



Kinetics of copper leaching from direct-to-blister copper flash smelting slag by sulfuric acid

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Abstract

Coppermaking from sulfide concentrates entails two major steps: smelting and converting. In continuous direct-to-copper smelting process these two steps are combined into one. The principal advantages of this process are: isolation of SO₂ emission to a single, continuous, SO₂-rich gas stream, minimization of energy consumption and minimization of capital and operating costs. Disadvantages of the process are that about 25% of the Cu entering a direct-to-copper smelting furnace ends up dissolved in the slag (when compared with < 10% in traditional Peirce–Smith converting) and the cost of recovering this Cu is significant. Decopperization process is based on the reduction of cuprous oxide and other metals, mainly lead and iron, in the liquid state in an electric furnace in the presence of coke and technological additives. This paper presents the results of laboratory tests on flash smelting slag leaching with sulfuric acid solutions. Hydrometallurgical treatment of the slag could be an alternative route to the presently used way of processing. The influence of a number of leaching parameters such as sulfuric acid concentration, amount of H₂O₂ added, liquid to solid phase (*l/s*) parameter and process temperature on the copper leaching efficiency was investigated. Under optimized process conditions, 95.6% of the copper contained in the original sample of slag was transferred into a solution. The experimental results obtained in the study were supplemented with the analysis of the kinetics of the copper leaching process from the flash smelting slag. The commonly known from the literature diffusion model and chemical reaction model were used. The activation energy of copper leaching from flash smelting slag was estimated in the range from 12.77 to 17.34 kJ/mol.

Keywords Direct-to-blister copper · Flash smelting slag · Decopperization · Grinding · Sulfuric acid leaching

1 Introduction

The annual production of copper in the direct-to-blister technology at the Głogów II smelter is around 220,000 tonnes. The specificity of the process is associated with

the need to copper remove from approximately 500,000 tons of slag with Cu content of 12–16%. Therefore, about 185,000 MWh of electricity is used annually in an electric furnace for slag processing [1] and about 16,000 tons of carbon in the form of coke and electrode mass are used annually for the reduction process [2]. As a result of the reduction of metal oxides, CO₂ is produced in an amount of almost 60,000 tons. Hydrometallurgical treatment of the slag could be an alternative route to the presently used way of processing. The processing of slag from direct-to-blister technology by hydrometallurgical methods requires its grinding [3]. The annual energy consumption for this processing stage is estimated at 33,000 MWh [4]. Specified amounts of energy would be needed to drive the conveying equipment, leach mixers, pumps, filter presses, and to maintain the temperature of the leaching solutions at the required level. Because the flash smelting process is a highly exothermic process, surplus thermal energy could be successfully used in the process of heating and

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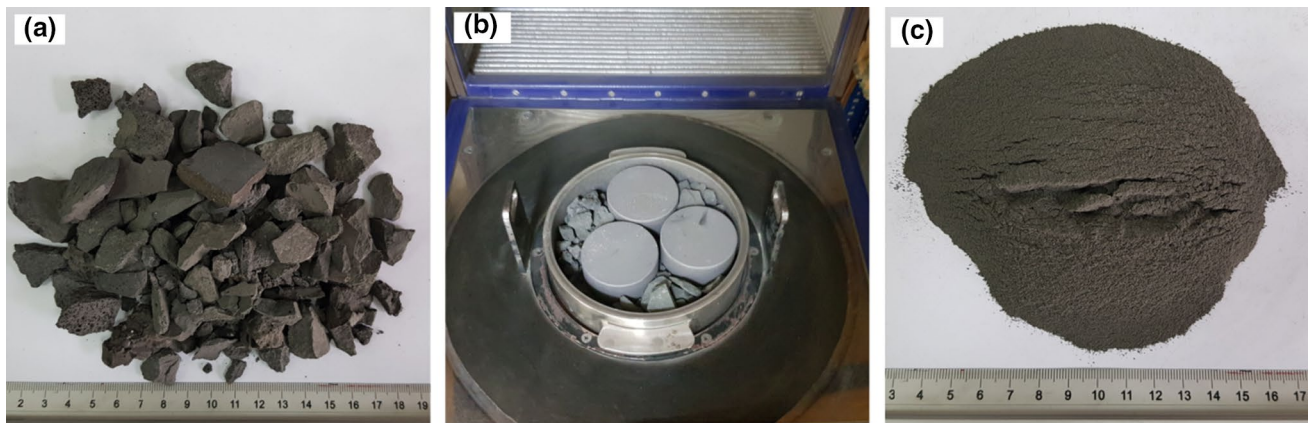


Fig. 1 Flash smelting slag before leaching process (**a**—slag pieces, **b**—grinding of slag, **c**—crushed slag)

maintaining the required temperature of the leaching solution. Assuming that, if all other auxiliary processes would consume another 33,000 MWh per year, the total energy consumption for hydrometallurgical processing would be approximately 66,000 MWh. Balancing the two methods of handling slag, the existing one and the one consisting of grinding and hydrometallurgical processing, it can be concluded that replacing the current technology would reduce energy consumption by almost 120,000 MWh per year [5]. Carbon consumption in the reduction process would drop by 16,000 tons, and as a consequence, almost 60,000 tons of CO₂ would not be emitted into the atmosphere [6].

There is a significant number of literature reports on leaching of copper oxide ores in sulfuric acid solutions [7–9], processing of flotation waste in H₂SO₄ solutions [10, 11], recovery of copper from waste of electrical [12, 13] and electronic equipment (WEEE) [14, 15] or extraction of copper from spent catalyst [16–18]. Hydrometallurgical processing of flash smelting slag was the subject of several papers [19, 20], and the results obtained there indicated the possibility of a wider application such methods [21]. In this paper, it was decided to conduct research on the leaching efficiency and kinetics of copper extraction from slag using hydrometallurgical methods with H₂SO₄ solutions.

2 Materials and methods

The slag used in the research came from the flash furnaces of the Głogów Copper Smelter II. Before leaching, it was crushed in a crusher to a grain size not exceeding 0.5 mm. Its image is shown in Fig. 1, and the result of the sieve analysis is presented in Table 1.

Further tests that were carried out on the flash smelting slag sample were performed by scanning electron

Table 1 The results of the sieve analysis of flash smelting slag

Grain size [mm]	Mass fraction share [%]
0.5 ÷ 0.4	8.49
0.4 ÷ 0.32	10.14
0.32 ÷ 0.25	6.67
0.25 ÷ 0.2	6.63
0.2 ÷ 0.16	21.12
0.16 ÷ 0.1	21.44
0.1 ÷ 0.071	18.14
0.071 ÷ 0.056	4.41
0.056 ÷ 0.028	2.92
0.028 ÷ 0	0.04

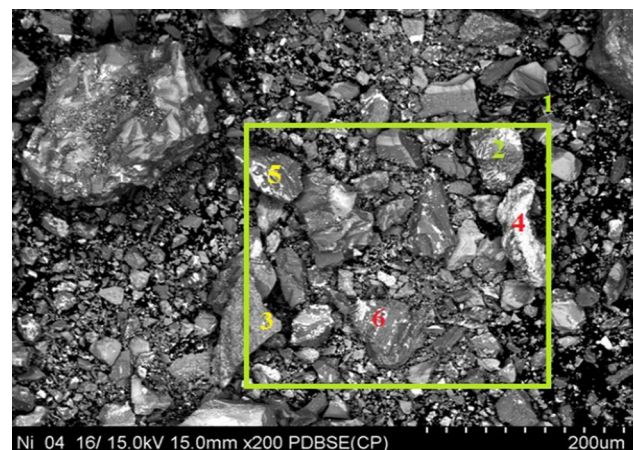
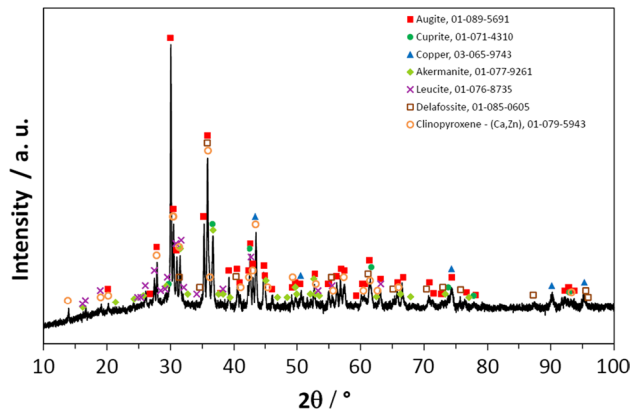


Fig. 2 SEM image of flash smelting slag sample before leaching

microscopy (Fig. 2), and EDS analysis of the slag (Table 2) as well as identification of the slag phase composition made by XRD (Fig. 3).

Table 2 EDS analysis of flash smelting slag in selected points (weight, %)

	O	Mg	Al	Si	Ca	Fe	Cu	Zn	Pb
Area1	36.4	2.5	5.2	14.7	10.8	12.4	12.4	1.6	3.6
pt2	43.7	0.2	12.9	30.8	3.7	2.5	0.9	0.3	4.5
pt3	33.0	1.7	4.4	15.2	17.6	14.0	7.4	2.4	3.8
pt4	10.8	0.1	0.5	1.0	0.3	0.7	86.1	0.0	0.2
pt5	24.7	2.9	4.0	18.1	19.8	15.4	8.4	1.8	4.4
pt6	52.9	4.9	5.1	17.0	11.8	7.3	0.1	0.5	0.1

**Fig. 3** XRD pattern of flash smelting slag sample

Owing to the fragmentation of the slag, more than 60% of the slag mass was within the grain diameter range of 0.071–0.2 mm. Copper content in the slag was 12.44% and as indicated by the EDS analysis, it was different depending on the place of the analysis. As the copper content in the sample, determined by the EDS method, is an approximate value, it was decided to test the copper content in the slag using the AAS method. The obtained value was 11.88%, which was used in further calculations of the copper leaching efficiency. Apart from Cu, there were also other metals in the sample, such as Zn, Pb and Fe. XRD analysis revealed a number of phases in which copper was identified:

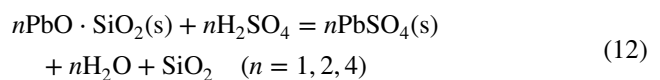
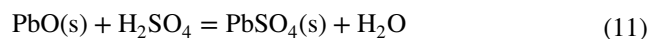
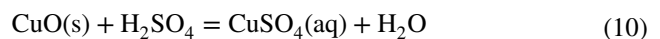
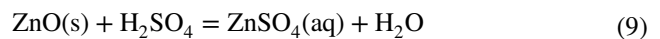
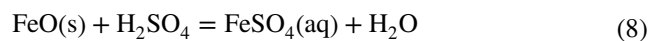
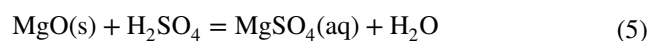
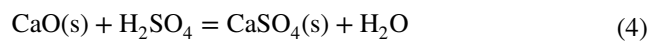
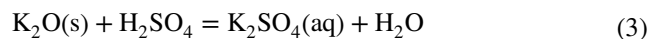
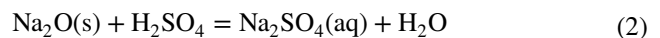
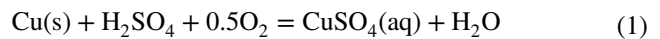
- cuprite—Cu₂O
- copper—Cu
- delafossite—CuFeO₂

and phases in which other elements were present:

- clinopyroxene—CaZn(Si₂O₆),
- augite—Ca(Mg,Fe,Al)(Si,Al)₂O₆,
- akermanite—Ca₂Mg(Si₂O₇)
- leucite—K(AlSi₂O₆).

It was assumed that by treating the slag with sulfuric acid, a number of reactions between the acid and the slag

components could occur [22, 23]. The most likely reactions are listed below:



The research methodology was based on cyclic sampling of the leaching solution, determining the concentration of copper in it, and then calculating the leaching efficiency. In this way, information was obtained on the efficiency of copper leaching and the kinetics of the process for the leaching parameters successively changed during the tests. The copper content of the leach solution was determined using a Minipal 4 EDXRF spectrometer. Before starting the tests, for five solutions with a strictly defined concentration of copper, a reference curve was made which defines the dependence of cps (counts per second) on the concentration of copper. The square of

the correlation coefficient (R^2) of the obtained curve was 0.9924 and should be considered as high. Due to the relationship it was possible to quickly and precisely convert cps from the analysis of samples obtained during the tests to the concentration of copper in the solution.

During the tests, the leaching solution consisting of sulfuric acid and distilled water (400 ml) was heated to the appropriate temperature using a water bath. A probe measuring the pH level was inserted into the beaker with the leaching solution. During the leaching, a mechanical agitator was used, the movement of which was to intensify the leaching process. After the planned solution temperature was reached, the stirrer was run at 250 rpm (constant speed for all tests—previous tests have shown that this is the maximum speed that can be obtained in the measuring system used; the solution splashes at higher speeds) and the initial pH of the solution was recorded. Then, the measurement was started by introducing an appropriate amount of flash smelting slag into the beaker with the leaching solution. With the passage of time, at appropriate intervals, i.e. after 5, 10, 20, 30, 60, 90 and 120 min, 5 ml of the solution for analysis was taken for Cu content and the pH value of the solution was recorded. In place of the solution taken from the beaker, a sufficient amount of sulfuric acid solution was fed to ensure a constant level of l/s (cm^3/g). In most of the tests, apart from sulfuric acid, the addition of perhydrol was also used, which caused the intensification of the copper leaching process in accordance with the reaction (1). The total perhydrol addition was divided into 4 parts and fed at 0, 30, 60 and 90 min of the leaching process.

The leaching efficiency of copper was calculated from the relationship:

$$\eta_{\text{Cu}} = \left(\frac{m_{\text{Cu}}}{m_{\text{Cu}}^0} \right) \quad (13)$$

where m_{Cu}^0 —the mass of copper in the slag sample before the process and m_{Cu} —the mass of copper in the solution after leaching process.

The measuring stand consisted of four main elements:

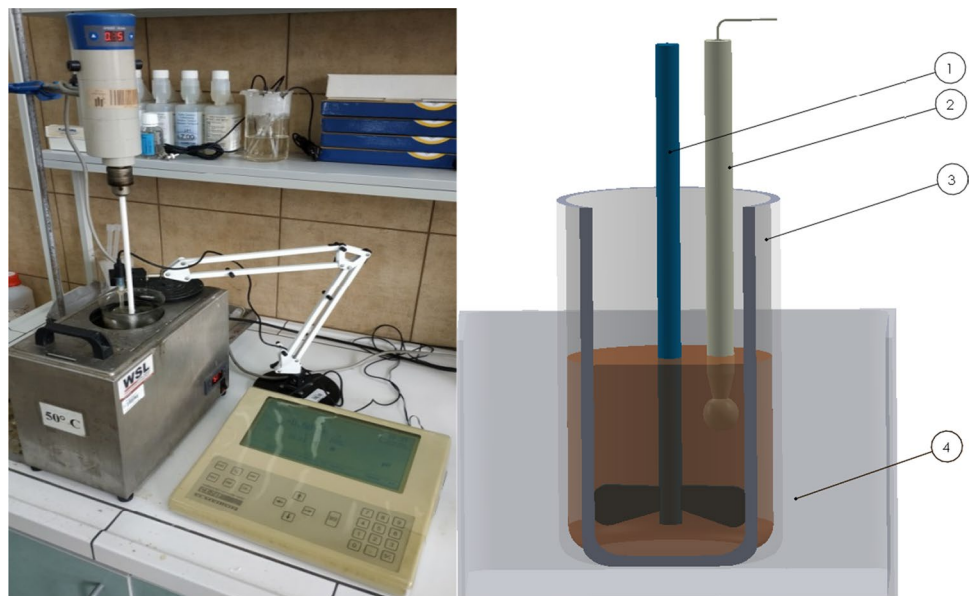
1. 600 ml beaker in which the leaching process was carried out,
2. pH analyzer consisting of a probe immersed in the solution during the entire leaching process and a panel from which numerical pH values were read,
3. a mechanical agitator ensuring uniform density and temperature of the solution throughout its volume and the proper course of the leaching process,
4. water bath ensuring constant and stable process temperature.

The measurement system is shown in Fig. 4.

3 Results

The results of studies on the efficiency of copper leaching and the kinetics of this process depending on the selected leaching parameters are presented below. Therefore, the influence of the concentration of H_2SO_4 , the amount of perhydrol addition, the parameter l/s (liquid phase/solid phase) and the temperature at which the process was carried out on the leaching of copper from flash smelting slag was investigated. After determining the parameter at which the process

Fig. 4 Image and diagram of the test stand for leaching of flash smelting slag (1—stirrer, 2—pH probe, 3—beaker, 4—water bath)



proceeds with the highest efficiency, the next parameter was changed in the next step. This procedure allowed for the minimization of the number of trials and led to the obtaining of a set of parameters allowing the process to be carried out with the maximum efficiency.

3.1 Effect of H_2SO_4 concentration on the efficiency of copper leaching

In this part of the research, it was decided to analyze the effect of sulfuric acid concentration on the leaching efficiency of copper from flash smelting slag. The concentration of the H_2SO_4 solution was varied from 50 through 100–200 g/l. The others leaching parameters were constant ($T = 50\text{ }^\circ\text{C}$, $l/s = 10$). The taken samples of the solution were analyzed for copper content and on this basis the copper leaching efficiency was determined. The obtained test results are presented in Table 3, the leaching efficiency calculated on their basis is shown in Fig. 5.

The highest copper leaching efficiencies were obtained for the highest sulfuric acid concentration (200 g/l) and the next stage of the research was started with the assumption that a solution of this concentration should be used.

3.2 Effect of perhydrol addition on copper leaching efficiency

In this series of measurements, it was decided to investigate how the copper leaching process is influenced by the addition of 30% perhydrol. The decomposition of H_2O_2 causes the release of a certain amount of oxygen necessary for the reaction (1) and H_2O_2 itself acts as a strong oxidant that causes intensification of the copper leaching process. H_2SO_4 solutions with a concentration of 200 g/l were used because at this concentration, in the previous series, the highest value of the leaching efficiency (0.812) was recorded. 10 ml and 20 ml of perhydrol divided into four portions were added.

Table 3 Results of copper leaching from flash smelting slag for different concentrations of H_2SO_4 in the leaching solution

Time (min)	50 g/l H_2SO_4		100 g/l H_2SO_4		200 g/l H_2SO_4	
	Cu in solution [g/l]	pH	Cu in solution [g/l]	pH	Cu in solution [g/l]	pH
0	0.00	−0.07	0.00	−0.36	0.00	−0.95
5	3.44	0.26	3.52	−0.24	4.04	−0.94
10	4.09	0.34	4.22	−0.18	4.84	−0.82
20	4.83	0.42	4.66	−0.13	5.35	−0.75
30	5.48	0.48	4.98	−0.09	5.71	−0.73
60	6.93	0.58	6.25	−0.07	7.17	−0.72
90	7.54	0.64	7.49	−0.05	8.59	−0.70
120	7.96	0.70	8.41	−0.04	9.64	−0.69

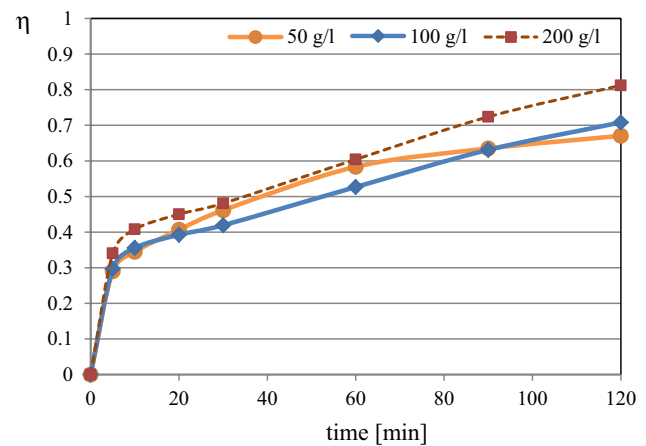


Fig. 5 Copper leaching efficiency vs. leaching time for different H_2SO_4 concentration. ($50\text{ }^\circ\text{C}$, $l/s = 10$)

The l/s parameter and temperature did not change in relation to the previous series. The test results are presented in Table 4 and the leaching yields are shown in Fig. 6.

The effect of perhydrol addition on the copper leaching process from flash smelting slag was observed. The highest copper leaching efficiency occurred with the highest addition of H_2O_2 , therefore, it was decided to start the next series of tests with the addition of 20 ml of perhydrol.

3.3 Effect of liquid phase to solid phase ratio (l/s) on the leaching efficiency

This series of tests was aimed at determining the effect of the l/s parameter on the course of the leaching process. It was assumed that the tests will be carried out with a leaching solution with a concentration of 200 g/l H_2SO_4 , with the addition of 20 ml of 30% H_2O_2 , at a temperature of $50\text{ }^\circ\text{C}$. The l/s parameter was changed from 5 through 10–20. The obtained results are presented in Table 5. The leaching yields are shown in Fig. 7.

Table 4 Results of copper leaching from flash smelting slag for various additives of perhydrol

Time [min]	0 ml of perhydrol		10 ml of perhydrol		20 ml of perhydrol	
	Cu in solution [g/l]	pH	Cu in solution [g/l]	pH	Cu in solution [g/l]	pH
0	0.00	-0.95	0.00	-0.95	0.00	-0.95
5	4.04	-0.94	4.56	-0.94	5.25	-0.93
10	4.84	-0.82	5.64	-0.81	5.94	-0.80
20	5.35	-0.75	6.55	-0.73	6.42	-0.72
30	5.71	-0.73	6.66	-0.71	6.94	-0.70
60	7.17	-0.72	9.09	-0.69	9.81	-0.68
90	8.59	-0.70	9.83	-0.67	10.39	-0.66
120	9.64	-0.69	10.39	-0.66	11.21	-0.65

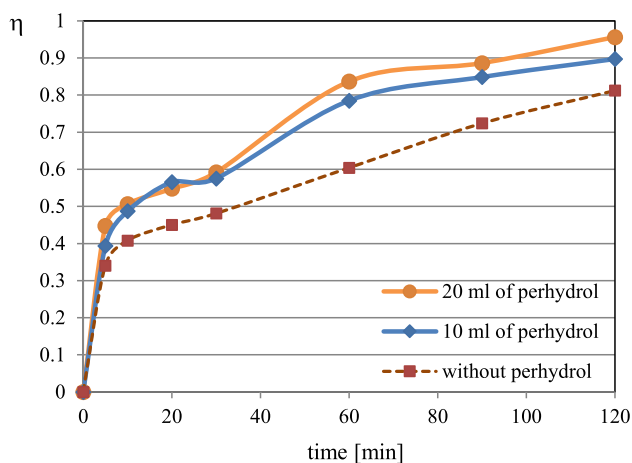


Fig. 6 Copper leaching efficiency vs. leaching time for different additives of perhydrol. (50 °C, $l/s = 10$, 200 g/l of H_2SO_4)

The test results indicate a significant influence of the l/s parameter on the copper leaching process. The highest leaching efficiencies in the entire process time range were obtained for $l/s = 20$, and therefore in the next series of tests it was decided to carry out the l/s parameter fixed at this level.

Table 5 Results of copper leaching from flash smelting slag for various l/s parameters

Time [min]	$l/s = 5$		$l/s = 10$		$l/s = 20$	
	Cu in solution [g/l]	pH	Cu in solution [g/l]	pH	Cu in solution [g/l]	pH
0	0.00	-0.95	0.00	-0.95	0.00	-0.95
5	4.88	-0.94	5.25	-0.93	3.35	-0.96
10	5.52	-0.92	5.94	-0.80	3.73	-0.75
20	5.97	-0.87	6.42	-0.72	4.09	-0.69
30	6.45	-0.79	6.94	-0.70	4.44	-0.70
60	9.11	-0.78	9.81	-0.68	5.01	-0.70
90	9.66	-0.77	10.39	-0.66	5.45	-0.69
120	10.42	-0.77	11.21	-0.65	5.61	-0.66

3.4 Influence of the process temperature on the efficiency of copper leaching

The last series of measurements was to determine the effect of temperature on the efficiency of copper leaching. Table 6 summarizes the results of tests carried out at 25, 50 and 75 °C. The other leaching parameters were fixed and amounted to 200 g/l of H_2SO_4 , 20 ml of perhydrol addition, $l/s = 20$. The calculated copper leaching yields in this series are presented in Fig. 8.

The obtained results indicate that the optimal temperature in the process of copper leaching from flash smelting slag is 50 °C. The highest process efficiencies over the entire leaching time range are then achieved. The highest copper leaching efficiency in the entire test cycle was 0.9562. The optimal leaching parameters for this result are: $T = 50$ °C, $l/s = 20$, 200 g/l of H_2SO_4 , 20 ml of perhydrol, $t = 120$ min.

3.5 Analysis of materials obtained after the leaching process under optimal conditions

It is understandable that after the leaching process, the slag changes its properties in terms of chemical composition, phase composition and graining, which also results in a

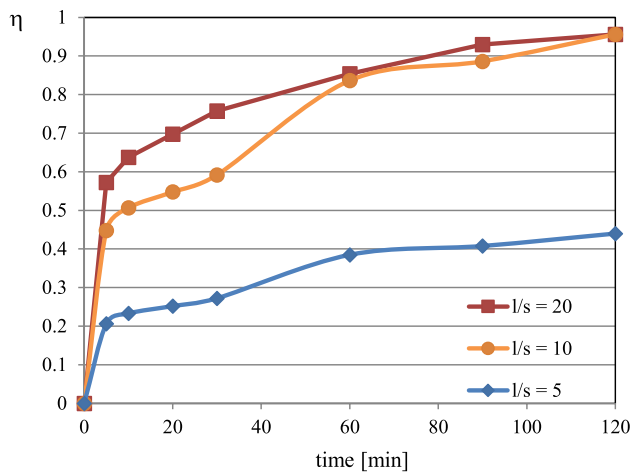


Fig. 7 Copper leaching efficiency vs. leaching time for different *l/s* parameters (50 °C, 200 g/l of H₂SO₄, 20 ml of perhydrol)

different appearance as compared to the period before the process. The image of the material after the test with the highest copper leaching efficiency is shown in Fig. 9.

This sample was tested for its chemical and phase composition. Figure 10 shows a scanning microscope image of this material, and Table 7 provides EDS analyzes of the residue sample after leaching. Figure 11 shows the results of the XRD analysis of obtained material after leaching. The residue after leaching was characterized by a much lower copper content (area1—1.12% Cu) as compared to the analogous value from the initial sample (area1—12.44% Cu). The phase composition of the sample after leaching was changed and XRD analysis did not reveal any copper-containing phases. Phases found in this material are:

- lead sulfate—PbSO₄,
- corundum—Al₂O₃,
- K₂Ca₂(SO₄)₃,
- clinoestatite—Mg(SiO₃) or Mg₂(Si₂O₆),

Table 6 Results of copper leaching from flash smelting slag for various temperatures

Time [min]	25 °C		50 °C		75 °C	
	Cu in solution [g/l]	pH	Cu in solution [g/l]	pH	Cu in solution [g/l]	pH
0	0.00	-0.44	0.00	-0.95	0.00	-1.03
5	2.13	-0.35	3.35	-0.96	2.89	-0.94
10	2.24	-0.27	3.73	-0.75	3.21	-0.89
20	2.44	-0.20	4.09	-0.69	3.53	-0.90
30	2.44	-0.18	4.44	-0.70	3.83	-0.88
60	3.09	-0.12	5.01	-0.70	4.78	-0.87
90	3.75	-0.11	5.45	-0.69	5.33	-0.86
120	4.30	-0.10	5.61	-0.66	5.63	-0.86

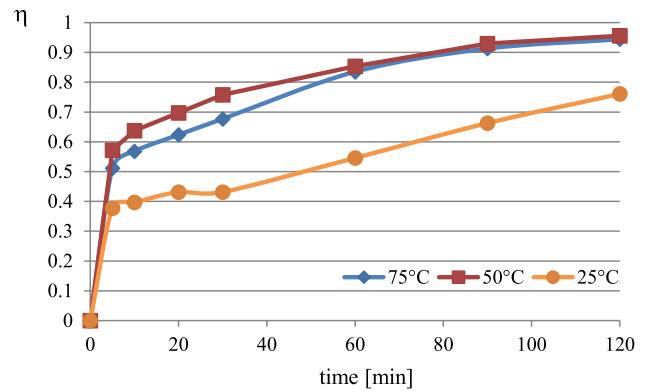


Fig. 8 Copper leaching efficiency vs. leaching time for different temperatures (*l/s* = 20, 200 g/l of H₂SO₄, 20 ml of perhydrol)



Fig. 9 Residue after leaching process under optimal conditions

- augite—Ca(Mg,Fe,Al)(Si,Al)₂O₆.

At the end of the research, the ICP analysis of the solution obtained from the test, in which copper was leached from the slag with the highest efficiency, was performed. The results of this analysis are presented in Table 8.

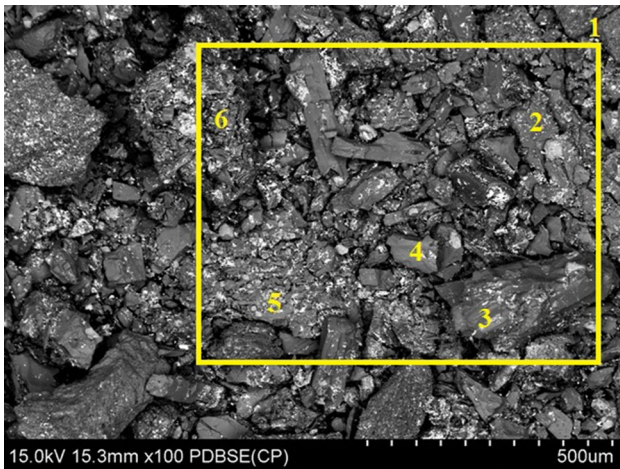


Fig. 10 SEM image of the residue sample after leaching under optimal conditions

4 Discussion

4.1 Optimization of leaching parameters

The conducted tests indicate a significant influence of the leaching parameters on the degree of Cu removal from the flash smelting slag. The results of tests in which the concentration of sulfuric acid was differentiated indicate that the increase in acid concentration positively influenced the obtained results, but the final leaching efficiency after 120 min of the process is not very high and amounts to 0.812 at most. Only the addition of an oxidant (perhydrol) allows the intensification of the copper leaching process and in the tests with the addition of this reagent, the copper leaching degree of 0.956 was obtained in the best test. The XRD tests performed in this study indicate the presence of the Cu₂O phase in the slag. According to the literature reports [24, 25], the leaching process of cuprous oxide in sulfuric acid is complex. To dissolve Cu₂O by sulfuric acid, the addition of oxidant is essential because of disproportionation reaction:

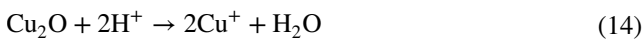


Table 7 EDS analysis of the material after leaching in selected points (weight, %)

	O	Mg	Al	Si	S	Ca	Fe	Cu	Zn	Pb
Area1	42.8	3.1	3.4	16.7	1.5	10.7	13.6	1.1	1.5	5.4
pt2	51.6	3.5	5.2	16.2	0.8	7.6	10.2	0.7	0.8	3.3
pt3	23.2	1.7	14.2	6.8	0.4	6.5	34.2	1.2	9.8	1.9
pt4	21.8	3.7	2.8	1.3	0.3	0.6	61.4	2.1	5.1	0.8
pt5	47.3	3.1	5.9	16.1	1.5	6.2	16.3	0.0	0.0	3.3
pt6	46.3	3.8	3.8	20.2	0.9	12.3	11.2	0.1	0.2	1.2

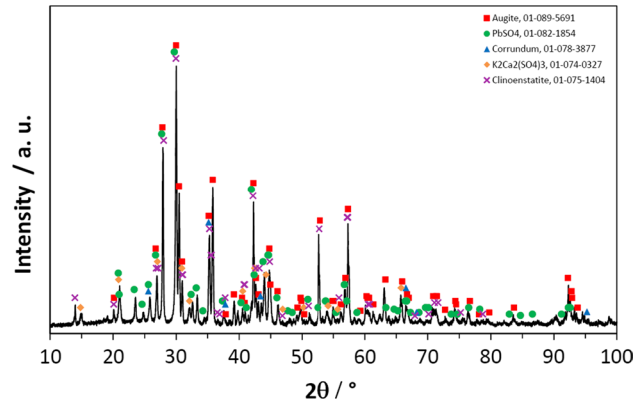


Fig. 11 XRD pattern of the residue obtained after leaching under optimal conditions

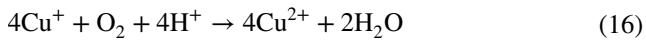
Table 8 Elemental concentrations in the solution after leaching under optimal conditions

Element	Concentration [mg/l]
Al	914
As	74
Ca	794
Co	12
Cu	5672
Fe	1352
K	1006
Mg	83
Mn	51
Mo	32
Na	84
Pb	9
S	53,231
V	39
Zn	355



Reaction (14) is very fast as compared to the dissolution of Cu, and thus all the results showed that Cu²⁺ was rapidly released for 5 min (Cu₂O dissolution), followed by sluggish increase in Cu²⁺ conc. (Cu dissolution). If the oxidant

(oxygen or H_2O_2) is present in the system, the disproportionation reaction will not occur:



This means that the tested process is conditioned by the access of oxygen in accordance with the previously indicated reaction (1, 16) and after supplying oxygen to the process, it was possible to increase the degree of copper leaching from the slag by over 17%. Two subsequent series of studies concerned the study of the effect of the liquid to solid ratio (l/s) and the process temperature on the efficiency of copper leaching from the slag. It was observed that with a low parameter ($l/s=5$) relatively low values of the leaching efficiency (<0.45) are obtained. Owing to the occurrence of reactions (2)–(3) and (5)–(9), apart from copper, a number of other elements pass into the solution, which causes a limited solubility of Cu under such conditions. An increase in l/s results in a directly proportional increase in leaching efficiency but only for a limited process time range (0–60 min). After more than 60 min of the process, the obtained results are similar both for $l/s=10$ and for $l/s=20$. A slightly different behavior of the system is observed in the case of examining the influence of the process temperature on copper leaching. At the temperature of 25 °C, the process is carried out with low efficiency and the increase in temperature increases the degree of copper leaching. However, the temperature of 50 °C seems to be optimal for this process because then the highest process efficiency is obtained in the whole range of the analyzed process time. Especially in the range of 0–60 min, it can be seen that the leaching yields at 50 °C are significantly higher than those obtained at 75 °C. It can be assumed that at a temperature of 75 °C, a rapid decomposition of H_2O_2 takes place, which causes a decrease in its concentration in the solution and a lower efficiency of copper leaching. For the time of carrying out the process above 60 min, the differences between the yields obtained in the two highest temperatures become blurred and after 120 min the obtained yields are practically the same.

The tests of the chemical and phase composition of the residue sample after leaching and the solution after the process confirm that the copper was transferred from the slag to the solution to a very high degree. XRD analysis does not even identify any copper-containing phase and indicates the existence of PbSO_4 in the material after leaching as a result of reactions (11) and (12). In addition to copper, the solution also contains large amounts of Fe, Al, Zn, K and Ca, which is a consequence of the chemical composition of the starting slag and the occurrence of a number of chemical reactions mentioned earlier.

On the basis of the data on the chemical composition of the solution after leaching (Table 8), using the HSC Chemistry 5.11 software, an Eh–pH diagram was prepared for the

Cu–S– H_2O system (Fig. 12). It can be seen that for the pH values observed throughout the leaching period (Table 6), the solution may contain, depending on the potential, Cu^{+2} cations, Cu_2S compound or metallic copper. It can be assumed that the addition of perhydrol to the leaching solution causes the process conditions to approach the upper dashed line ($2\text{H}_2\text{O}=\text{O}_2+4\text{H}^++4\text{e}^-$) and the solution contains mainly Cu^{2+} ions.

4.2 Investigations of the kinetics of the copper leaching process from flash smelting slag

The leaching process of copper from copper flash smelting slag is a solid–liquid reaction. The condition of the leaching process to take place is to supply the reagents to the surface of the solid phase. Therefore, the speed of the process may be primarily determined by the factors regulating the rate of mass transport between the dissolved phase and the solution. The slowest stage determines the overall rate of the reaction. If the slowest stage of the reaction is the transport of the reactants to the phase boundary, then the process takes place in the diffusion region. If the leaching rate is independent of transport processes, then the slow stage of the process is a chemical reaction that runs on the surface of the solid and the reaction runs in the kinetic region. Under such conditions, an increase in the reaction rate is usually achieved by increasing the temperature. For the analysis of the kinetics of the leaching process the models of control of the diffusion process through the product layer [26] and the chemical reaction [27], commonly known from the literature, were used. The mathematical relationships for both models are presented below.

Equation of the diffusion process through the product layer [28–30]:

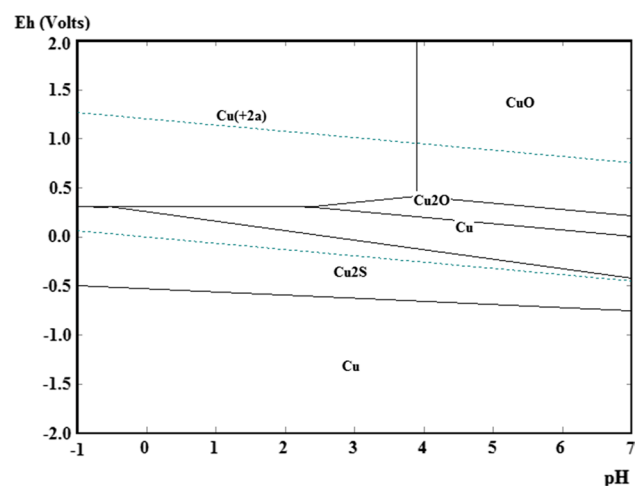


Fig. 12 E–pH diagram for Cu–S– H_2O system

$$1 - 2/3 \cdot \eta - (1 - \eta)^{2/3} = k_1 t \tag{17}$$

Chemical reaction model equation [31, 32]:

$$1 - (1 - \eta)^{1/3} = k_2 t \tag{18}$$

where k_1, k_2 —speed constants. η —efficiency of the copper leaching process.

The speed constants for both models were obtained by approximating the points calculated on the basis of experimental values. Owing to the fact that the course of the curves describing the measurement data is different in the range of 0–5 min and 5–120 min, the experimental results were used for model calculations, not taking into account the moment of starting the measurements ($t=0$ min.) The values of the left-hand sides of model Eqs. (17) and (18) are on the ordinate axis, and the process time is marked on the abscissa axis. The directional coefficients of the obtained lines are the speed constants of the respective models. As in the case of the presentation of data on the efficiency of copper leaching, the following figures show the results for different concentrations of H_2SO_4 , different perhydrol additives, various l/s parameters and different process temperatures (Table 9; Figs. 13, 14, 15 and 16).

Analyzing the obtained results, it can be concluded that due to the high R^2 values, both models describe the kinetics of the copper leaching process just as well. It is generally accepted that a chemically controlled process is strongly dependent on the temperature. The variation of the reaction

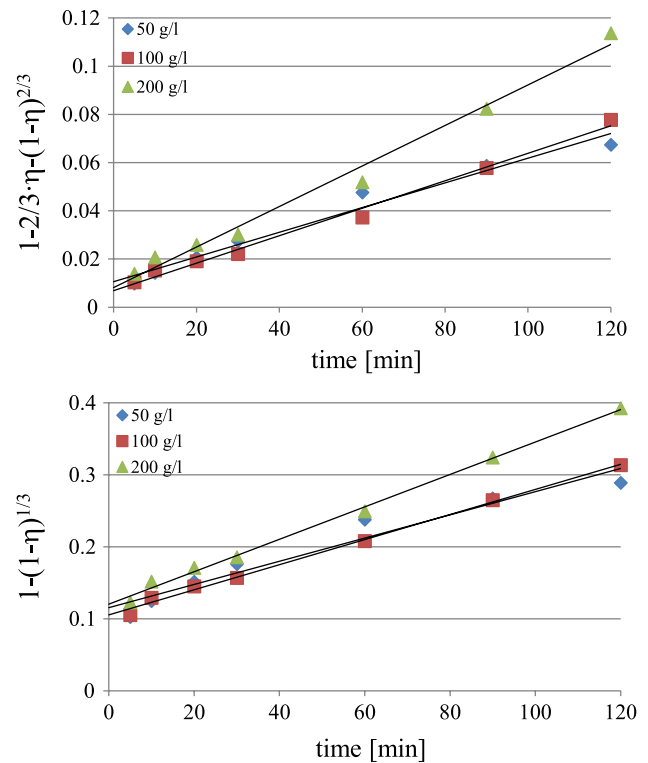


Fig. 13 The course of model curves (17) and (18) relative to the experimental points obtained during the leaching tests (various concentrations of H_2SO_4)

Table 9 Speed constants and R^2 leaching reaction of copper depending on process parameters obtained for the models used

Parameter/values	Diffusion process model		Chemical reaction model	
	k	R^2	K	R^2
H_2SO_4 concentration [g/dm³]				
50	5.13E-04	0.9741	1.61E-03	0.9445
100	5.70E-04	0.9913	1.74E-03	0.9956
200	8.41E-04	0.9878	2.25E-03	0.9960
Perhydrol addition [ml]				
0	8.41E-04	0.9878	2.25E-03	0.9960
10	1.21E-03	0.9810	2.86E-03	0.9662
20	1.77E-03	0.9832	3.93E-03	0.9824
l/s [ml/g]				
5	2.01E-04	0.9661	9.14E-04	0.9497
10	1.77E-03	0.9832	3.93E-03	0.9824
20	1.56E-03	0.9876	3.30E-03	0.9823
Temperature [°C]				
25	6.52E-04	0.9641	1.83E-03	0.9843
50	1.56E-03	0.9876	3.30E-03	0.9823
75	1.75E-03	0.9974	3.80E-03	0.9980

rate with temperature is commonly described using the empirical Arrhenius law:

$$k = k_0 \exp \left[-E_a / (RT) \right] \tag{19}$$

where k_0 , pre-exponential factor, E_a , apparent activation energy and R , mole gas constant.

According to the empirical Arrhenius law shown in Eq. (19), the plot of $\ln k$ versus T^{-1} was constructed and the results are shown in Fig. 17 (the $\ln k$ values were determined from Table 9). The slope of the straight line is equal $t_0 - E_a/R$. It was calculated that the activation energy of copper leaching from flash smelting slag is 12.77 kJ/mol when the k constants based on the chemical reaction model are used, and 17.34 kJ/mol when the constants from the diffusion process model are used. A higher numerical value of the activation energy obtained on the basis of the diffusion model may indicate that the diffusion of products and substrates during the leaching process determines the speed of the entire process.

5 Conclusions

The research carried out in the work contributed to the drawing of the following conclusions:

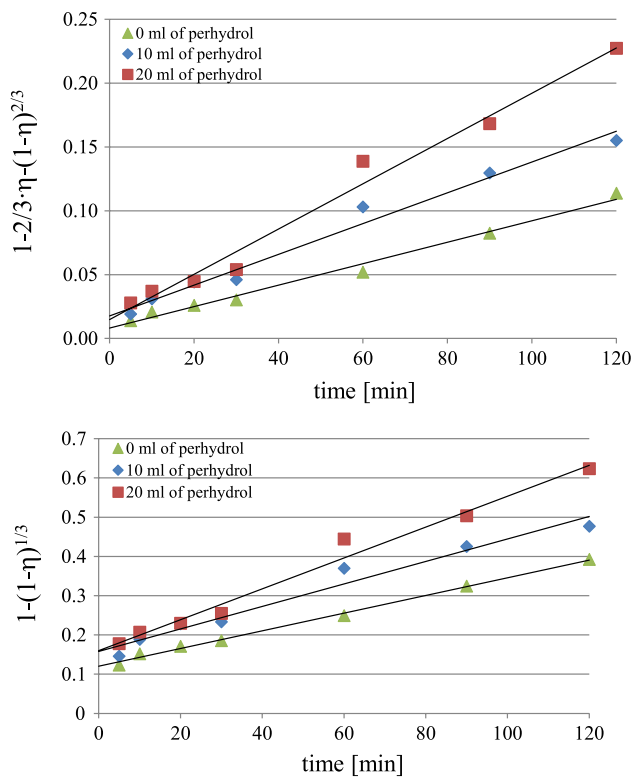


Fig. 14 The course of model curves (17) and (18) relative to the experimental points obtained during the leaching tests (different additives of perhydrol)

1. The effect of the concentration of H_2SO_4 in the solution on the efficiency of copper leaching from flash smelting slag is observed; copper leaching is intensified when the process is carried out under oxidizing conditions,
2. Copper leaching efficiency is the highest in the case of using high l/s parameters,
3. The optimal temperature of the copper leaching process is 50°C —raising the temperature does not have a positive effect on the obtained results,
4. The highest copper leaching efficiency of 0.9562 was obtained with the following set of process parameters:
5. $T = 50^\circ\text{C}$, $l/s = 20$, 200 g/l of H_2SO_4 , 20 ml of perhydrol, $t = 120\text{ min}$,
6. The residue after leaching contains more than 5% of lead in the form of sulfate and therefore should be processed for the recovery of this component.

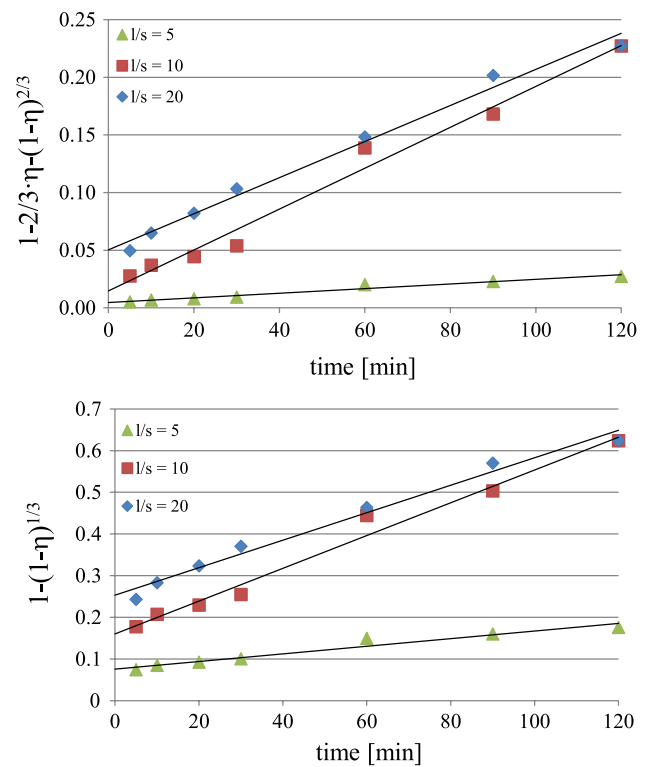


Fig. 15 The course of model curves (17) and (18) relative to the experimental points obtained during the leaching tests (different l/s parameters)

7. Both diffusion model and chemical reaction model describe the kinetics of copper leaching from flash smelting slag with H_2SO_4 solutions just as well,
8. The value of activation energy of copper leaching from flash smelting slag depending on the estimation method, ranges from 12.77 to 17.34 kJ/mol; due to the higher activation energy obtained on the basis of the diffusion model, it can be assumed that under certain conditions, this step may have a more significant effect on the speed of the overall process compared to the chemical reaction step.
9. Copper recovery using hydrometallurgical processes can significantly reduce electricity consumption and CO_2 emissions to the atmosphere compared to the currently used technology.

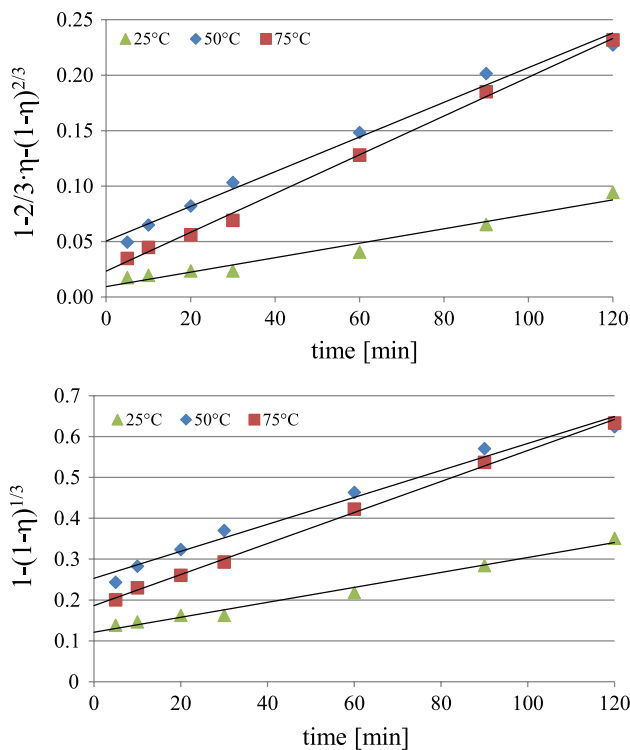


Fig. 16 The course of model curves (17) and (18) relative to the experimental points obtained during the leaching tests (different process temperatures)

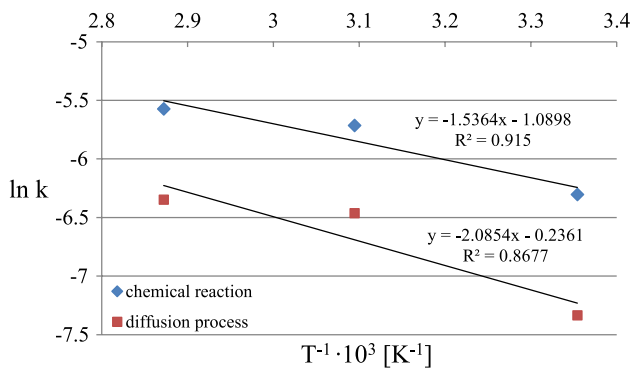


Fig. 17 Arrhenius plot for leaching of copper from flash smelting slag

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Declarations

Conflict of interest The authors declare no conflict of interest.

Ethical approval This article does not contain any studies with human participants or animals performed by any of the authors.

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