

Article

Kinetics of Chalcopyrite Leaching by Hydrogen Peroxide in Sulfuric Acid

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Received: 4 September 2019; Accepted: 26 October 2019; Published: 30 October 2019



Abstract: In ores, chalcopyrite is usually associated with other sulfide minerals, such as sphalerite, galena, and pyrite, in a dispersed form, with complex mineralogical structures. Concentrates obtained by flotation of such ores are unsuitable for pyrometallurgical processing owing to their poor quality and low metal recovery. This paper presents the leaching of chalcopyrite concentrate from the location “Rudnik, Serbia”. The samples from the flotation plant were treated with hydrogen peroxide in sulfuric acid. The influences of temperature, particle size, stirring speed, as well as the concentrations of hydrogen peroxide and sulfuric acid were followed and discussed. Hence, the main objective was to optimize the relevant conditions and to determine the reaction kinetics. It was remarked that the increase in temperature, hydrogen peroxide content, and sulfuric acid concentration, as well as the decrease in particle size and stirring speed, contribute to the dissolution of chalcopyrite. The dissolution kinetics follow a model controlled by diffusion, and the lixiviant diffusion controls the rate of reaction through the sulfur layer. Finally, the main characterization methods used to corroborate the obtained results were X-ray diffraction (XRD) as well as qualitative and quantitative light microscopy of the chalcopyrite concentrate samples and the leach residue.

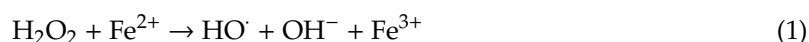
Keywords: chalcopyrite concentrate; hydrogen peroxide; sulfuric acid; leaching kinetics

1. Introduction

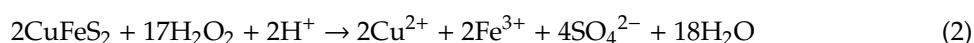
The global demand for copper is increasing while its content in mined ores decreases. Chalcopyrite, as the most abundant copper mineral in the earth’s crust, has a very stable crystal structure, and usually co-exists with other sulfide minerals such as sphalerite, galena, pyrite, and gangue minerals. Copper producers are forced to cope with low-grade ores dominated by chalcopyrite [1,2]. Due to the complex mineralogy and/or presence of toxic chemical elements, such as arsenic, some ores are not suitable for concentration by froth flotation. Therefore, it is convenient to treat these ores using some of the hydrometallurgical processes. Leaching of copper from chalcopyrite requires the presence of the oxidants in an acidic environment; some of the frequently present oxidants are: the ferric ions [3–9], the cupric ions [10–12], some acidophilic bacteria [13–18], the nitrate ions [19,20], the nitrite ions [21,22], the dichromate ions [23,24], the manganese ions [25,26], the permanganate ions [27], the chlorate ions [28], the oxygen ions [29–34], ozone [35], the silver ions [36,37], and the use of microwaves [38,39].

Hydrogen peroxide was used as a relatively cheap and strong oxidizing agent, with a redox potential of +1.77 mV in the acidic medium [40]. The application of hydrogen peroxide for the leaching of chalcopyrite in sulfuric acid solution has previously been examined by several authors [40–53].

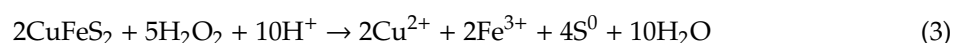
Oxidative activity of the hydrogen peroxide is based on its dissociation to the reactive hydroxyl anion group (OH^-) and hydroxyl radical (HO^\cdot), dissociation is catalyzed by ferric ion, this reaction occurs according to the chemical Equation (1) [40,54]:



A dominant mechanism of chalcopyrite dissolution by the hydrogen peroxide in acidic solution is given by the Equation (2) [42]:



At the same time, a small part of sulfide sulfur is oxidized to its elemental form, this is confirmed by XRD analysis of the leach residue and a leaching degree of 55%, the reaction is presented by Equation (3):



Agacayak et al. obtained similar results [46]. They did not confirm the formation of elemental sulfur in the leaching process, as confirmed by the XRD analysis of the leach residues. Simultaneously, they found a pH decrease in the solution, which confirms that sulfide sulfur transforms to sulfate during the leaching. On the other hand, Misra and Fuerstenau [43] have shown that most of the sulfide sulfur was transformed into its elemental form.

Adebayo et al. [40] examined the leaching kinetics of chalcopyrite and found that increasing the concentration of sulfuric acid and hydrogen peroxide could increase the copper leaching rate; also, the chalcopyrite dissolution reaction takes place by a shrinking-core model with the surface reaction as the rate-controlling step with an activation energy of 39 kJ/mol.

Hydrogen peroxide is unstable and quickly decomposes in the leaching process of sulfide minerals in the presence of iron and copper ions, mineral particles, and different impurities. Intensive depletion of hydrogen peroxide by metal cations and discontinuation of chalcopyrite leaching after 60 min were confirmed by Olubambi and Potgieter [40], and Agacayak et al. [46]. They also confirmed the decomposition of hydrogen peroxide at elevated temperatures.

To reduce the decomposition of peroxide and reduce the decomposition of peroxide, polar organic solvents can be used as its stabilizers. Mahajan et al. [51] confirmed that in the presence of ethylene glycol, chalcopyrite dissolution was possible at low peroxide concentrations. They also confirmed the presence of elemental sulfur at the chalcopyrite surface in the form of separate crystalline particles instead of a continuous sulfur layer; these particles cause the passivation of the chalcopyrite surface. In their experiments, the activation energy was 30 kJ/mol, and the leaching rate was controlled by the surface reaction. Similar results of chalcopyrite leaching in the presence of ethylene glycol and methanol were obtained by Ruiz-Sanchez and Lapidus [52], and Solís Marcial et al. [53].

This work is related to the study of kinetics and the mechanism of dissolution of chalcopyrite from its concentrate by hydrogen peroxide in sulfuric acid solution. The main reason to perform this study was significant differences (~50%) observed in leaching rates of eleven different chalcopyrite samples from different localities under various leaching conditions [55]. The same concentrate was used for the previous study by Sokić et al. [56], where he studied the influence of chalcopyrite structure on leaching by sodium nitrate in sulfuric acid.

In order to optimize parameters for copper leaching, effects of the particle size, temperature, leaching time, concentrations of hydrogen peroxide on copper extraction yield were measured. The obtained results were used to select and to determine the adequate reaction kinetic model.

2. Materials and Methods

2.1. Experimental Procedure

All leaching experiments were performed in the glass reactor of 1.2 dm³ equipped with the Heidolph RZR 2021 model mechanic stirrer (Heidolph Instruments GmbH & CO. KG, Schwabach, Germany) with a Teflon-covered propeller, the condenser to prevent evaporation, the thermometer, the funnel for adding solid samples, and the sampling device. The temperature in the glass reactor was controlled by a heating mantle station (Electrothermal, Staffordshire, UK). The 600 mL sulfuric acid-hydrogen peroxide solution of a definite concentration was poured into the reactor and heated to the set temperature. A 1.2 g concentrate samples were added to the reactor in all experiments when the desired temperature was reached. Samples of the leaching solution were collected in the selected time intervals, and then analyzed on dissolved copper, zinc and iron by atomic absorption spectrophotometry. The solid residues obtained by leaching were washed, dried, and characterized.

Analytical grade chemicals (sulfuric acid, hydrogen peroxide, and distilled water) (MOSS & HEMOSS, Belgrade, Serbia) were used for preparation leaching solutions.

In the leaching experiments, the influence of the stirring speed up to 300 rpm, the temperature in the range 25–45 °C, the hydrogen peroxide concentration in the range of 0.2–2.0 M, and the particle size range was –37, +37–50, +50–75, and +75 µm were investigated.

2.2. Methods

In order to determine the characteristics of the chalcopyrite concentrate, leaching solutions and leach residues, detailed chemical and qualitative and quantitative mineralogical examinations were done. The following methods were used: atomic absorption spectrophotometry (AAS), X-ray diffraction (XRD), and qualitative and quantitative light microscopy.

For chemical analysis, samples were dissolved in aqua regia, and then the concentration of the selected chemical elements was measured by the atomic absorption spectrophotometer PERKIN ELMER 703 model (Perkin Elmer, Norwalk, CT, USA).

The mineralogical compositions of the concentrate and leaching residue were determined using Philips PW-1710 X-ray diffractometer (Philips, Eindhoven, Netherlands). Data obtained by X-ray diffraction were analyzed by Powder Cell computer software [57]. Qualitative and quantitative microscopic investigations were performed in reflected light on Carl Zeiss-Jena, JENAPOL-U microscope (Carl Zeiss, Jena, Germany).

2.3. Material

The chalcopyrite concentrate samples were provided by the “Rudnik” flotation plant (Rudnik, Serbia), and their granulometric and chemical composition for each size fraction are presented in Table 1.

Table 1. Granulometric and chemical composition of the chalcopyrite concentrate samples.

Class, µm	Mass Fraction, %	Content (%)				
		Cu	Zn	Pb	Fe	S
+75	7.32	23.38	3.43	4.08	22.25	28.31
–75 + 50	21.15	26.55	4.28	1.70	24.43	30.19
–50 + 37	5.18	26.95	4.36	1.85	24.75	30.92
–37	66.35	27.08	4.15	2.28	25.12	31.12

The chemical analysis showed that chalcopyrite concentrate contains significant amounts of zinc, lead, and iron.

X-ray diffraction (XRD) analysis shows that the main phase in concentrate is chalcopyrite, with small amounts of sphalerite (Figure 1).

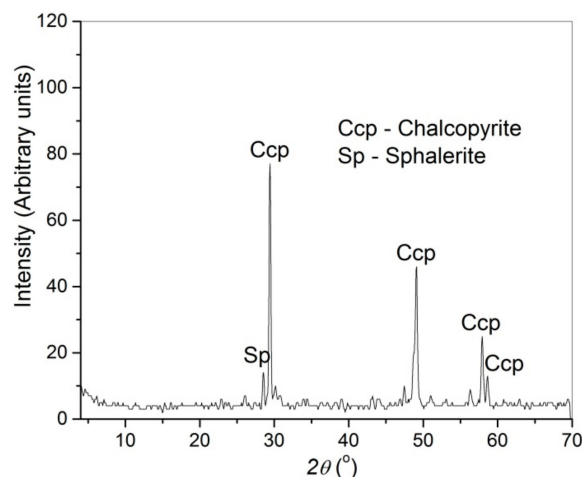


Figure 1. X-ray diffraction analysis of the chalcopyrite concentrate sample [56].

The complete mineralogical composition of the sample is shown in Table 2; the qualitative and quantitative analyses are done using light microscopy, with corrections of Cu, Zn, and Pb content using AAS. Qualitative and quantitative mineralogical analyses show that total sulfides content was 88.7%, while the share of the liberated sulphide grains was 91% and liberated chalcopyrite grains were about 95%.

Table 2. Mineral composition of the chalcopyrite concentrate [56].

Mineral	Mass %
Chalcopyrite	78.247
Sphalerite	6.249
Galena	2.633
Pyrrhotite	1.161
Pyrite	0.099
Arsenopyrite	0.211
Covellite	0.081
Native bismuth	0.031
Limonite	0.118
Gangue	11.170
Total:	100.000

The reflected light microscopic examination of chalcopyrite concentrate is shown in Figure 2. Figure 2 shows the presence of chalcopyrite in the form of free grains and simple intergrowths with sphalerite.

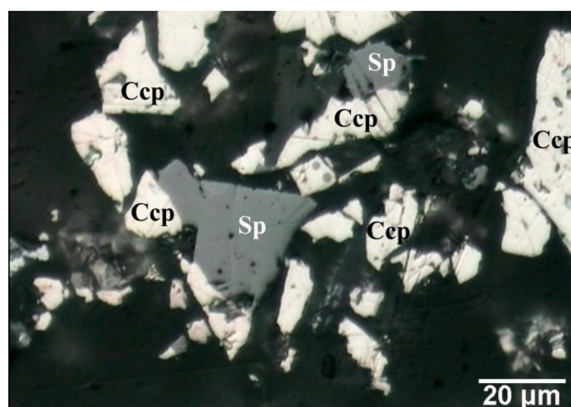


Figure 2. Optical micrograms of the chalcopyrite concentrate sample [56].

3. Results and Discussion

3.1. Effect of Particle Size

The influence of the particle size on the leaching degree of copper was determined under the following conditions: the temperature—40 °C, stirring speed—100 rpm, concentrations of H₂SO₄—1.5 M, H₂O₂—1 M, and solid/liquid ratio—2 gdm⁻³. The results of these experiments are presented in Figure 3.

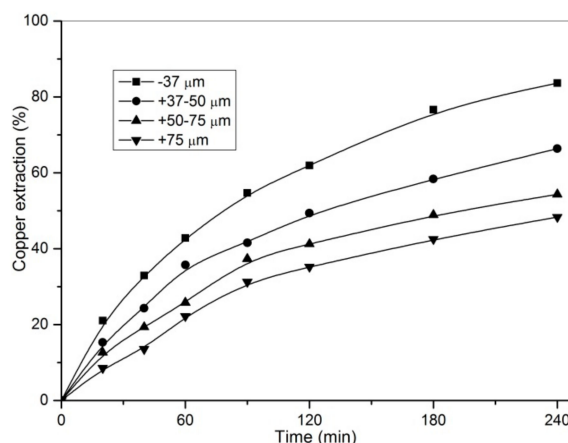


Figure 3. Influence of the particle size on the copper extraction yield (temperature—40 °C, stirring speed—100 rpm, solid/liquid ratio—2 g/dm³, —1.5 M H₂SO₄, —1 M H₂O₂).

As can be seen from Figure 3, with decreasing particle size, copper extraction under the same conditions increases. The similar results were obtained by other authors [40,46,50]. The contact surface between oxidant and chalcopyrite increases, for smaller particles compared to large ones, significantly improving copper extraction; thus, particles with size −37 μm was used for testing other parameters.

3.2. Effect of Temperature and Leaching Time

Influences of the temperature and leaching time on a copper extraction yields from chalcopyrite concentrate was measured at temperatures 25, 30, 35, 40, and 45 °C and leaching time from 0 to 240 min. The grain size was 100% −37 μm, the stirring speed was 100 rpm, and the were of H₂SO₄ and H₂O₂ 1.5 M, and 1 M, respectively. The amount of concentrate in the solution was 2 gdm⁻³. The leaching degree of copper as a function of temperature and leaching time is shown in Figure 4. The copper extraction yield sharply increased with temperature up to 40 °C. After 240 min, at 25 °C, 33.21% of the copper was extracted, compared to 83.64% at 40 °C. At temperatures above 40 °C, copper leaching yields decreased due to a reduction in the amount of H₂O₂ from the solution, caused by its decomposition, as confirmed by Antonijevic et al. [41,42] and Mahajan et al. [51]. Agacayak et al. [46] found that during the leaching with H₂O₂, increasing of the temperature above 50 °C decreases the copper extraction yield due to the promoted decomposition of the hydrogen peroxide. They also noticed that the copper extraction increased with increasing temperatures until the leaching time reached 90 min. After that time, Cu extraction does not change significantly at temperatures above 50 °C. Accordingly, a temperature of 40 °C was used in other experiments.

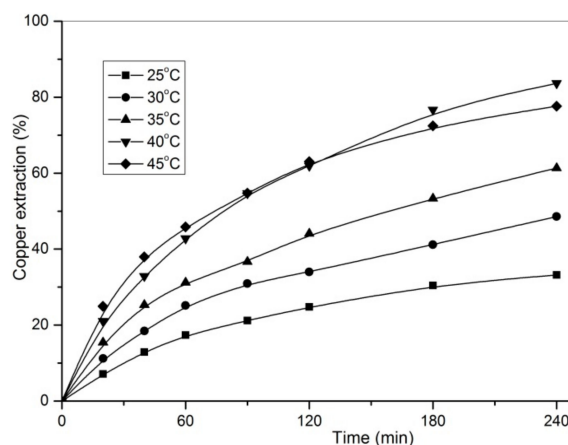


Figure 4. Influence of the temperature and time on the copper extraction yield (particle size $-37\ \mu\text{m}$, stirring speed—100 rpm, solid/liquid ratio— $2\ \text{g}/\text{dm}^3$, $1.5\ \text{M}\ \text{H}_2\text{SO}_4$, $1\ \text{M}\ \text{H}_2\text{O}_2$).

3.3. Effect of Stirring Speed

The influence of the stirring speed was examined on the sample with the particle size 100% $-37\ \mu\text{m}$, temperature of $40\ ^\circ\text{C}$, concentrations of H_2SO_4 $1.5\ \text{M}$, and H_2O_2 $1\ \text{M}$, and solid/liquid ratio— $2\ \text{g}/\text{dm}^3$. These experimental results are shown in Figure 5.

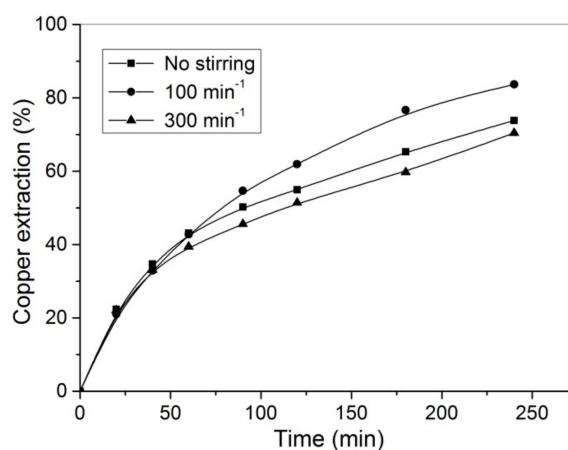


Figure 5. Influence of the stirring speed on copper extraction yield (temperature— $40\ ^\circ\text{C}$, particle size $-37\ \mu\text{m}$, solid/liquid ratio— $2\ \text{g}/\text{dm}^3$, $1.5\ \text{M}\ \text{H}_2\text{SO}_4$, $1\ \text{M}\ \text{H}_2\text{O}_2$).

Maximal leaching degree was achieved at the stirring speed of 100 rpm, which is in line with the results published by Mahajan et al. [51]. Accordingly, the stirring speed of the 100 rpm was optimal, and it has been used in other experiments.

A similar result was obtained by Hu et al. [50], who confirmed that the copper dissolution increased slowly with increasing stirring speed up to 200 rpm, after which it does not change.

The increase of steering speed possibly interferes with the adsorption of hydrogen peroxide on the chalcopyrite and sulfure surface and facilitates the decomposition of the hydrogen peroxide [41]. Adebayo et al. [40] observed the highest dissolution rate when there was no mechanical mixing, indicating that better contacts were made. The decomposition of H_2O_2 is associated with a stirring speed by the evolution of molecular oxygen adsorbed at the particle surface, thus aggravating particle/peroxide contact. In addition, peroxide decomposition was catalyzed by cations as well as Cu^{2+} , Fe^{3+} , and Fe^{2+} [40,52]. On the other hand, Antonijević et al. [42] and Agacayak et al. [46] concluded that stirring speed does not affect the yield of copper during the leaching with hydrogen-peroxide. During the chalcopyrite leaching with potassium dichromate in sulfuric acid solution, Aydogan et al. [24] showed that chalcopyrite dissolution increased up to 400 rpm stirring

speed, and after that, the dissolution rate significantly decreased. The same result was obtained by Petrović et al. [48] during chalcopyrite leaching with peroxide in hydrochloric acid solution.

3.4. Effect of Hydrogen Peroxide Concentration

The influence of the concentration of hydrogen peroxide was examined on the sample size 100% –37 μm , temperature 40 $^{\circ}\text{C}$, the concentration of H_2SO_4 1.5 M, and concentration of solid phase 2 gdm^{-3} . The experimental results are shown in Figure 6.

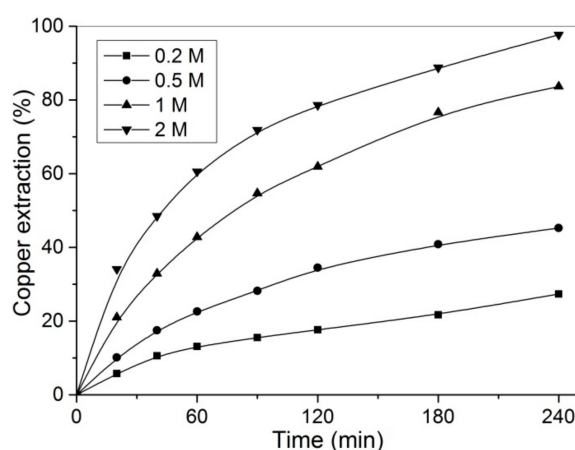


Figure 6. Influence of H_2O_2 concentration on the copper extraction yield (temperature—40 $^{\circ}\text{C}$, particle size –37 μm , stirring speed—100 rpm, solid/liquid ratio—2 gdm^{-3} , —1.5 M H_2SO_4).

Increasing the hydrogen peroxide concentration in the solution has a significant influence on the copper leaching rate. The copper extraction yield increased from 27.35% to 97.96% after 240 min, while the concentration of H_2O_2 was increased from 0.2 to 2.0 M, which shows that the increase of peroxide concentration had a positive effect on the chalcopyrite leaching. The influence of peroxide concentration is larger as the concentration increased from 0.2 to 1.0 M, while the smaller influence was noticed in increasing the peroxide concentration from 1.0 to 2.0 M. These results are in agreement with the earlier results that the decomposition rate of peroxide was proportional to its concentration [40,41,48]. Because of that, the concentration of 1.0 M hydrogen peroxide was used for the investigation of other parameters.

3.5. Characterization of Leach Residue

The chemical analysis of the leach residue, obtained at 40 $^{\circ}\text{C}$, grain size –37 μm , stirring speed—100 rpm, time—240 min, concentrations of H_2SO_4 —1.5 M and H_2O_2 —1 M, and a concentration of solid phase of 2 gdm^{-3} is shown in Table 3. As can be seen in Table 3, the zinc, copper, and iron content in the residue decreases, while the lead content increases. This confirms that in the leaching process, copper, zinc, and iron dissolve, while lead in the form of poorly soluble anglesite remains in the residue. The sulfur content is increased, which confirms that the part of the sulfide sulfur oxidized to its elemental form.

Table 3. Chemical composition of the leach residue.

Mass of the Leach Residue (g)	Content (%)				
	Cu	Zn	Pb	Fe	S
0.38	21.80	0.14	4.95	20.12	41.34

The XRD analysis of the leach residue is shown in Figure 7. The presence of chalcopyrite and elemental sulfur as the major phases was determined.

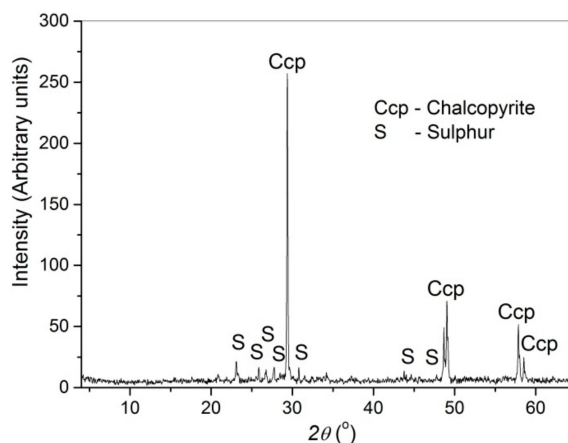


Figure 7. X-ray diffraction analysis of the leach residue sample.

The leach residue was analyzed using light microscopy, and mineral composition is shown in Table 4; the total sulfides content was 64.8%, with liberated sulfide grains of about 87% and liberate chalcopyrite grains of about 89%.

Table 4. Mineral composition of leach residue.

Mineral	Mass %
Chalcopyrite	63.002
Sphalerite	0.222
Galena	0.417
Pyrrhotite	1.215
Anglesite	6.754
Elemental sulfur	18.887
Quartz	9.503
Total:	100.000

The reflected light microscopic examination of leach residues is shown in Figure 8. The leach residue obtained at 25 °C, as seen from Figure 8a, displays corroded chalcopyrite grains and elemental sulfur crystals, while the leach residue obtained at 40 °C as seen from Figure 8b only contains elemental sulfur.

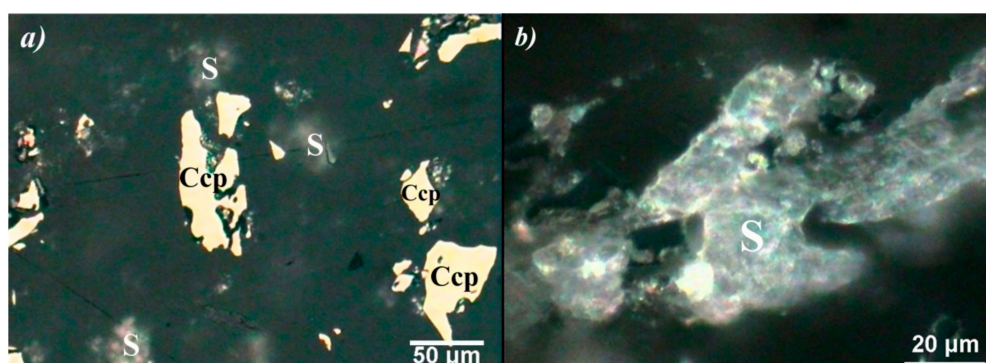


Figure 8. Optical micrograms of the leach residue for different temperatures of leaching (particle size—37 μm, stirring speed—100 rpm, time—240 min, solid/liquid ratio—2 g/dm³, —1.5 M H₂SO₄, —1 M H₂O₂): (a) temperature 25 °C, (b) temperature 40 °C.

3.6. Leaching Kinetics

The process of copper leaching from chalcopyrite concentrate with H₂SO₄ + H₂O₂ solution is a complex heterogeneous process. The kinetic model applied for linearization of the experimental

results was selected based on Sharp’s method, including the reduced reaction half time [19,50,58,59]. The reduced reaction half time is given in Equation (4):

$$F(\alpha) = A(\tau/\tau_{0.5}) \tag{4}$$

where: α is the extraction degree, τ is the extraction time, $\tau_{0.5}$ is the time required to reach $\alpha = 50\%$, while constant A depends on a function $F(\alpha)$. For the isotherms presented in Figure 4, it is possible to determine the values of the reaction half time and time for different copper extraction yields for each temperature. According to the data obtained by such an analysis, the experimental results ($\tau/\tau_{0.5}$) and values for different kinetic models may be compared, as shown in Figure 9.

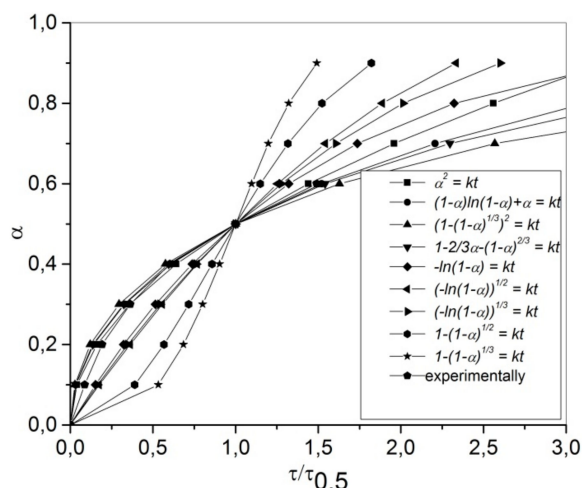


Figure 9. Selection of the kinetic model for linearization of the experimental results.

From Figure 9 it can be seen that the experimental data could be approximated with values that are presented by the kinetic Equation (5)

$$\alpha^2 = kt \tag{5}$$

where k is the rate constant and t is the reaction time. This kinetic model is used for a description of the process controlled by diffusion. The rate of reaction may be limited by diffusion of the reactants through the sulfur layer, precipitated at the surfaces of the particles.

In order to determine the activation energy, Equation (5) was used for the linearization of the kinetic curves from Figure 4. The variation in $\alpha^2 = kt$ with time at different temperatures is shown in Figure 10.

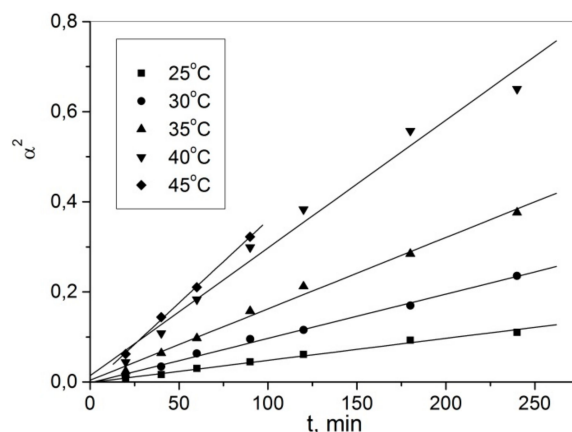


Figure 10. The plot of α^2 vs time for Cu extraction at different temperatures.

The activation energy was calculated from the slopes of the lines in Figure 10; for the chalcopyrite oxidation in the $\text{H}_2\text{SO}_4\text{-H}_2\text{O}_2\text{-H}_2\text{O}$ system, activation energy is 80 kJ/mol (Arrhenius equation $k = A \cdot e^{-E_a/RT}$ was used—Figure 11).

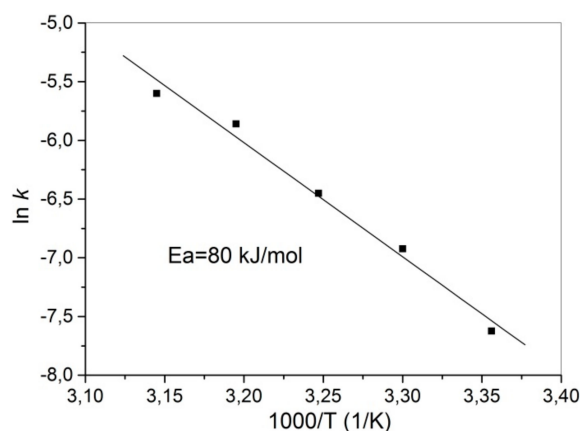


Figure 11. Arrhenius plot of the chalcopyrite oxidation in the $\text{H}_2\text{SO}_4\text{-H}_2\text{O}_2\text{-H}_2\text{O}$ system.

Relatively high activation energy suggests that the chemical surface reaction might control the kinetics of the reaction. At the same time, some of the reported results indicate high activation energy in the reactions controlled by the diffusion mechanism [3,60].

Considering that the experimental data obtained at the temperature range from 25–45 °C best fit to the linearization equation $\alpha^2 = kt$; it can be concluded that the rate of the chemical reaction was most likely controlled by diffusion of reactants through the compact layer of the elemental sulfur. The chemical surface reaction mechanism is probably important only throughout the initial stages of the process.

Other authors also confirmed the existence of elemental sulfur at the surface of the leach residue. Thus, Misra and Fuerstenau [43], and Mahajan et al. [51] have shown that most sulfide sulfur is transformed into its elemental form. Also, Antonijevic et al. [42] confirmed the presence of elemental sulfur in the leach residue and found an activation energy value of 59 kJ/mol, using a kinetic model for the process controlled by chemical reaction. Unlike them, Olubambi and Potgeiter [44] proved that elemental sulfur on the mineral surface was oxidized by hydrogen peroxide to sulfates, which increased the permeability of the passivation layer and thus promoted oxidation of the chalcopyrite. Adebayo et al. [40] found that the dissolution kinetics follow a shrinking-core model, controlled by surface chemical reaction mechanism as the rate-determining step, and they have reported an activation energy value of 39 kJmol⁻¹. Hu et al. [50] examined chalcopyrite leaching with hydrogen peroxide in 1-hexyl-3-methyl-imidazolium hydrogen sulfate solution and found that the process was chemically controlled with an activation energy of 52 kJ/mol and with the formation of sulfur as the main leaching product located near unleached chalcopyrite. Similar results with a chemically controlled mechanism, activation energy of 39.9 kJ/mol, and elemental sulfur in the residues were obtained by Ahn et al. [49].

4. Conclusions

Chalcopyrite concentrate from the “Rudnik” polymetallic ore, containing 27.08% of copper can be effectively leached using the hydrogen peroxide, as an oxidant, in the sulfuric acid medium. The copper extraction yield increased with increasing sulfuric acid and hydrogen peroxide concentrations and with smaller particles. The maximal reaction rate was obtained with a stirring speed of 100 rpm. Copper extraction yield increased with temperatures up to 40 °C; after that, the yield begins to decline due to the decomposition of hydrogen peroxide at higher temperatures. The highest yield of copper, 97.69% was obtained under the following conditions: particle size 100% –37 μm, temperature of 40 °C, leaching time of 240 min, stirring speed of 100 rpm, concentrations of H_2SO_4 1.5 M and H_2O_2 2.0 M, and a concentration of solid phase at 2 gdm⁻³. The kinetic data for the copper leaching process show a good

fit for the model controlled by diffusion, and the rate of reaction controlled by the lixiviant diffusion through the sulfur layer. This sulfur layer is formed as the reaction product during the leaching process. The calculated activation energy value is 80 kJ/mol. The formation of elemental sulfur was confirmed by XRD and mineralogical analysis, showing sulfur precipitation at the particle surfaces.

Author Contributions: Conceptualization, M.S. and B.M.; methodology, M.S. and V.M.; formal analysis, S.S., N.Š. and V.M.; investigation, M.S., N.P. and B.M.; writing—original draft preparation, S.S.; writing—review and editing, M.S. and Ž.K.; visualization, B.M. and V.M.; supervision, M.S. and Ž.K.; project administration, M.S. and B.M.

Funding: This work was realized in the frame of projects TR 34023 and TR 34033, supported by the Ministry of Education, Science and Technological Development of the Republic of Serbia.

Conflicts of Interest: The authors declare no conflict of interest.

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