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Agitation Leaching of Zinc from Sal-ammoniac Flux Residue in HCl

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This paper presents the results of the laboratory investigation of acid leaching of sal-ammoniac flux residue. Sal-ammoniac flux residue is a waste product originated during wet hot dip galvanizing process consisting about 40 % of zinc. Zinc is the most abundant element in the sal-ammoniac flux residue and in the supplied sample occurred in the form of following phases: 70.83 % $Zn_5(OH)_8Cl_2 \cdot H_2O$, 24.02 % $(NH_4)_2(ZnCl_4)$ and 5.5 % $ZnCl_2(NH_3)_2$. The leaching test of sal-ammoniac flux residue in distilled water and aqueous solution of hydrochloric acid has been carried out under agitation. The experimental parameters of HCl concentration, leaching time and temperature were varied. The results obtained are as follows: The apparent activation energy of the 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:

Sal-ammoniac flux – Leaching – Zinc – Hydrochloric acid – Apparent activation energy – Apparent order of reaction

Rührlaugung von Zink aus Salmiak-Flussmittelrückständen in HCl

Dieser Beitrag stellt die Ergebnisse experimenteller Untersuchungen im Labormaßstab zur Säurelaugung von Rückständen des Flussmittels Salmiak dar, einem Abfallprodukt aus dem Feuerverzinkungsprozess, das ca. 40 % Zink enthält. Zink ist das häufigste Element in Salmiak-Flussmittelrückständen. In der untersuchten Probe trat es in Form der folgenden Verbindungen auf: $Zn_5(OH)_8Cl_2 \cdot H_2O$ in Höhe von 70,83 %, $(NH_4)_2(ZnCl_4)$ in Höhe von 24,02 % und $ZnCl_2(NH_3)_2$ zu 5,5 %. Die Laugungsversuche des Salmiak-Flussmittelrückstands wurden in destilliertem Wasser und wässriger Chlorwasserstoffsäurelösung unter Rühren durchgeführt. Die experimentellen Parameter der HCl-Konzentration, der Laugungszeit und der Temperatur wurden variiert. Die Ergebnisse der Untersuchung sind wie folgt: Die ermittelte Aktivierungsenergie der Laugungsreaktion der Salzsäurelösung betrug E_a = 6.28 kJ mol^{-1}. Die Reaktionsordnung wurde zu n = 0.33 geschätzt.

Schlüsselwörter:

Laugung – Salmiak-Flussmittel – Zink – Salzsäure – Aktivierungsenergie – Reaktionsordnung

Lixiviation de Zn par agitation sur la base des résidus de fondant de sel ammoniac dans le HCl

Lixiviación de zinc por agitación desde residuos de fundentes de amoníaco en HCl

1 Introduction

The amount of zinc production in the world has 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, residues etc. are generated in various chemical and metallurgical industries. The materials contain different levels of impurities depending on the source. Hydrometallurgical processing is effective and flexible for treating such materials as it can control the different levels 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:

- the chemical and phase composition of the sal-ammoniac flux residue,
- the effect of leaching time on the rate of zinc leaching in distilled water as well as in aqueous solution of hydrochloric acid,
- the effect of leaching temperature on the rate of zinc leaching,
- the effect of concentration of hydrochloric acid on the rate of zinc leaching,
- the value of apparent activation energy E_a and apparent order n of reaction based on the above results.

2 Material and methods

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

Table 1: Chemical composition of sal-ammoniac flux sample

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

The phase analysis of the investigated samples was carried out by X-ray diffraction method on Seifert XRD 3003/PTS under following conditions: Co-Kα 35 kV, 40 mA radiation, scan step 0.02° θ. The range of measurements: from 10 to 130° 2θ. The weight of samples subjected to leaching tests was 20 g each. The leaching tests were carried out in 1000 ml glass containers. 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 a rate of 200 rpm. The leaching tests were carried out at the following temperatures: 20 °C, 40 °C, 60 °C and 80 °C respectively. The constant temperature was maintained in each experiment by water thermostat. Samples of leaching solution (volume 5 ml) were taken periodically for quantitative analysis to determine the amount of dissolved zinc by AAS method.

3 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 Figure 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 on the leaching rate of zinc using distilled water.

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

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

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

Table 2: Effect of leaching time at temperatures of 20 to 80 °C in distilled water on X_{Zn}

Leaching time [min]	Fraction of dissolved Zn [–] 20 °C	40 °C	60 °C	80 °C
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

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

$$Zn_5(OH)_8Cl_2 \cdot (H_2O) + 8HCl \rightarrow 5ZnCl_2 + 9H_2O \qquad (2)$$

takes place.

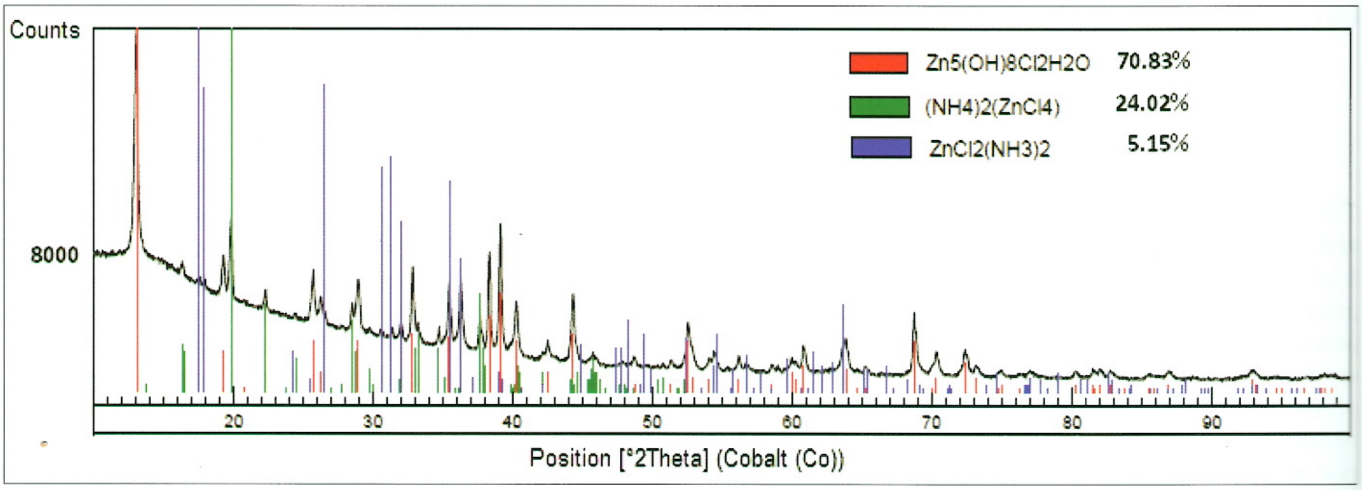

Fig. 1: XRD pattern of sal-ammoniac flux residue with quantitative analysis

3.1 Effect of temperature on the leaching rate of zinc

The effect of temperature on the leaching rate of zinc in 0.25 mol dm^{-3} HCl is shown in Figure 2.

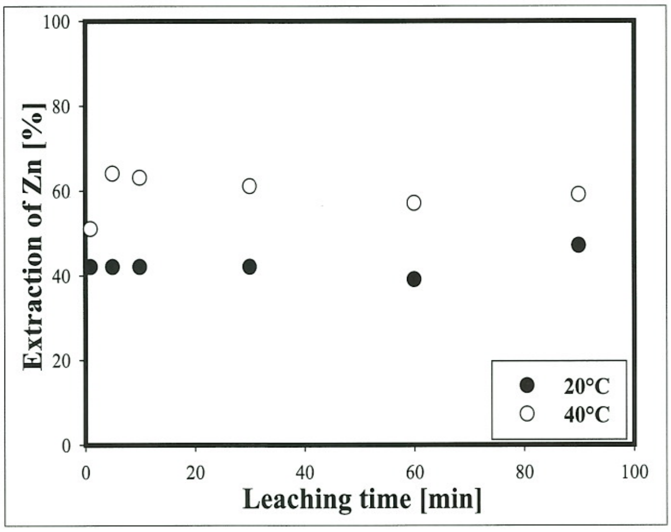

Fig. 2: Effect of temperature on the rate of zinc leaching in 0.25 mol dm^{-3} HCl

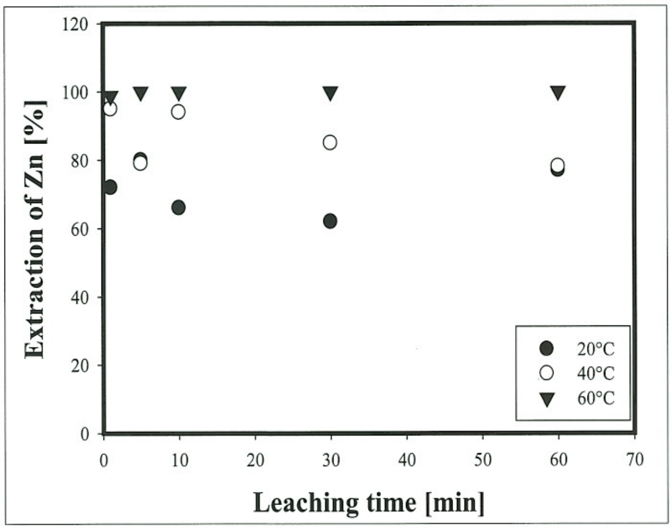

Fig. 3: Effect of temperature on the rate of zinc leaching in 1 mol dm^{-3} HCl

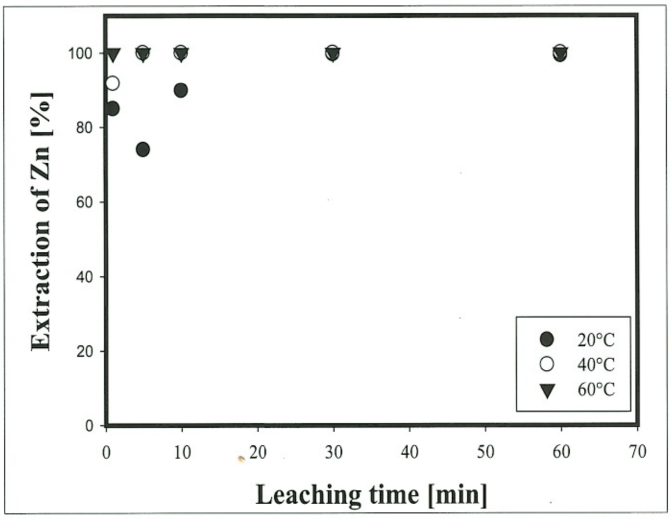

Fig. 4: Effect of temperature on the rate of zinc leaching in 2 mol dm^{-3} HCl

The leaching rate of zinc was higher at higher temperature in all time intervals, as it can be seen from Figure 2. The highest increase of leaching rate was found in 0.25 mol dm^{-3} HCl after 5 minutes of leaching, when leaching rate at a temperature of 20 °C was 42 % Zn, respectively 64 % Zn at a temperature of 40 °C. The effect of temperature on the leaching rate of zinc in 1 mol dm^{-3} HCl is show in Figure 3 and in 2 mol dm^{-3} HCl in Figure 4.

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

- The leaching rate of zinc x_{Zn} = 100 % was achieved after sal-ammoniac flux sample leaching in 2 mol dm^{-3} as well as in 1 mol dm^{-3} at a temperature of 60 °C in all time intervals.
- The leaching rate of zinc x_{Zn} = 100 % was achieved after leaching in 2 mol dm^{-3} HCl at a temperature of 40 °C within 5 minutes of leaching.
- The leaching rate of zinc x_{Zn} = 100 % within 5 minutes of leaching at temperatures of 40 °C and 60 °C in 2 mol dm^{-3} was achieved, so leaching time longer than 5 minutes is not necessary.
- A leaching time of 30 minutes is necessary to achieve a leaching rate of zinc x_{Zn} = 100 % using 2 mol dm^{-3} HCl at a temperature of 20 °C.
- The most favourable conditions in terms of achieving maximum leaching rate of the zinc are: temperature of 40 °C and leaching time 5 minutes using 2 mol dm^{-3} HCl as leaching media. Leaching time of 30 minutes is required for leaching at lower temperature i.e. 20 °C.

3.2 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 to 60 seconds (Figure 5). Temperature of 80 °C was not considered for determination of E_a, because of the decreasing leaching rate of zinc at this temperature, which is evident from Figure 5. Concentration of the leaching media c_{HCl} was 1 mol dm^{-3}.

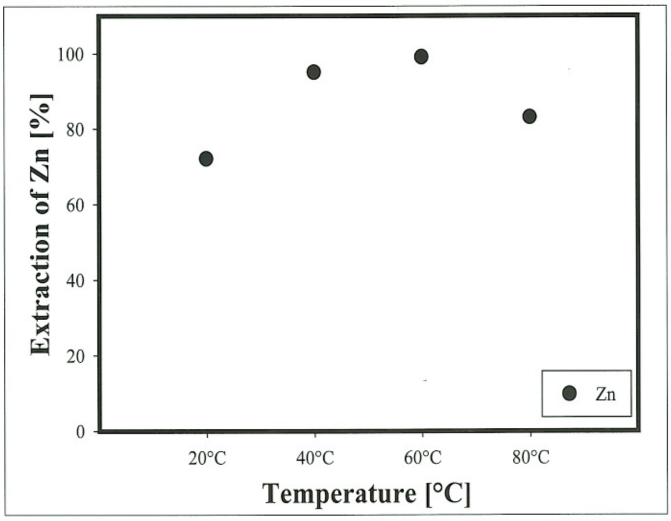

Fig. 5: Temperature dependence of the leaching rate of zinc in 1 mol dm^{-3} HCl

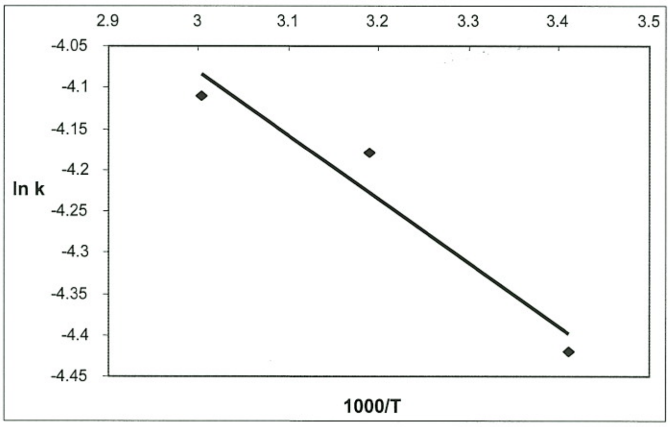

Fig. 6: Arrhenius plot for zinc extracting – correlation coefficient R = –0.9607

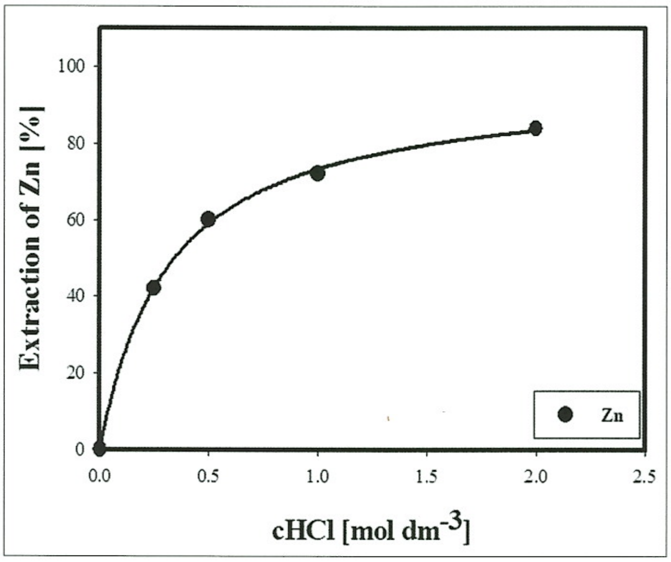

Fig. 7: Effect of HCl concentration on the leaching rate of zinc at 20 °C

The Arrhenius equation was used to determine the activation energy:

$$\ln k = \ln A - E_a/R \cdot T \quad (3)$$

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 20 °C to 60 °C, 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 diffusion-controlled processes [8, 9]. Estimated value of apparent activated energy indicates that leaching of the sample is controlled by diffusion. The corresponding relationship between ln k and 1000/T is shown in Figure 6, which indicates, that the mechanism for sample leaching in temperature interval 20 °C to 60 °C does not change.

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

3.3 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} (Figure 7) was studied with the aim of determination the order of reaction. The experimental conditions were: temperature 20 °C and leaching time 60 seconds.

Figure 7 displays the positive effect of increasing concentration of HCl on the leaching rate of zinc. The leaching rate of zinc was 42 % using 0.25 mol dm^{-3} HCl and 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 the leaching solution was determined according to the following equation:

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

or in logarithmic form:

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

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

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

or in logarithmic form:

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

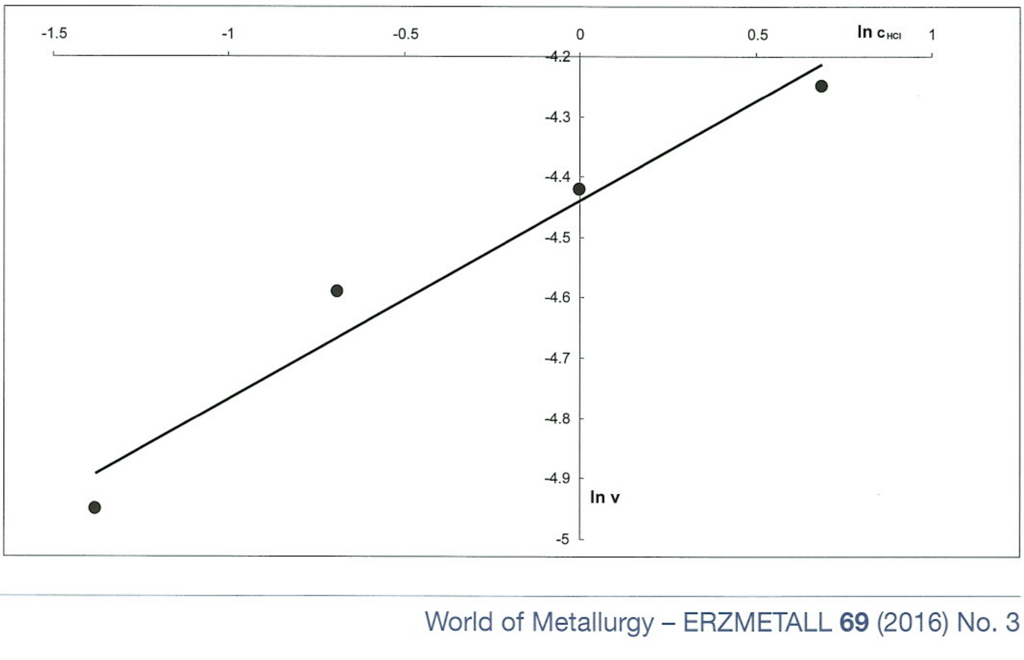

Fig. 8:
Linear dependence ln v = f(ln c_{HCl}) at 20 °C, correlation coefficient R = 0.9806

The 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}. A 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 a leaching time of 60 seconds.

As an example, at a leaching temperature of 40 °C using 0.5 M HCl the value of X_{Zn} is 64 % and using 1M HCl the value of X_{Zn} is 91 %.

Table 3: Effect of HCl concentration on rate of leaching of zinc at temperatures of 20 °C and 40 °C within 60 seconds of leaching

Temperature [°C]	Extraction of Zn [%]			
	0.25 M HCl	0.5 M HCl	1 M HCl	2 M HCl
20	42	60	72	84
40	51	64	91	91

4 Conclusions

The following conclusions were drawn for the leaching zinc of sal-ammoniac flux residue by HCl.

- 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.
- Leaching of waste in distilled water results in low zinc recoveries.
- The zinc recovery increases with increasing concentrations of HCl.
- The apparent activation energy E_a = 6.28 kJ mol^{-1} suggests that the leaching process is taking place within the diffusion region.
- The apparent order of reaction determined for leaching in HCl solutions in the concentration range from 0.25 mol dm^{-3} to 2 mol dm^{-3} is n = 0.33.

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