

## Recovery of zinc from copper smelter slag by sulfuric acid leaching in an aqueous and alcoholic environment

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The content of zinc in copper smelter slags obtained from pyrometallurgical copper production is comparable to the content of this metal in zinc ores. Therefore, these slags are considered a valuable secondary resource for zinc recovery. At the same time, the features of the mineralogical composition of the slag make the extraction of zinc from it very problematic. Most of the zinc is concentrated in the refractory zinc ferrite ( $ZnFe_2O_4$ ). To avoid the formation of a viscous pulp when leaching copper smelter slag with an aqueous solution of sulfuric acid, in this work, the slag was leached with sulfuric acid also in isopropanol and n-pentanol, under the following conditions: 0.5 M  $H_2SO_4$ , pulp density 50 g/L, magnetic stirrer rotation speed 600 rpm. The influence of the duration and temperature of leaching milled ( $\leq 100 \mu m$ ) copper smelter slag of the Balkhash copper smelter on the extraction of zinc into solution was investigated. It was found that the maximum zinc recovery into an aqueous solution was  $75 \pm 2\%$  at 363 K and 210 min. Replacing water with isopropanol or n-pentanol led to an increase in zinc recovery to  $82 \pm 2\%$  at 210 min and a lower temperature (353 K) than in an aqueous environment. An increase in temperature to 383 K during leaching in n-pentanol made it possible to extract  $92 \pm 2\%$  of zinc. A shrinking core model was used to describe the kinetics of the zinc leaching process. It was found that the limiting stage of the process under all investigated conditions is the chemical leaching reaction. Some kinetic characteristics of the leaching process were calculated, in particular, the apparent reaction rate constants, as well as the activation energy.

**Keywords:** copper smelter slag; leaching; zinc recovery; isopropanol; n-pentanol.

## Су және спирт орталарында күкірт қышқылды сілтілеу арқылы үйінді мыс шлағынан мырышты алу

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Пирометаллургиялық мыс өндірісінің үйінді мыс шлактарындағы мырыштың құрамы мырыш кендеріндегі осы металдың құрамымен салыстырылады. Сондықтан бұл шлактар мырыш алу үшін құнды ресурс ретінде қарастырылады. Сонымен қатар, шлақтың минералогиялық құрамының ерекшеліктері одан мырыш алуды өте проблемалы етеді. Мырыштың негізгі бөлігі мырыш ферритінде ( $ZnFe_2O_4$ ) шоғырланған. Үйінді мыс шлағын күкірт қышқылының сулы ерітіндісімен шаймалау кезінде тұтқыр қойыртпақтың пайда болуын болдырмау үшін осы жұмыста қожды күкірт қышқылымен, сондай-ақ изопропанол және н-пентанол ортасында шаймалау жүргізілді, мынадай жағдайларда: 0,5 M  $H_2SO_4$ , қойыртпақтың тығыздығы 50 г/л, магнитті араластырғыштың айналу жылдамдығы 600 айн/мин. Мырышты ерітіндіге өткізуде Балқаш мыс балқыту зауытының ұсақталған ( $\leq 100 \mu m$ ) үйінді мыс шлағын шаймалау ұзақтығы мен температураның әсері зерттелді. 363 K және 210 мин кезінде сулы ерітіндіде мырыштың максималды алынуы  $75 \pm 2\%$  құрады. Суды изопропанолмен немесе н-пентанолмен ауыстыру арқылы мырыштың алынуын 210 мин ішінде  $82 \pm 2\%$  -ға дейін жоғарлатты және сулы ортаға қарағанда төмен температурада (353 K) алуға мүмкіндік берді. Н-пентанолда шаймалау кезінде температураның 383 K дейін көтерілуі ерітіндіге  $92 \pm 2\%$  мырыш алуға мүмкіндік берді. Мырышты шаймалау процесінің кинетикасын сипаттау үшін қысқартатын сфера моделі қолданылды. Барлық зерттелген жағдайларда процестің шектеулі кезеңі химиялық шаймалау реакциясы болып табылады. Шаймалау процесінің кейбір кинетикалық сипаттамалары, атап айтқанда реакция жылдамдығының константалары, сондай-ақ активтендіру энергиясы есептелген.

**Түйін сөздер:** үйінді мыс шлағы; шаймалау; мырыш алу; изопропанол; н-пентанол.

## Извлечение цинка из отвального медного шлака серноокислотным выщелачиванием в водной и спиртовых средах

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Содержание цинка в отвальных медных шлаках пирометаллургического производства меди сопоставимо с содержанием этого металла в цинковых рудах. Поэтому эти шлаки рассматриваются как ценный вторичный ресурс для извлечения цинка. В то же время особенности минералогического состава шлака делают извлечение цинка из него весьма проблематичным. Основная часть цинка сосредоточена в упорном феррите цинка ( $ZnFe_2O_4$ ). Во избежание образования вязкой пульпы при выщелачивании отвального медного шлака водным раствором серной кислоты, в настоящей работе проведено выщелачивание шлака серной кислотой также и в среде изопропанола и н-пентанола, при следующих условиях: 0,5 M  $H_2SO_4$ , плотность пульпы 50 г/л, скорость вращения магнитной мешалки 600 об/мин. Исследовано влияние продолжительности и температуры выщелачивания измельченного ( $\leq 100 \mu m$ ) отвального медного шлака Балхашского медеплавильного завода на извлечение цинка в раствор. Найдено, что в водном растворе максимальное извлечение цинка составило  $75 \pm 2\%$  при 363 K и 210 мин. Замена воды на изопропанол или н-пентанол привела к повышению извлечения цинка до  $82 \pm 2\%$  при 210 мин и более низкой температуре (353 K), нежели в водной среде. Повышение температуры до 383 K при выщелачивании в н-пентаноле позволило извлечь  $92 \pm 2\%$  цинка. Для описания кинетики процесса выщелачивания цинка была использована модель сокращающейся сферы. Найдено, что лимитирующей стадией процесса при всех исследованных условиях является химическая реакция выщелачивания. Рассчитаны некоторые кинетические характеристики процесса выщелачивания, в частности, кажущиеся константы скорости реакции, а также энергии активации.

**Ключевые слова:** отвальный медный шлак; выщелачивание; извлечение цинка; изопропанол; н-пентанол.



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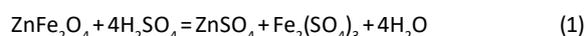
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### 1. Introduction

Non-ferrous metallurgical slags produced by pyrometallurgical processing of copper concentrates are potential secondary raw materials because they contain a considerable concentration of valuable metals [1-3]. For instance, the content of zinc in copper smelter slag is comparable to that of zinc ores, which makes this slag an attractive resource for zinc recovery [4]. However, the peculiarities of the mineralogical composition of the copper smelter slag make its processing very problematic. Slag is a glassy matrix with a predominance of fayalite ( $\text{Fe}_2\text{SiO}_4$ ), in which the target components, in particular, zinc, are impregnated. Typically, the zinc in the slag is in the form of zinc ferrite ( $\text{ZnFe}_2\text{O}_4$ ), which is a highly stable chemical compound [5,6].

There are several ways to recover zinc from the copper slag. Most of them involve heat treatment of the material by roasting together with ammonium chloride [7], calcium chloride [8], sulfuric acid [9], pyrite [10], as well as ferric sulfate [11]. In some cases, high-temperature reduction of zinc ferrite was used with the release of the target metal in the form of an oxide [12-16]. However, the roasting stages are quite energy-intensive; besides, the risk of air pollution with gaseous products increases.

The most attractive is the hydrometallurgical processing of copper smelter slag with sulfuric acid solutions. The choice of sulfuric acid is due to its production in sufficiently large quantities at non-ferrous metallurgy enterprises, in particular, at copper smelters. The interaction of sulfuric acid with zinc ferrite is described by the following equation [17]:



Despite the negative value of the Gibbs free energy of the above reaction (about 6.7 kJ/mol at 298 K), its proceeding is

very difficult at room temperature due to kinetic limitations; these limitations can be largely eliminated by heating the pulp.

There is one more problem that significantly impedes the hydrometallurgical processing of copper smelter slag. The silicon that has passed into the solution during leaching undergoes polymerization, which makes it very difficult to filter the viscous slurry. This problem can be solved by using non-aqueous solvents. This approach, called solvometallurgical (in contrast to the hydrometallurgical approach, non-aqueous solvents are used here), has been successfully used for leaching non-ferrous, rare and noble metals [18-20]. We have previously described hydrochloric acid leaching of copper smelter slag in isopropyl alcohol for copper recovery [21]. To the best of our knowledge, this article remains the only one in peer-reviewed journals dedicated to the solvometallurgical processing of waste copper slag. In this work, we investigated the process of extracting zinc from copper smelter slag by sulfuric acid leaching in isopropanol, as well as in n-pentanol. The aim of the work was a comparative study of the leaching processes in aqueous and alcoholic environments, as well as the determination of some kinetic parameters of the leaching reaction. Possible reasons for the difference in zinc recoveries, as well as in the values of kinetic parameters, are also discussed in the article.

### 2. Experiment

#### 2.1 Materials

Copper smelter slag samples were collected from Balkhash copper smelter (Kazakhstan). The slag was milled and sieved; more than 90% of slag particles used in leaching experiments were smaller or equal to 100  $\mu\text{m}$ .

Sulfuric acid (96%), isopropanol ( $\geq 98\%$ ), and n-pentanol ( $\geq 98\%$ ) purchased from Sigma-Aldrich were used without further purification.

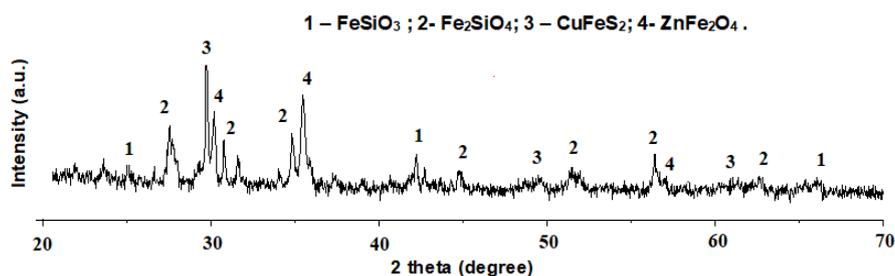


Figure 1 – XRD pattern of the initial slag

## 2.2 Leaching experiments

The batch leaching tests of milled slag with 0.5 M sulfuric acid solution were performed in a 250-mL round-bottom glass thermostated reactor equipped with a magnetic stirrer. Distilled water, isopropanol and n-pentanol were used separately as a solvent. Every 30 min of leaching, for 210 min, a sample of the solution was taken to determine the zinc content. All the zinc determinations were performed 3 times; mean values of three measurements are presented in Figures. In the Tables, calculated values of standard deviation are also given along with a mean.

## 2.3 Characterization

The elemental composition of the slag sample was determined by inductively coupled plasma atomic emission spectroscopy (ICP-AES, Perkin Elmer, Optima 8000) with preliminary microwave sample decomposition. The content of zinc in liquid samples was also determined by ICP-AES. The XRD pattern was recorded by using a D8 Advance diffractometer (Bruker) with  $\alpha$ -Cu irradiation (40 kV, 40 mA).

## 3. Results and Discussion

### 3.1 Characterization of used slag

The elemental composition of the copper smelter slag sample determined by atomic emission spectroscopy was as follows, wt %: Fe 28.7, Si 17.9, Ca 1.8, Zn 4.2, Cu 0.7.

In the slag, fayalite (Fe<sub>2</sub>SiO<sub>4</sub>) and ferrosilite (FeSiO<sub>3</sub>) were determined by XRD analysis as major components; zinc ferrite (ZnFe<sub>2</sub>SO<sub>4</sub>) and chalcopyrite (CuFeS<sub>2</sub>) were also presented in the sample (Figure 1).

### 3.2 Leaching in an aqueous environment

Figure 2 demonstrates the dependences of the zinc recovery from copper smelter slag into an aqueous solution of sulfuric acid (0.5 M) on the temperature and leaching duration.

The data presented in Figure 2 indicate that an increase in temperature led to an increase in zinc recovery into solution. For all three studied temperatures, an increase in the leaching duration from 30 to 120 min also led to an increase in the zinc recovery into solution, and this effect slowed down with the course of leaching: in the first 30 min, zinc recovery into solution was 2, 16, and 32% (hereinafter, the mean values of

three measurements are given) for 303, 333 and 363 K, respectively, while after 210 min the recoveries were 5±1, 45±1, and 75±2%, respectively. Such a significant effect of temperature on Zn recovery is because zinc ferrite is very resistant to the action of inorganic acids, in particular, sulfuric acid. Although reaction (1) can be expected even at room temperature on thermodynamic considerations, an acceptable degree of dissolution of zinc ferrite is observed only at elevated temperatures.

The shrinking core model (SCM) that adequately describes the dissolution process of minerals as long as the conversion increases with time was applied in this work for obtaining kinetic characteristics of zinc releasing from copper slag. As a rule, the rate of agitational leaching processes is limited by the chemical reaction of the leaching agent with the mineral surface. We hypothesized that in our case the limiting stage is also a chemical reaction of zinc ferrite with sulfuric acid.

For surface reaction controlled processes the SRM of a mineral leaching can be presented as the following equation (Equation 2):

$$1 - (1 - X)^{1/3} = kt \quad (2)$$

where X is the fraction of the target component (Zn, in this case) recovered into the solution at the leaching time t, k is the apparent rate constant of the chemical reaction.

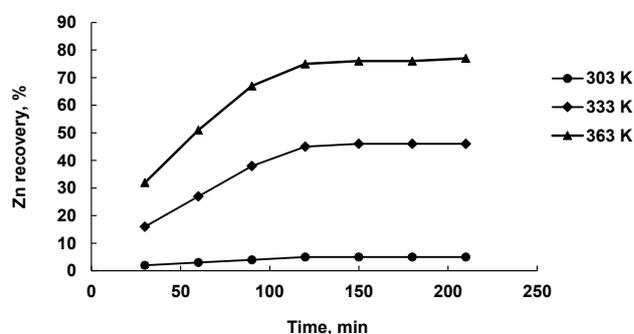
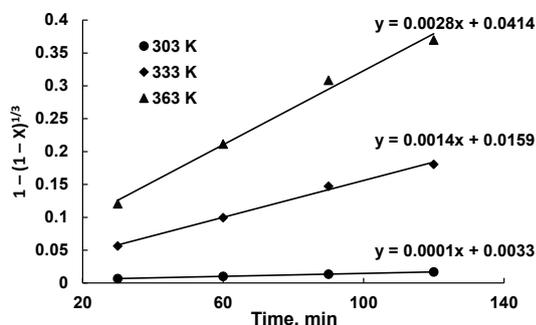


Figure 2 – Effect of leaching duration and temperature on zinc recovery from copper smelter slag into an aqueous solution (0.5 M H<sub>2</sub>SO<sub>4</sub>, pulp density 50 g/L, 600 rpm)

The  $1 - (1 - X)^{1/3}$  plots vs time for three operating temperatures are presented in Figure 3; equations of straight lines are also shown.



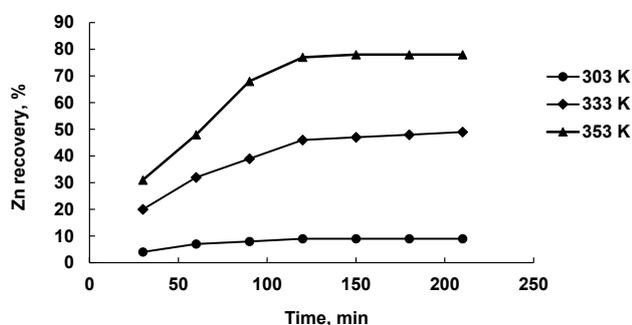
**Figure 3** – Plot of  $1 - (1 - X)^{1/3}$  plots vs time for zinc recovery from copper smelter slag into an aqueous solution (0.5 M  $H_2SO_4$ , pulp density 50 g/L, 600 rpm)

Since after 120 min of leaching, the zinc recoveries reached a plateau for all temperatures investigated, the recovery values at times over 120 min were not included in Figure 3.

Straight-line dependencies indicate the applicability of SCM for surface reaction controlled processes in describing the process of sulfuric acid leaching of zinc from copper smelter slag. The apparent rate constants for the Zn releasing from copper smelter slag under the conditions of sulfuric acid leaching were 0.0001, 0.0014, and 0.0028  $min^{-1}$  at 303, 333, and 363 K, respectively (see equations of straight lines in Figure 3).

### 3.3 Leaching in an alcohol environment

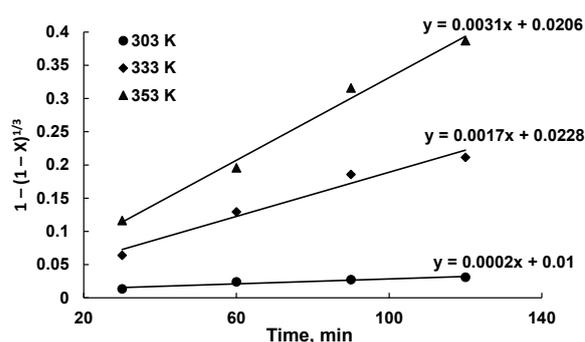
The dependences of the zinc recovery from copper smelter slag into an isopropanol solution of sulfuric acid (0.5 M) on the temperature and leaching duration are shown in Figure 4. Due to the low boiling point of isopropanol (about 355 K), leaching was carried out at 303, 333 and 353 K.



**Figure 4** – Effect of leaching duration and temperature on zinc recovery from copper smelter slag into isopropanol solution (0.5 M  $H_2SO_4$ , pulp density 50 g/L, 600 rpm)

As it was observed for aqueous solutions, with increasing leaching duration, Zn recovery demonstrated an upward trend up to 120-150 min for all investigated temperatures; at the same time, Zn recovery in the case of an isopropanol solution was higher than in aqueous solution, at 303 and 333 K. The Zn recoveries at 353 K in an isopropanol solution and 363 K in an aqueous solution were approximately at the same level, which indicates a favourable role of isopropyl alcohol in the leaching of Zn from slag.

The  $1 - (1 - X)^{1/3}$  plots vs time for Zn sulfuric acid leaching in isopropanol solution are presented in Figure 5.



**Figure 5** – Plot of  $1 - (1 - X)^{1/3}$  vs time for zinc recovery from copper smelter slag into isopropanol solution (0.5 M  $H_2SO_4$ , pulp density 50 g/L, 600 rpm)

Linear dependences  $1 - (1 - X)^{1/3}$  vs time also testify in favour of kinetic control of the Zn leaching process, as in the case of leaching in an aqueous solution. However, the apparent rate of constants at 333 and 363 K in an alcoholic medium is 1.2-2.0 times higher than in an aqueous one; moreover, apparent rate constant at 353 K in isopropanol environment is about 1.1 times higher than that obtained in aqueous solution.

To study the effect of the alcohol chain length on Zn releasing from copper slag, leaching tests using n-pentanol were performed. Despite the high boiling point of n-pentanol (about 411 K), the upper limit for leaching was set at 353 K, to correctly compare the results of leaching in isopropanol and n-pentanol. Zn recoveries, as well as apparent rate constants at three investigated temperatures, are presented in Table 1.

Comparison of the data in Table 1 with those in Figures 4 and 5 reveals that replacing isopropanol with n-pentanol did not lead to any noticeable changes in zinc recovery, taking into account the experimental error; the values of apparent rate constants of leaching reaction also remained at the same level.

Since n-pentanol has a much higher boiling point than isopropanol (411 K vs 355 K), it seemed informative to perform leaching in n-pentanol at elevated temperatures. Table 2 shows the effect of leaching duration and temperature on zinc recovery from copper smelter slag into n-pentanol solution (0.5 M  $H_2SO_4$ , pulp density 50 g/L, 600 rpm) at the temperatures of 363, 383 and 403 K.

**Table 1** – Effect of leaching duration and temperature on zinc recovery from copper smelter slag into n-pentanol solution (0.5 M H<sub>2</sub>SO<sub>4</sub>, pulp density 50 g/L, 600 rpm) and apparent rate constants of leaching reaction

Temperature, K	Zn recovery (%) at leaching duration, min							Apparent rate constant of Zn leaching reaction, min <sup>-1</sup>
	30	60	90	120	150	180	210	
303	6±1	8±1	10±1	11±1	12±1	12±1	12±1	0.0002
333	23±1	35±1	43±1	49±1	50±1	51±1	52±1	0.0017
353	34±1	51±1	70±2	78±2	81±2	81±1	82±2	0.0031

**Table 2** – Effect of leaching duration and temperature on zinc recovery from copper smelter slag into n-pentanol solution (0.5 M H<sub>2</sub>SO<sub>4</sub>, pulp density 50 g/L, 600 rpm) at elevated temperatures

Temperature, K	Zn recovery (%) at leaching duration, min						
	30	60	90	120	150	180	210
363	35±1	54±1	73±2	84±2	87±2	87±2	87±2
383	41±1	63±1	79±2	89±2	91±1	91±2	91±2
403	42±1	64±2	80±2	89±2	91±2	92±2	92±2

It can be seen that raising the leaching temperature generally increased the zinc recovery into solution. The maximum extraction of zinc at 383 K was 91% vs 82% at 353 K. Noteworthy is the fact that an increase in temperature from 383 to 403 K practically did not change the Zn recovery. This led to the fact that the rate constants of the leaching reaction at both temperatures mentioned were the same (0.0031 min<sup>-1</sup> vs 0.0029 min<sup>-1</sup> at 363 K). For the subsequent construction of the dependence 1/T – ln k (not shown) to determine the activation energy (E<sub>A</sub>) of the zinc leaching reaction, the slag was leached at 373 K. The reaction rate constant was 0.0030 min<sup>-1</sup>.

Table 3 shows the calculated activation energies for the zinc leaching reaction under various conditions described in this work.

Comparison of the activation energies of zinc leaching shows that the use of isopropanol and n-pentanol reduced the activation energy of the main reaction of zinc leaching from the slag (reaction 1). Elgersma et al [22] demonstrated that the activation energy of sulfuric acid leaching (aqueous solution, 0.5 M H<sub>2</sub>SO<sub>4</sub>) of synthetic zinc ferrite is 74±2 kJ/mol, in the temperature range of 75-95°C. The lower value of the activation energy in our case (51±1 kJ/mol) can be explained as follows. In the copper smelter slag, zinc is not only in the form of zinc ferrite but also in the form of more reactive compounds

(sulfides and oxides). Due to their low content, these compounds were not detected by XRD analysis. Sulfuric acid leaching reactions of these compounds have lower activation energies than zinc ferrite leaching; it is this circumstance that reduces the energy activation of the whole process of zinc recovery.

A favourable effect on the leaching of minerals in alcoholic solvents in comparison with an aqueous environment was observed in several works [23-26]. In particular, the positive effect of ethanol on hydrochloric leaching of scheelite was explained by the better solvating ability of this alcohol concerning chloride ions [25]. Jana et al showed that in hydrochloric acid solutions of some alcohols, in particular, in methanol and ethanol, the activity of chloride ions increases; this circumstance led to an increase in the leaching efficiency of sea nodules [26].

We assume that as the proton is hydrogen-bonded to alcohols (i.e. C<sub>3</sub>H<sub>7</sub>OH<sub>2</sub><sup>+</sup> and C<sub>5</sub>H<sub>11</sub>OH<sub>2</sub><sup>+</sup> in our case) alcohol can be considered to be a good cationic collector. Therefore, solvated protons are more active than hydrated ones (in aqueous solution), which increases the efficiency of leaching in an alcohol environment. The Gibbs free energy of protons solvation in alcohol is lower than that of proton hydration in aqueous solutions [27]. This indicates a higher concentration of

**Table 3** – Activation energies of Zn leaching reaction under different conditions

Activation energy (E <sub>A</sub> ), kJ/mol	Leaching conditions			
	Aqueous solution (303-363 K)	Isopropanol solution (303-353 K)	N-pentanol solution (303-353 K)	N-pentanol solution (363-383 K)
	51±1	42±1	42±1	6±1

hydronium ions in alcoholic environment than in aqueous one at the same acid concentration. Since the protonation of the surface of zinc ferrite with hydronium ions is an obligatory stage of its leaching [22], replacing water with alcohol as a solvent has a favorable effect on the leaching process. This argument is in good agreement with that described by Jana et al [26].

The sharp decrease in the activation energy during leaching in n-pentanol in the temperature range of 363-383 K is explained by a change in the mechanism of slag leaching at elevated temperatures. In this case, a change in temperature within the above limits has practically no effect on the degree of zinc recovery and the rate of the process.

#### 3.4 Economic feasibility of using alcohols in copper smelter slag leaching

Despite the higher cost of alcohols in comparison with the cost of water, the possible use of alcohols, in particular isopropanol or n-pentanol, for leaching copper slag seems to be justified. First, the use of a non-aqueous environment avoids the formation of a hard-to-filter slurry due to the polymerization of silicic acid in an aqueous solution. This aspect is very important and determines the advantages of solvometallurgy over hydrometallurgy. Secondly, the use of alcohol as a solvent makes it possible to increase the extraction of zinc into solution. After processing the solution, the alcohol can be reused for leaching. Thus, the prospects for using alcohol as a solvent in copper slag leaching appear to be favorable.

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#### 4. Conclusions

Isopropanol and n-pentanol are demonstrated to be feasible solvents for sulfuric acid leaching of zinc from copper smelter slag. The dissolution rate of zinc-containing minerals, predominantly zinc ferrite ( $\text{ZnFe}_2\text{O}_4$ ), was increased with increasing leaching duration and temperature in all three investigated solvents, including water, isopropanol and n-pentanol. The zinc recovery into solution during leaching with 0.5 M  $\text{H}_2\text{SO}_4$  in alcohol environment was  $82\pm 2\%$  at 210 min and 353 K, while in an aqueous solution it was possible to extract only  $75\pm 2\%$  at 363 K and the same leaching duration. An increase in temperature to 383 K during leaching in n-pentanol increased zinc recovery to  $92\pm 2\%$ . According to XRD analysis, the main zinc-containing compound in the slag was zinc ferrite; at the same time, the relatively low value of the activation energy during leaching in an aqueous solution indicates the presence of other, more reactive zinc minerals in the slag. The results obtained indicate that the use of aliphatic alcohols, in particular, isopropanol and n-pentanol, is promising for the sulfuric acid leaching of zinc from copper smelter slag.

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