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KINETIC STUDY OF ZINC LEACHING FROM SAL-AMMONIAC FLUX IN ACIDIC MEDIA

This paper presents the results of the laboratory investigation of acid leaching of sal-ammoniac flux. Sal-ammoniac is waste product originated during wet hot dip galvanizing process having about 40 % of zinc. Zinc is the most abundant element in the sal-ammoniac flux and in the supplied sample was occurred in the form of following phases: $Zn_5(OH)_8Cl_2{\cdot}H_2O$ in amount of 70.83 %, $(NH_4)_2(ZnCl_4)$ in amount of 24.02 % and $ZnCl_2(NH_3)_2$ in amount of 5.5 %. Leaching test of sal-ammoniac flux in distilled water and aqueous solution of hydrochloric acid has been carried out kinetically. The experimental parameters of HCl concentration, leaching time and temperature were varied. The results obtained are as follows: The apparent activation energy of leaching reaction by hydrochloric acid solution was $E_a = 6.28$ kJ mol^{-1}. The apparent order of reaction n = 0.33 was estimated.

Keywords: leaching, sal-ammoniac flux, zinc, hydrochloric acid, apparent activation energy, apparent order of reaction

BADANIE KINETYKI ŁUGOWANIA CYNKU Z ODPADOWEGO SALMIAKU W ŚRODOWISKU KWAŚNYM

W artykule przedstawiono wyniki badań laboratoryjnych kwaśnego ługowania odpadowego salmiaku. Salmiak ten jest produktem powstającym podczas gorącej zanurzeniowej galwanizacji zawierający ok. 40 % mas. cynku. Cynk jest pierwiastkiem występującym w największej ilości, dostarczona (badana) próbka zawierała następujące fazy: $Zn_5(OH)_8Cl_2{\cdot}H_2O$ — 70,83 %, $(NH_4)_2(ZnCl_4)$ — 24,02 % i $ZnCl_2(NH_3)_2$ — 5,5 %. Testy ługowania prowadzono w wodzie destylowanej i w wodnych roztworach kwasu solnego. W testach zmiennymi parametrami były: stężenie HCl, czas i temperatura ługowania. Uzyskano następujące wyniki: pozorna energia aktywacji ługowania roztworem kwasu solnego $E_a = 6,28$ kJ mol^{-1}, pozorny rząd reakcji n = 0,33.

Słowa kluczowe: ługowanie, salmiak, cynk, kwas solny, pozorna energia aktywacji, pozorny rząd reakcji

Introduction

The amount of zinc production in the world have increased and reached more than 13 million tons. Zinc is produced from various primary and secondary raw materials. The primary processes use concentrates, while in secondary processes recycled products from other metallurgical operations are employed. In practice, a clear distinction of primary and secondary zinc production is often difficult because many smelters use both primary and secondary raw materials. Zinc containing wastes as zinc ash, dross, flue dusts, sludge, residue etc. are generated in various chemical and metallurgical industries. The materials contain different level of impurities depending on the source. The hydrometallurgical processing is effective and flexible for treating such materials as it can control the different level of impurities. Studying kinetic aspects of the leaching process is one of the key elements before establishing the flowsheet for hydrometallurgical method of processing the zinc-bearing ores, minerals or secondary materials. The rate of zinc leaching may be affected by selection of leaching solution as well as parameters as leaching temperature, leaching time, concentration of leaching solution, solid to liquid ratio and other [1÷6].

In this work distilled water and aqueous solution of hydrochloric acid were chosen as leaching agents because of chlorine content in the waste.

The aim of the study was to determine:

1. The chemical and phase composition of the sal-ammoniac flux.

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2. The effect of leaching time on the rate of zinc leaching in distilled water as well as in aqueous solution of hydrochloric acid.
3. The effect of leaching temperature on the rate of zinc leaching.
4. The effect of the concentration of hydrochloric acid on the rate of zinc leaching.
5. Value of apparent activation energy Ea and apparent order n of reaction based on the above (2, 3, 4) results.

Material and methods

A sal-ammonic flux sample was provided by a Czech galvanizing plant which applies the wet hot dip galvanizing process. The sample was crushed and milled. Representative sample after quartation process was subjected to chemical analysis. The results of chemical composition are shown in Table 1.

The phase analysis of the investigated samples was carried out by X-ray diffraction method on SEIFERT XRD 3003/PTS (Germany) under following conditions: Co 35 kV, 40 mA radiation, scan step 0.02 theta. The range of measurements: from 10 to 130° 2theta. The weight of samples subjected to leaching tests was always 20 g. The leaching tests were carried out in 1000 ml glass container. In each leaching test 400 ml of aqueous solution were used. Concentrations of HCl in leaching experiments were: 0.25 mol·dm^{-3}, 1 mol·dm^{-3} and 2 mol·dm^{-3}. Samples and solutions were agitated in all experiments at the rate 200 rpm. The leaching tests were carried out at the following temperatures: 293 K, 313 K, 333 K and 353 K respectively. The con stant temperature was maintained in each experiment by water thermostat. Samples of leaching solution (volume 5 ml) were withdrawn periodically for quantitative analysis to determine the amount of dissolved zinc by AAS method.

Table 1

Chemical composition of sal-ammoniac flux sample

Tablica 1

Skład chemiczny próbki odpadu salmiaku

Element	Zn	Cl^-	Fe	Al	Pb
wt. %	43.94	33.34	0.16	0.21	0.02

Results and discussion

The phase analysis revealed that the sample contained $Zn_5(OH)_8Cl_2 \cdot H_2O$, $(NH_4)_2(ZnCl_4)$ and $ZnCl_2(NH_3)_2$. Other zinc-containing phases were not identified. The XRD pattern of the sample is shown in Fig. 1.

Results of zinc leaching in distilled water are shown in Table 2. From the results it can be stated, that the zinc leaching rates are low, within the range 0.11 to 0.18. The leaching temperature and leaching time have no effect of the leaching rate of zinc using distilled water.

Fraction of dissolved zinc was calculated according to the following equation:

$$X_{Zn} = (m_0 - m) \;/\; m_0 \tag{1}$$

Where

m_0 is the amount of zinc in original sample in time $t = 0$ s,

m is the amount of zinc in time $t \neq 0$ s.

Table 2

Effect of X_{Zn} on leaching time at temperatures of 293 K, 313 K, 333 K, 353 K in distilled water

Tablica 2

Wpływ X_{Zn} na czas ługowania w wodzie destylowanej w temperaturze 293 K, 313 K, 333 K, 353 K

Leaching time min	Fraction of dissolved Zn, [-]			
	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

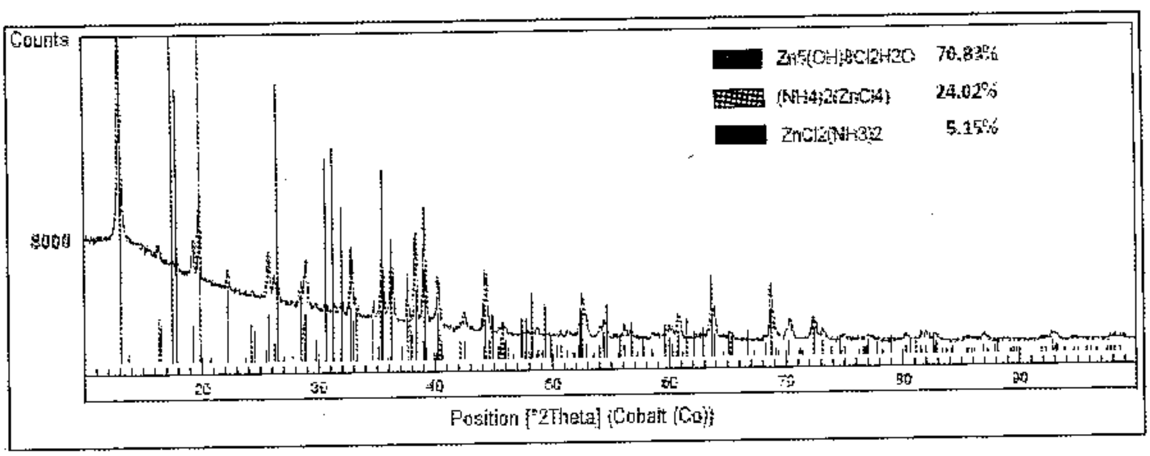

Fig. 1. XRD pattern of sal-ammoniac flux with quantitative analysis

Rys. 1. Ilościowa dyfrakcyjna XRD analiza odpadu salmiakowego

The results show that distilled water is not suitable leaching agent for studied sample of sal-ammoniac flux. Therefore in subsequent leaching experiments HCl was used as leaching agent. It can be assumed according Sithole [7], that during leaching of major flux phase $Zn_5(OH)_8Cl_2\cdot(H_2O)$, the course of chemical reaction takes place

$$Zn_5(OH)_8Cl_2\cdot(H_2O)_s + 8HCl_{(aq)} = 5ZnCl_{2(aq)} + 9H_2O_{(l)} \quad (2)$$

Effect of the temperature on leaching rate of zinc

The effect of temperature on leaching rate of zinc in 0.25 $mol\cdot dm^{-3}$ HCl is shown in Fig. 2.

The leaching rate of zinc was higher at higher temperature in all time intervals, as it can be seen form Fig. 2. The highest increase of leaching rate was found in 0.25 $mol\cdot dm^{-3}$ HCl after 5 minutes of leaching, when leaching rate at a temperature of 293 K was 0.42, respectively 0.64 at a temperature of 313 K. The effect of temperature on leaching rate of zinc in 1 $mol\cdot dm^{-3}$ HCl is show in Fig. 3 and in 2 $mol\cdot dm^{-3}$ HCl in Fig. 4.

Based on the experimental results shown in Fig. 3 and Fig. 4 it can be stated:

a — The leaching rate of zinc $x_{Zn} = 1$ (equal 1) was achieved after sal-ammoniac flux sample leaching in 2 $mol\cdot dm^{-3}$ as well as in 1 $mol\cdot dm^{-3}$ at a temperature of 333 K in all time intervals.

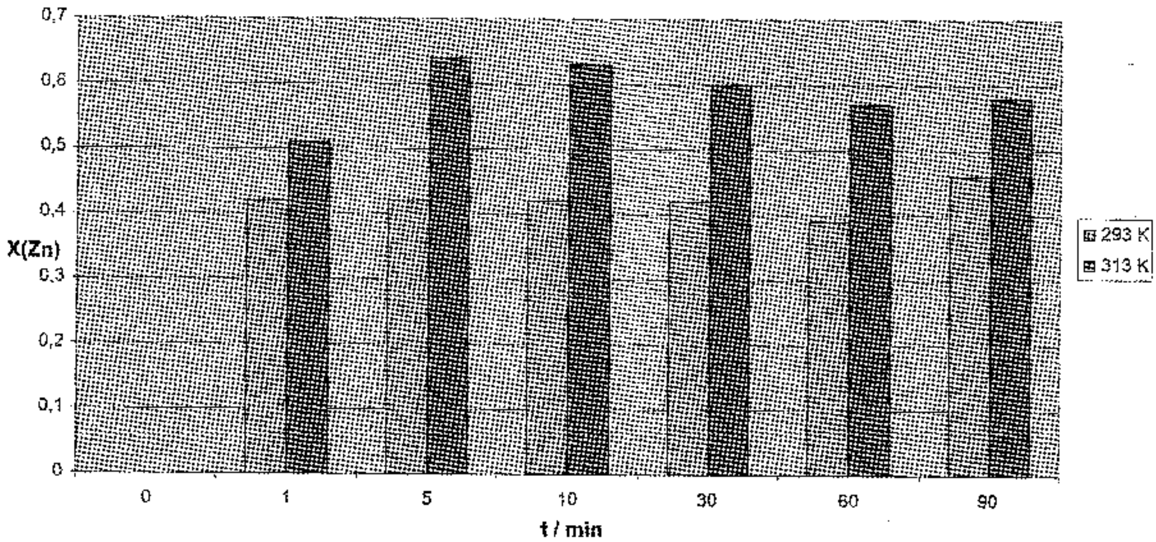

Fig. 2. Effect of the temperature on leaching rate of zinc in 0.25 $mol\cdot dm^{-3}$ HCl

Rys. 2. Wpływ czasu i temperatury na stopień wyługowania cynku z roztworu 0,25 $mol\cdot dm^{-3}$ HCl

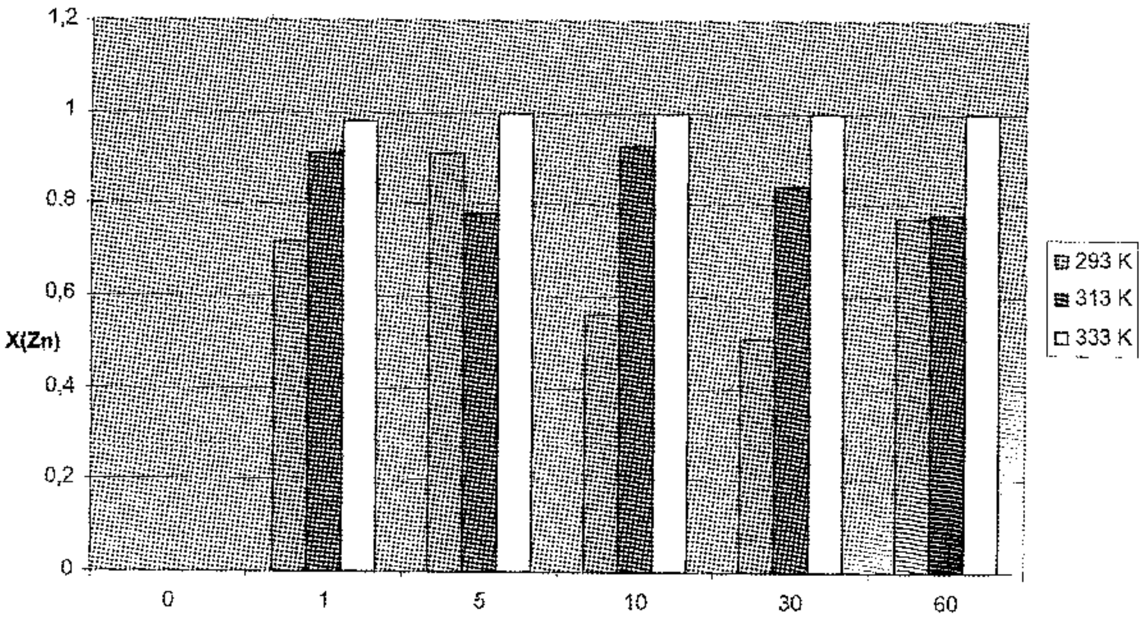

Fig. 3. Effect of the temperature on leaching rate of zinc in 1 $mol\cdot dm^{-3}$ HCl

Rys. 3. Wpływ czasu i temperatury na stopień wyługowania cynku z roztworu 1 $mol\cdot dm^{-3}$ HCl

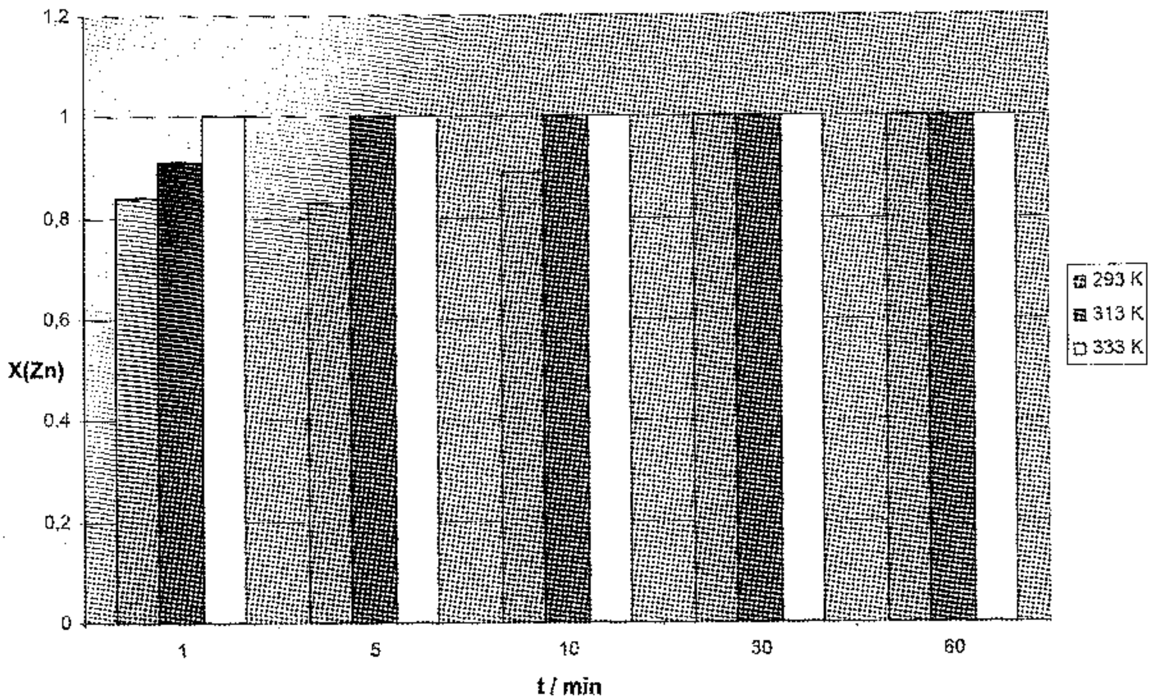

Fig. 4. Effect of the temperature on leaching rate of zinc in 2 mol·dm^{-3} HCl

Rys. 4. Wpływ czasu i temperatury na stopień wyługowania cynku z roztworu 2 mol·dm^{-3} HCl

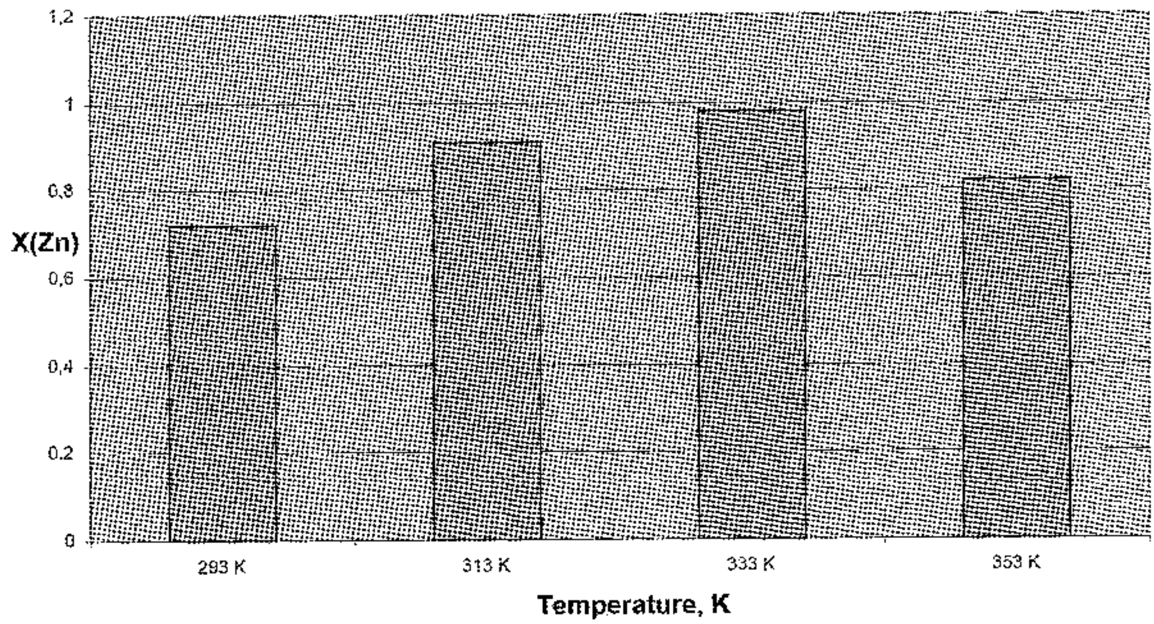

Fig. 5. Temperature dependence of the leaching rate of zinc in 1 mol·dm^{-3} HCl

Rys. 5. Zależność stopnia wyługowania cynku z roztworu 1 mol·dm^{-3} HC1 od temperatury

b — The leaching rate of zinc x_{Zn} = 1 was achieved after leaching in 2 mol·dm^{-3} HCl at a temperature of 313 K within 5 minutes of leaching.

c — The leaching rate of zinc x_{Zn} = 1 within 5 minutes of leaching at a temperatures of 313 K and 333 K in 2 mol·dm^{-3} was achieved, so longer leaching time than 5 minutes is not necessary.

d — Leaching time of 30 minutes is necessary to achieve leaching rate of zinc X_{Zn} = 1 using 2 mol·dm^{-3} HCl at a temperature of 293 K.

e — The most favourable conditions in terms of achieving maximum leaching rate of the zinc are: temperature of 313 K and leaching time 5 minutes using 2 mol·dm^{-3} as leaching media. Leaching time of 30 minutes is required at leaching in lower temperature i.e. 293 K.

Apparent activation energy "E_a" and apparent order of reaction "n" determination

Apparent activation energy E_a was determined experimentally by measuring the initial dissolution rate of zinc at different temperatures T for time interval 0÷60 seconds, (Fig. 5). Temperature of 353 K was not considered for determination of E_a, because of decrease the leaching rate of zinc at this temperature, which is evident from Fig. 5. Concentration of leaching media c_{HCl} was 1 mol·dm^{-3}.

Arrhenius equation was used to determine the activation energy

$$\ln k = \ln A - E_a/R{\cdot}T \qquad (3)$$

where

k is the rate constant, A is the frequency factor, R is the universal gas constant and T is the temperature. Estimated apparent activation energy is E_a = 6.28 kJ·mol^{-1} in temperature interval from 293 K to 333 K and frequency factor is A = 0.162 s^{-1}. It is generally believed that high values of activation energy (>40 kJ/mol) indicate chemical control whereas values <20 kJ/mol imply in diffusion-controlled processes [8, 9]. Estimated value of apparent activated energy indicates that leaching of sample is controlled by diffusion.

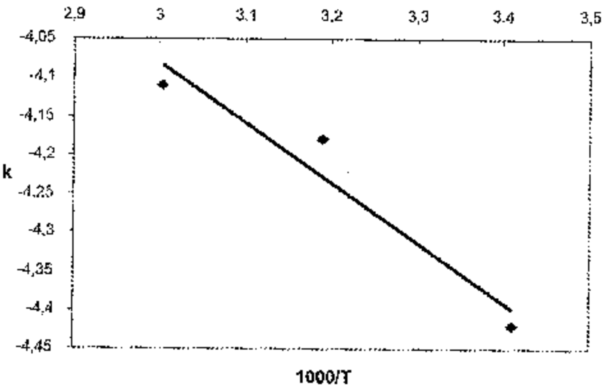

Fig. 6. Arrhenius plot for zinc extracting.
Correlation coefficient R = –0.9607

Rys. 6. Wykres Arrheniusa dla ekstrakcji cynku.
Współczynnik korelacji R = –0,9607

The corresponding relationship between ln k and 1000/T is shown in Fig. 6, which indicates, that mechanism for sample leaching in temperature interval 293÷333 K does not change.

Arrhenius plot shows the effect of temperature on the rate constant of sample leaching.

The effect of HCl concentration

The effect of HCl concentration on the leaching rate of zinc in the interval from 0.25 mol·dm^{-3} to 2 mol·dm^{-3} (Fig. 7) was studied with the aim of determination the order of reaction. The experimental conditions were: temperature of 293 K and leaching time 60 seconds.

It can be seen from Fig. 7 positive effect of increasing concentration of HCl on the leaching rate of zinc. The leaching rate of zinc was 0.42 using 0.25 mol·dm^{-3} HCl and 0.84 using 2 mol·dm^{-3} HCl within 1 minute of leaching.

The apparent order of reaction in respect of initial concentration of HCl in leaching solution was determined according to the following equation

$$v_{0,Zn} = k \cdot c^n_{HCl} \qquad (4)$$

or in logarithmic form

$$\ln v = \ln k + n \cdot \ln c_{HCl} \qquad (5)$$

where

n is slope of a graph of $\ln v_{0,Zn} = f(\ln c_{HCl})$, shown in Fig. 8. Value of n = 0.33 and $\ln k$ = –4.443. Dissolution of the zinc at temperature of 293 K can be represented as

$$v = 0.0117 \cdot c^{0.33} \qquad (6)$$

or in logarithmic form

$$\ln v = -4.443 + 0.33 \cdot \ln c_{HCl} \qquad (7)$$

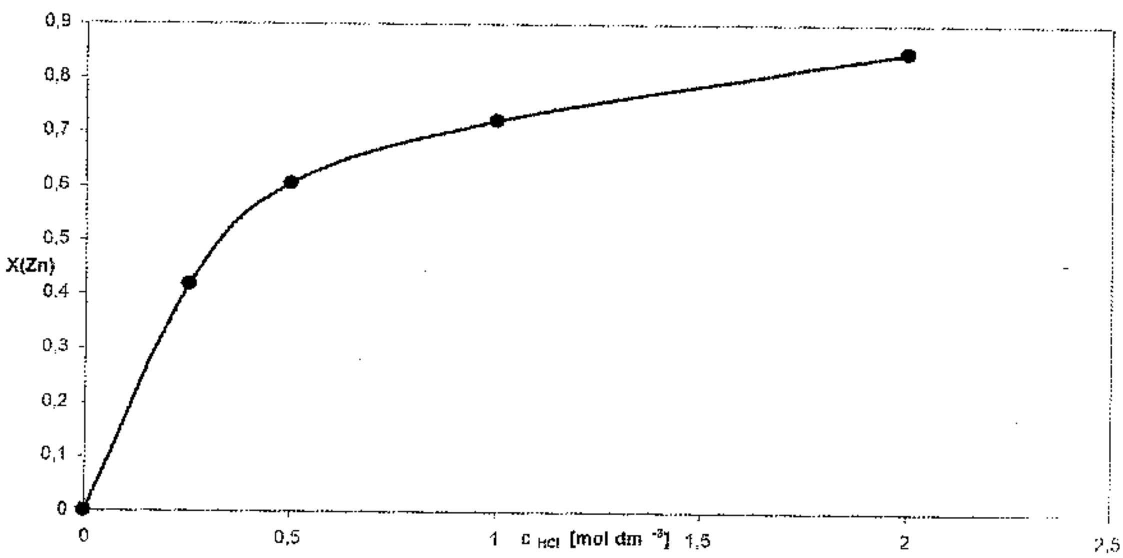

Fig. 7. Effect of HCl concentration on the leaching rate of zinc at 293 K

Rys. 7. Wpływ stężenia HCl na stopień wyługowania cynku w 293 K

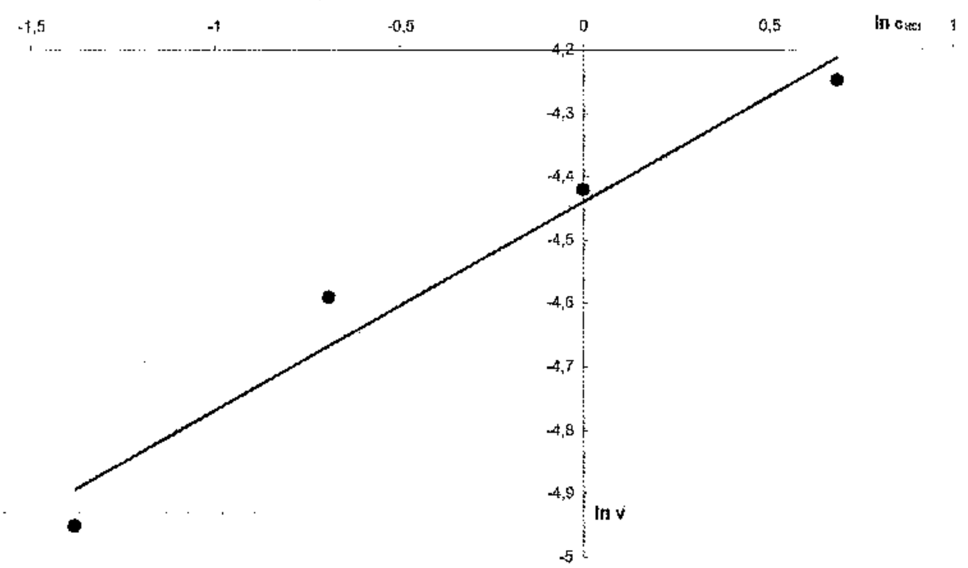

Fig. 8. Linear dependence ln $v = f(\ln c_{HCl})$ at temperature of 293 K. Correlation coefficient R = 0.9806

Rys. 8. Liniowa zależność ln $v = f(\ln c_{HCl})$ w temperaturze 293 K. Współczynnik korelacji R = 0,9806

Apparent order of reaction in respect of initial concentration of HCl in leaching solution is $n = 0.33$ for concentration interval from 0.25 mol·dm^{-3} to 2 mol·dm^{-3}. Positive effect of increasing HCl concentration on the leaching rate of zinc was found also at higher temperatures, as it can be seen in Table 3, (at leaching time of 60 seconds).
As an example it can be present: at leaching temperature of 313 K using v 0.5 M HCl value of $X_{Zn} = 0.64$ and using 1M HCl value of $X_{Zn} = 0.91$.

Table 3

Effect of HCl concentration on rate of leaching of zinc at temperatures of 293 K and 313 K within 60 seconds of leaching

Tablica 3

Wpływ stężenia HCl na stopień wyługowania cynku w temperaturze 293 K i 313 K w czasie 60-sekundowego ługowania

Temperature	Fraction of dissolved Zn [-]			
	0.25 M HCl	0.5 M HCl	1 M HCl	2 M HCl
293 K	0.42	0.60	0.72	0.84
313 K	0.51	0.64	0.91	0.91

Conclusions

The following conclusions were arrived at for the leaching zinc of sal-ammoniac flux by HCl:

1 — The sample used for leaching consisted of $Zn_5(OH)_8Cl_2 \cdot H_2O$, $(NH_4)_2(ZnCl_4)$ and $ZnCl_2(NH_3)_2$ as was confirmed by X-ray diffraction analysis.

2 — Leaching of waste on distilled water results in low zinc recoveries.

3 — The zinc recovery increases with the increasing concentrations of HCl.

4 — The apparent activation energy $E_a = 6.28$ kJ·mol^{-1} s gests that the leaching process is taking place wi the diffusion region.

5 — The apparent order of reaction determined for lea ing in HCl solutions in the concentration range fr 0.25 mol·dm^{-3} to 2 mol·dm^{-3} is $n = 0.33$.

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Bibliophil

[9] Chang J. et al. 2015. „Kinetics of microwave roasting of slag oxidation dust with concentrated sulfuric acid and w leaching". *Chemical Engineering and Processing* 97: 75-83.

[2] Dvořák P., J. Jandová. 2006. „Zinc recovery from chloride-bea galvanizing waste". *Acta Metallurgica Slovaca* 12: 90-94.

[3] Dvořák P., Jandová, J. 2005. „Hydrometallurgical recover zinc from hot dip galvanizing ash". *Hydrometallurgy* 77: 29

[8] Fabiano M. F. S. et al. 2010. „The kinetics of zinc silicite lea ing in sodium hydroxide". *Hydrometallurgy* 102: 43-49.

[4] Gotfryd L., A. Chmielarz, Z. Szołomicki. 2011. „Recovery of from arduous wastes using solvent extraction technique Pa Preliminary laboratory studies". *Physicochemical Problem Mineral Processing* 47: 149-158.

[1] Jha, M. K., V. Kumar, R. J. Singh. 2001. „Review of hydrom lurgical recovery of zinc from industrial wastes". *Resou Conservation & Recycling* 33: 1-22.

[5] Rabah M. A., A. S. El-Sayed. 1995. „Recovery of zinc and so of its valuable salts from secondary resources and wast *Hydrometallurgy* 37: 23-32.

[7] Sithole J. et al. 2012. „Simonkolleite nano-platelest: Systh at temperature effect on hydrogen gas sensing properties" *Applied Surface Science* 258: 7839-7843.

[6] Yoshida T. 2003. „Leaching of zinc oxide in acidic soluti *Materials Transactions* 44: 2489-2493