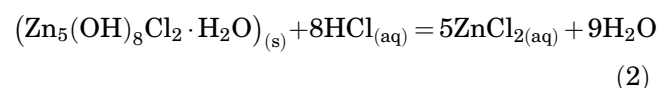
The concentration of the leaching solution at the reaction interface and the interface area determine the rate of the chemical reaction. The study of leaching kinetics of samples with zinc in the

hydrochloric acid solution requires a time-dependent experimental determination of zinc recovery under different conditions (temperature, concentration of leaching solution, liquid to solid ratio), i.e., determination of $X(\mathrm{Zn})$ as a function of the time t.

The amount of the dissolved Zn was calculated according to the formula:

$$X(\mathrm{Zn}) = \frac{m_0 - m}{m_0} \qquad (3)$$

where m_0 is the amount of zinc in the original sample in time $t = 0$ s, m is the amount of zinc in time $t \neq 0$ s.

The aim of the present investigation was to determine the following:

1. The mineralogical and chemical composition of the zinc-containing wastes.
2. The comparison of zinc recovery for both samples in time-dependent leaching experiments using distilled water and hydrochloric acid solution.
3. The zinc recovery during the agitated leaching of waste material under different parameters: liquid to solid ratio, reaction temperature, leaching times and HCl concentrations.
4. Based on kinetics measurement, values of the apparent activated energy "E_a" and values of the apparent order of reactions "n" with regard to the initial concentration of HCl for both waste samples.

EXPERIMENTAL STUDY

The samples of spent skimmings under investigation were supplied by two plants (A and B). The chemical composition of the flux skimming samples (A and B) in weight percentage is summarized in Table I.

Prior to the leaching tests, the samples were crushed ($d \geq 1.25$ mm) and ground ($d \leq 1.25$ mm). After homogenization, the sample was adjusted by quantation with the aim of obtaining a representative sample. The zinc concentration in the leaching solutions was analyzed by the atomic absorbance spectrophotometry (AAS) method. The parameters used for the analyses were: supply current 10 mA, wavelength 213.9 nm, gap 1.0 nm, and range of calibration 0.01–2 μg cm^{-3}. Chlorides were estimated by the titration method using 5% AgNO$_3$ solution and K$_2$CrO$_4$ indicator.

The phase analysis of the investigated samples was carried out by the x-ray diffraction method on a SEIFERT XRD 3,003/PTS (Germany) under the following conditions: Co 35 kV, 40 mA radiations, scan step 0.02 2θ. The range of measurements was from 10 to 130° 2θ. Analytical reagent grade chemicals and distilled water were used in all experiments.

The experimental conditions of the leaching samples in HCl solutions were: volume of leaching solution: 400 cm^3, sample weight: 20 g, rate of rotation of the stirrer: 3.3 s^{-1}.

The leaching tests were carried out in 1000-cm^3 glass containers. A glass stirrer which rotated at the constant speed of 3.3 s^{-1} agitated both solid and liquid phases. The leaching solutions were prepared by dissolving HCl in distilled water. The temperatures at which the leaching tests were performed were maintained at the constant level by a water thermostat.

RESULTS AND DISCUSSION

The phase analysis revealed that the sample (A) contained two phases, i.e. Zn(OH)Cl and NH$_4$Cl. Other zinc-containing phases were not identified. The x-ray diffraction pattern of the sample A is plotted in Fig. 1.

The phase analysis revealed that the sample (B) contained three phases, Zn$_5$(OH)$_8$Cl$_2$·H$_2$O, (NH$_4$)$_2$(ZnCl$_4$) and ZnCl$_2$(NH$_3$)$_2$. The x-ray diffraction pattern of sample B is plotted in Fig. 2.

Effect of Leaching Time

The effect of leaching time on the degree of zinc leaching from sample A (46.8% Zn) and from sample B (43.94% Zn) in distilled water at the temperature of 293 K, at the stirring rate of 3.3 s^{-1} and for a time period of 90 min is shown in Fig. 3.

As seen in Fig. 3, higher degrees of zinc extraction were achieved for sample A than for sample B using distilled water at all time intervals. The degree of zinc leaching for sample B was 0.13, while it was 0.63 for sample A after 10 min of leaching. This is likely due to the different phase composition. An extension of leaching time over 10 min using distilled water as a leaching medium had no effect under the given conditions. As sample A also contains NH$_4$Cl, it is suitable to consider the reaction of ammonium chloride with water. Almost all ammonium salts are soluble in water, and they are completely ionized. The NH$_4^+$ cation has an acidic character, which is expressed by the protolytic reaction with water:[9]

$$\mathrm{NH_{4(aq)}^+ + H_2O_{(l)} = NH_{3(aq)} + H_3O_{(aq)}^+} \qquad (4)$$
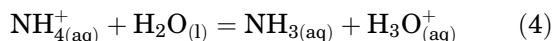
Table I. Chemical analyses of the flux skimming samples used for the kinetic study

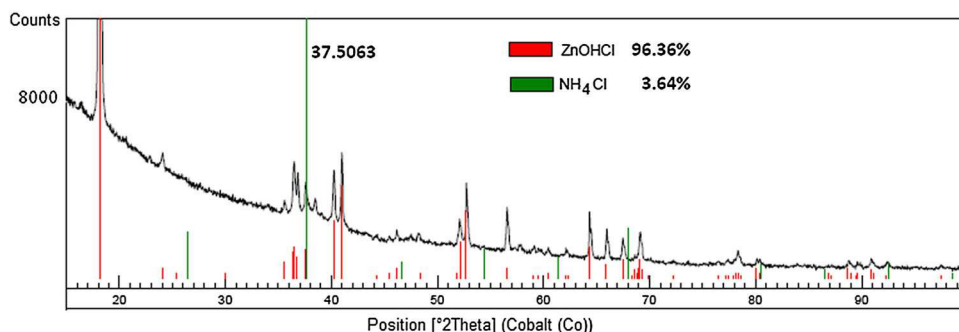| Element	Zn	Fe	Al	Pb	Cl$^-$
Weight% A	46.8	0.03	0.12	0.005	22.7
Weight% B	43.94	0.16	0.21	0.02	33.34

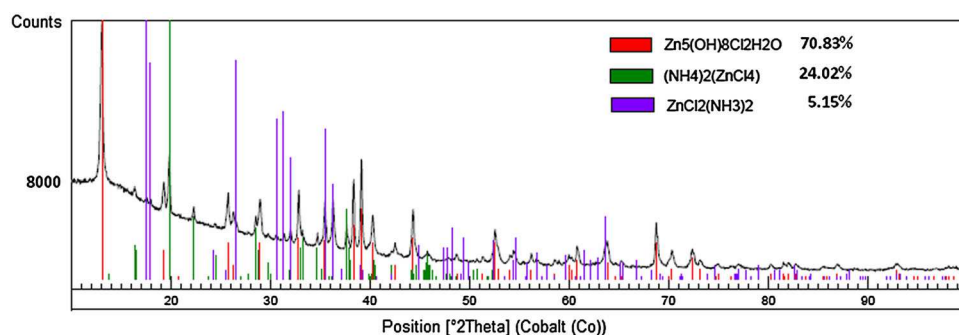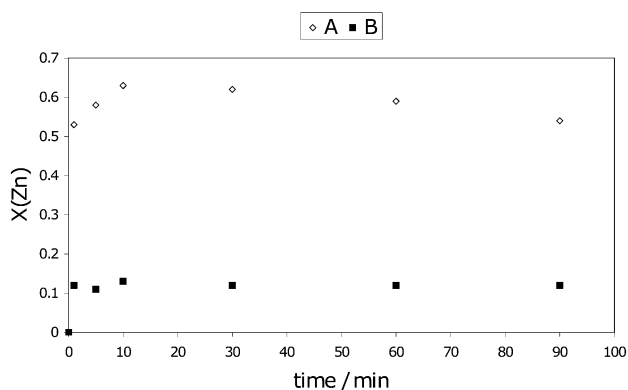Fig. 1. The results of x-ray diffraction analysis of sample (A).

Fig. 2. The results of x-ray diffraction analysis of sample (B).

Fig. 3. The effect of leaching time on the zinc recovery for samples A and B. (temperature 293 K; distilled water; stirring rate 3.3 s^{-1}; l:s = 20:1).

The water solution of ammonium chloride is acidic. If the product of dissolving ammonium chloride is only a small amount of NH_3 and HCl,[10] then the reaction in the acidic environment should probably look as follows:

$$Zn(OH)Cl_{(s)} + HCl_{(aq)} = ZnCl_2 + H_2O \qquad (5)$$
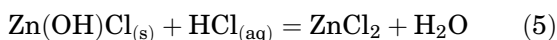
In these series of experiments, the time-dependent effect of temperature on the zinc extraction using distilled water for sample B was also studied. The reason was that the degree of zinc leaching at the temperature of 293 K in sample B

was below that for sample A. The determined values of the degree of zinc leaching in the temperature interval between 293 K and 353 K are presented in Table II.

The results presented in Table II showed that the use of distilled water as a leaching medium is unfavorable for sample B, because no significant increase of the zinc extraction was achieved in this sample even at the increased temperature of 353 K. Values of $X(Zn) = 0.12$ at the temperature of 293 K and $X(Zn) = 0.13$ at temperature of 353 K, respectively, after 1 h of leaching were achieved. Simonkolleite, which is major phase (70.83%) in sample B is insoluble in distilled water, so it follows that zinc is leached from the rest of the phases. A similar, not significant, effect of temperature on zinc leaching from sample A in distilled water was determined.[11]

The effect of the leaching time on the degree of zinc leaching using 0.25 mol dm^{-3} of hydrochloric acid as the leaching medium for both samples was experimentally studied. The results of the zinc extraction for the temperature of 293 K are shown in Fig. 4, and the results for the temperature of 313 K are shown in Fig. 5.

The degrees of zinc leaching $X(Zn) = 0.42$ in 0.25 mol dm^{-3} HCl for sample B and twice as high, $X(Zn) = 0.86$, for sample A at the temperature of 293 K after 10 min of leaching were achieved. The same trend was observed at all time intervals (Fig. 4). The degrees of zinc leaching $X(Zn) = 0.63$

Table II. Time-dependent effect of X_{Zn} at various temperature of 293 K, 313 K, 333 K and 353 K using distilled water for sample B

Time (min)	Degree of zinc leaching [−]			
	293 K	313 K	333 K	353 K
1	0.12	0.13	0.18	0.17
5	0.11	0.14	0.14	0.14
10	0.13	0.13	0.14	0.13
30	0.12	0.13	0.15	0.14
60	0.12	0.14	0.14	0.13
90	0.12	0.15	0.13	0.12
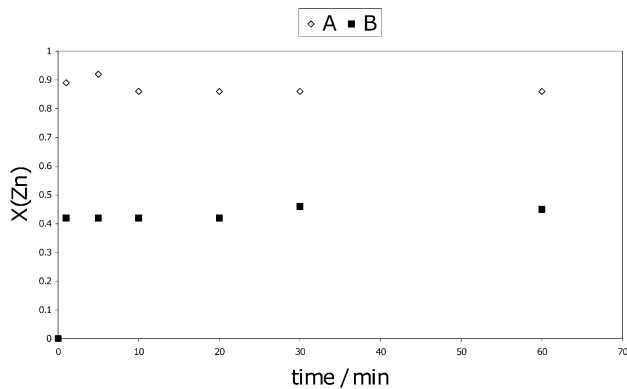
Fig. 4. The effect of leaching time on the degree of zinc leaching using 0.25 mol dm^{-3} HCl for both samples with various phase compositions (temperature 293 K; stirring rate 3.3 s^{-1}; l:s = 20:1).
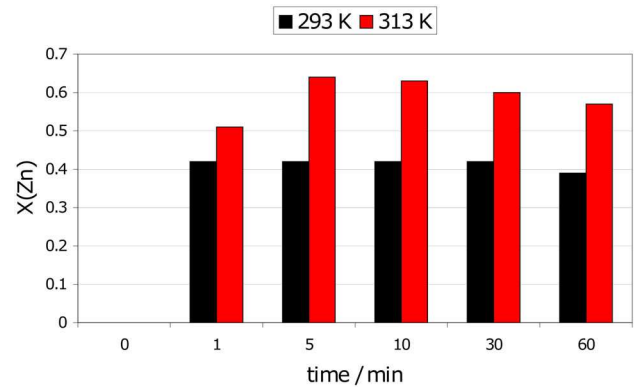
Fig. 6. The effect of the temperature on the leaching rate of zinc in 0.25 mol dm^{-3} HCl. (sample B; l:s = 20:1; stirring rate 3.3 s^{-1}).
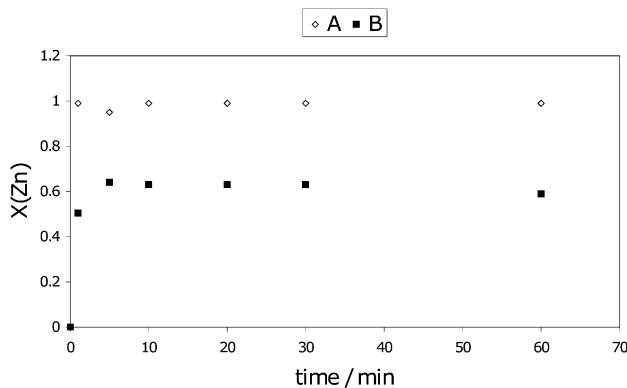
Fig. 5. The effect of leaching time on the degree of zinc leaching using 0.25 mol dm^{-3} HCl for both samples with various phase compositions. (temperature 313 K; stirring rate 3.3 s^{-1}; l:s = 20:1).

for sample B and $X(Zn) = 0.99$ for sample A were achieved at the temperature of 313 K after 10 min of leaching (Fig. 5).

Effect of Temperature

The positive effect of the increasing leaching temperature on the zinc recovery is shown in Fig. 6, where leaching in 0.25 mol dm^{-3} HCl

aqueous solution was carried out on sample (B) containing $Zn_5(OH)_8Cl_2 \cdot H_2O$, $(NH_4)_2(ZnCl_4)$ and $ZnCl_2(NH_3)_2$.

The effect of the temperature on the degree of zinc leaching using 1 mol dm^{-3} HCl for sample B was investigated in the temperature interval between 293 K and 353 K for 60 min. The results are presented in Table III. The time-dependent effect of the temperature on the degree of zinc leaching in 0.01 mol dm^{-3} HCl was experimentally studied for sample A because using 0.25 mol dm^{-3} HCl at the temperature of 293 K resulted in achieving the degree of zinc leaching equal to 0.86 at the temperature of 293 K, and even 0.99 at the temperature of 313 K.

The results presented in Table III showed a slight effect of the temperature on the degree of zinc leaching. The extension of leaching time over 5 min is also not efficient.

Effect of HCl Concentration

The effect of the HCl concentration on the degree of zinc leaching for sample B at the temperature of 293 K in particular time intervals is described by experimentally determined values of $X(Zn)$ presented in Table IV.

Table III. Time-dependent effect of $X_{(Zn)}$ at temperatures of 293 K, 313 K, 333 K and 353 K using 1 mol dm^{-3} HCl

Leaching time (min)	Degree of zinc leaching [−]			
	293 K	313 K	333 K	353 K
1	0.72	0.91	0.98	0.82
5	0.91	0.78	1	0.85
10	0.56	0.93	1	0.97
30	0.51	0.84	1	0.96
60	0.77	0.78	1	0.92

Experimental conditions: Sample B; l:s = 20:1; stirring rate 3.3 s^{-1}.

Table IV. Effect of HCl concentration on the degree of zinc leaching for sample B (Experimental conditions l:s = 20:1; 3.3 s^{-1}; 293 K)

Leaching time (min)	Degree of zinc leaching [−]			
	0.25 mol dm^{-3}	0.5 mol dm^{-3}	1 mol dm^{-3}	2 mol dm^{-3}
1	0.42	0.604	0.72	0.849
5	0.42	0.779	0.91	0.839
10	0.42	0.772	0.56	0.898
30	0.46	0.742	0.51	1.0
60	0.45	0.785	0.77	1.0

Based on data shown in Table IV, it is obvious that the increasing concentration of HCl has a positive effect on $X(Zn)$ in all time intervals at constant temperature. Leaching time of 30 min is necessary to achieve $X(Zn) = 1$ under conditions of temperature 293 K, l:s = 20:1 and stirring rate 3.3 s^{-1} using 2 mol dm^{-3}.

Apparent Activation Energy "Ea" and Apparent Order of Reaction "n" Determination

The following were used for the determination of apparent activation energy in the temperature interval of 293–333 K: 0.01 mol dm^{-3} HCl for sample A; 1 mol dm^{-3} HCl for sample B.

The apparent activation energy E_a was determined experimentally by measuring the initial dissolution rate of zinc at different temperatures T for the time interval 0–60 s. The temperature of 353 K was not considered for the determination of E_a, because of the decrease of the leaching rate of zinc at this temperature, which is evident from the values in Table III for sample B.

The Arrhenius equation was used to determine the activation energy:

$$\ln k = \ln A - Ea/R.T \qquad (6)$$

where k is the rate constant, A is the frequency factor, R is the universal gas constant and T is the temperature. The estimated apparent activation energy for sample B is $E_a = 6.28$ kJ mol^{-1} in the temperature interval from 293 K to 333 K and the

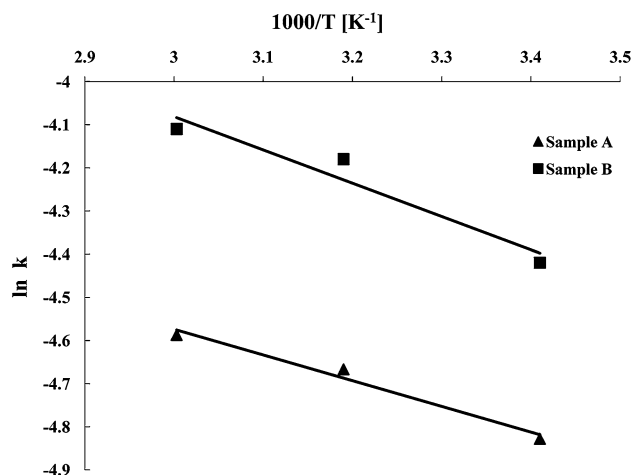

Fig. 7. The Arrhenius plot for zinc extracting (Samples A and B). Sample A: Correlation coefficient $R = -0.9924$; Sample B: Correlation coefficient $R = -0.9607$.

frequency factor is $A = 0.162$ s^{-1}. The apparent activation energy for sample A is $E_a = 4.61$ kJ mol^{-1} and the frequency factor $A = 1.0711$ s^{-1}. It is generally believed that high values of activation energy (>40 kJ/mol) indicate chemical control, whereas values <20 kJ/mol imply diffusion-controlled processes.[12,13] Estimated values of the apparent activation energy indicate that leaching of samples A and B is controlled by diffusion. The corresponding relationships between
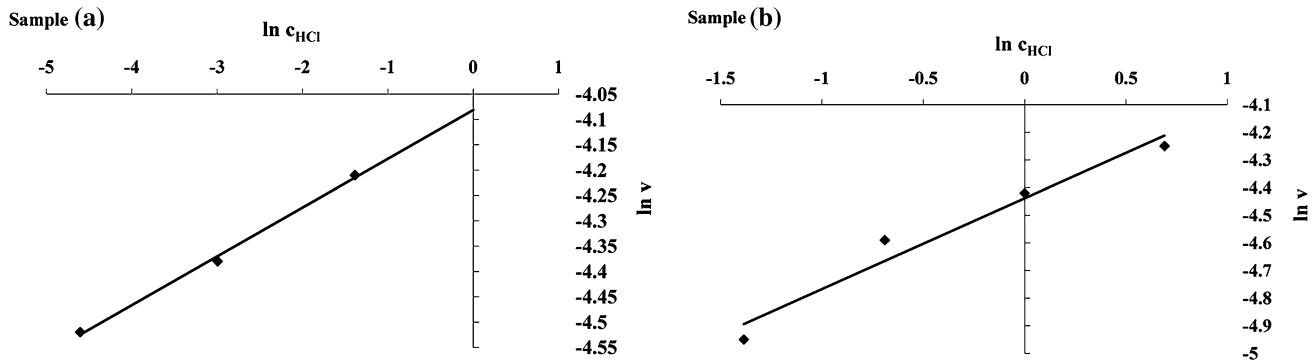
Fig. 8. The logarithmic plot ln v versus ln c_{HCl} for samples A and B. Sample A: Correlation coefficient $R = 0.9984$; Sample B: Correlation coefficient $R = 0.9806$.

ln k and $1000/T$ are shown in Fig. 7, which indicates that the mechanism for samples leaching in the temperature interval 293–333 K does not change.

The apparent activation energy, E_a, and the apparent order of reaction, n, were determined by the linear regression method from Eqs. 6 and 7, respectively.[12]

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

$$v_{Zn} = k \cdot c_{HCl}^n \qquad (7)$$

or in logarithmic form:

$$\ln v = \ln k + n \cdot \ln c_{HCl} \qquad (8)$$

where n is the slope of a graph of $\ln v_{Zn} = f(\ln c_{HCl})$, shown in Fig. 8 (Sample B). The value of $n = 0.33$, and ln $k = -4.443$. The dissolution of zinc at the temperature of 293 K can be represented as:

$$v = 0.0117 . c^{0.33} \qquad (9)$$

or in logarithmic form:

$$\ln v = -4.443 + 0.33 \cdot \ln c_{HCl} \qquad (10)$$

The dissolution of zinc for sample A can be represented as:

$$v = 0.0193 . c_{HCl}^{0.18} \qquad (11)$$

or in logarithmic form:

$$\ln v = -3.944 + 0.18 \ln c_{HCl} \qquad (12)$$

The following concentration interval was used for the determination of the apparent order of reaction at the temperature of 293 K: from 0.01 mol dm^{-3} to 0.25 mol dm^{-3} HCl for sample A, and from 0.25 mol dm^{-3} to 2 mol dm^{-3} HCl for sample B.

Experimentally Determined Values of E_a and n are Summarized in Table V

Relatively low values of the apparent activation energy suggest that the leaching process in both samples is diffusion-controlled.[12,13] The low values of E_a, as well as the dependence of the degree of zinc

Table V. Values of the apparent activation energy E_a and the apparent order of reaction n

Sample	E_a kJ mol^{-1})	Apparent reaction order n
A	4.61	0.18
B	6.28	0.33

leaching on the stirring rate indicate that the leaching of zinc from spent flux skimmings in hydrochloric acid is controlled by diffusion, and the mechanism in temperature interval of 293–353 K does not change. The effect of the stirring rate on the degree of zinc leaching was proved in the literature.[11] The optimum stirring rate of 3.3 s^{-1} was determined. The higher value of the apparent reaction order in sample B ($n = 0.33$) than in sample A ($n = 0.18$) confirms that the zinc leaching from sample B is more dependent on the concentration of leaching medium. This result is consistent with the results shown in Table IV and is related to the phase composition (presence of the insoluble in water phase of simonkolleite).

Precipitation is proposed for further treatment of the leached solution with the aim of obtaining zinc from the solution in the form of a saleable compound (ZnO). Two precipitation agents were used in the experiments for the purposes of examination: Na_2CO_3 and NaOH. Results of the experiments are published in the literature, Trpčevská et al.[14]

CONCLUSION

The effect of temperature and concentration of hydrochloric acid on the leaching rate of zinc from spent flux skimmings was studied by the agitated leaching process. The results show that:

- The samples of spent flux skimmings coming from two plants have similar high content of zinc (more than 40%).
- The phase composition of the samples is different. Sample A contains two phases, Zn(OH)Cl

and NH$_4$Cl. In sample B, the presence of three phases, Zn$_5$(OH)$_8$Cl$_2$·H$_2$O, (NH$_4$)$_2$(ZnCl$_4$) and ZnCl$_2$(NH$_3$)$_2$, was proved.

- The temperature has no significant effect on the leaching rate of zinc. According to the Arrhenius equation, the apparent activation energy values of zinc reaction for sample A and B are calculated to be 4.61 kJ mol^{-1} and 6.28 kJ mol^{-1}, respectively. The energy value falls in the range of 4 kJ mol^{-1}–12 kJ mol^{-1} for the typical inner diffusion-controlled process.[15,16]

- The effect of increasing the concentration of HCl in the leaching solution from 0.01 mol dm^{-3} to 0.25 mol dm^{-3} is favorable. The apparent order of reaction $n = 0.18$ for sample A was determined.

- The effect of increasing the concentration of HCl in the leaching solution from 0.25 mol dm^{-3} to 2 mol dm^{-3} is favorable. The apparent order of reaction $n = 0.33$ for sample B was determined.

- The recovery of zinc from sample B requires using hydrochloric acid with the concentration higher than 0.25 mol dm^{-3}, whereas for the recovery of zinc from sample A, hydrochloric acid with the concentration less than 0.25 mol dm^{-3} is sufficient at the same temperature. This observation is related to different phase compositions.

- The leaching rate of zinc from spent flux skimmings using hydrochloric acid depends on the stirring conditions. The optimum stirring rate 3.3 s^{-1} was used in all leaching tests.

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