

KINETICS AND MECHANISM OF SPHALERITE LEACHING BY SODIUM NITRATE IN SULPHURIC ACID SOLUTION

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Abstract

Interest for application of hydrometallurgical processes in a processing of complex sulphide ores and concentrates has increased in recent years. Their application provides better metal recoveries and reduced emission of gaseous and toxic ageneses in the environment. The kinetics and mechanism of sphalerite leaching from complex sulphide concentrate with sulphuric acid and sodium nitrate solution at standard conditions was presented in this paper. The influences of temperature and time on the leaching degree of zinc were investigated and kinetic analysis of the process was accomplished. With temperature increasing from 60 to 90°C, the zinc leaching increased from 25.23% to 71.66% after 2 hours, i.e. from 59.40% to 99.83% after 4 hours. The selected kinetic model indicated that the diffusion through the product layer was the rate-controlling step during the sphalerite leaching. The activation energy was determined to be 55 kJ/mol in the temperature range 60-90°C. XRD, light microscopy and SEM/EDX analyses of the complex concentrate and leach residue confirmed formation of elemental sulphur and diffusion-controlled leaching mechanism.

Keywords: sphalerite leaching, sodium nitrate, sulphuric acid, kinetics, mechanism

1. Introduction

Sphalerite is the most important zinc sulphide minerals. It is commonly associated

with other sulphide minerals, such as chalcopyrite, galena and pyrite, in disseminated form with complex mineralogical composition and fine-grained

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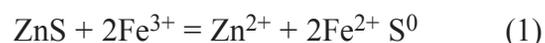
structures. Both pyrometallurgical and hydrometallurgical processes are applied for processing zinc sulphide ores and concentrates. The conventional methods usually follow roasting-leaching and electrowinning steps. regulation on discharge of sulphur dioxide becomes more and more strict, hydrometallurgical processes of direct leaching of sulphide ores and concentrates becomes more attractive. The preferences of direct leaching are the treatment low grade materials, the increase of metal recoveries and conversion of sulphide sulphur to elemental form, which remains in the leach residue, thus thoroughly eliminating discharge of sulphur dioxide into the atmosphere. On the other hand, elemental sulfur formed as the main leaching product precipitates at the particle surfaces and tends to inhibit the reaction rate [1-5].

The presence of iron in sphalerite mineral has a significant influence on dissolution rate. Kammel et al. [6] and Crundwell [7] reported that the dissolution rate of sphalerite was directly proportional to the concentration of substitutional iron impurity in the solid. Palencia Perez and Dutrizac [8], noticed that the sphalerite leaching rate increases and the activation energy decreases with increasing iron content in sphalerite structure. At the sphalerite leaching with 0.04 wt. % of iron by ferric chloride, the activation energy was about 70 kJ / mol, while the sphalerite leaching with 12.5 wt.% of iron, activation energy was about 40 kJ / mol. The presence of 5% galena in sphalerite concentrate decreases the leaching rate of zinc up to 13%, while the presence of 10% pyrite increases zinc dissolution [9]. On the other hand, Souza et al. [10], suggested that

the iron content has small affect on the leaching kinetics of the silicate concentrate by sulphuric acid.

Ferric and cupric ions, bacteria, oxygen, and other oxidants have been used as leaching agents of sphalerite in sulphate and chloride media under atmospheric or pressure leaching conditions.

Ferric ion, in either sulphate or chloride media, can be used to leach sphalerite, according to the reaction [2, 11, 12]:

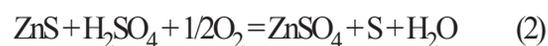


Oxidizing agents such O_2 or H_2O_2 may be used for oxidation of ferrous ions formed through reaction 1 [12,13].

Cheng et al. [14] leached zinc sulphide concentrate in a solution of ferric sulphate, sulphuric acid and sodium chloride. The dissolution process was limited by electrochemical reaction until 60-70% conversions, after which the formed sulfur layer was limited the rate of reaction.

Atmospheric leaching of a sphalerite concentrate in sulphate and chloride media was studied by Santos et al. [12]. The results showed that using a solid /liquid ratio of 5% (w/v) it was possible to leach 95% of zinc after 2 h, at 80°C. The oxidation of Fe(II) by H_2O_2 during the leaching was studied and improvement of 20% zinc extraction was observed.

Oxygen pressure leaching, at high temperatures, in sulphuric acid have been reported in several publications [15-18], and it is represented by the following chemical reactions:



Habashi [16] studied the mechanism of sphalerite oxidation process and found that

the dissolution rate is independent of oxygen pressure in the low sulphuric acid concentrations, but only on the concentration of sulphuric acid. For the higher concentrations of sulphuric acid the dissolution rate depends only on the oxygen pressure.

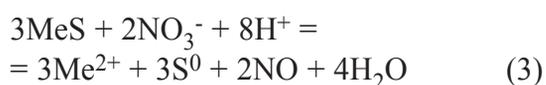
During the pressure leaching, the leach temperatures were limited to below the melting point of sulphur, because molten sulphur would encapsulate unleached sulphide and limit dissolution. The certain surface-active reagents inhibited the molten sulphur from sulphide particles and allowed leaching at temperatures above the melting point of sulfur [19]. The Additive was lignin sulphionate; zinc extractions increased to 96-98%. Li et al. [18] investigated oxygen pressure leaching process of sphalerite concentrate in sulphuric acid in the addition of sodium lignosulfonate lignin. The leaching of 99% zinc was achieved from the concentrate under oxygen partial pressure of 800 kPa at leaching temperature of 150°C for 2h, and the amount of sulphide sulphur oxidized to sulphate during leaching of 81%.

Babu et al. [20] investigated oxidative leaching of sphalerite with ammonium persulphate in sulphuric acid media. They achieved of 95% zinc extraction at a temperature of 60°C for 5 h in the presence of 20% (w/v) ammonium persulphate.

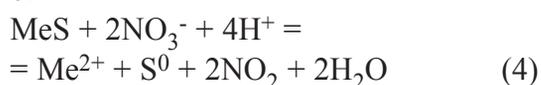
Nitrate ion, due to their high oxidation potential, can be used as an oxidant for leaching sulphide minerals by sulfuric acid [21-22]. Habashi [21], indicated that metal sulphide oxidation by nitric acid can be achieved in two ways. In the first case, NO ion is the oxidant, and during the reaction it is reduced to NO or NO₂. In the second case,

oxygen that arises from nitric acid decomposition is the oxidant.

Oxidative dissolution of a sulphide concentrate using nitrate as an oxidant in sulphuric acid solution takes place with formation of elemental sulphur, and it can be represented by one of the following chemical reactions [23-27]:



or



A small part of the sulphide sulfur, under certain conditions, is oxidized to sulfate [28].

Peng et al. [27], were studied the enhanced leaching of sphalerite concentrate in H₂SO₄-HNO₃ solutions and the extraction of sulphur with tetrachloroethylene. The zinc extraction without C₂Cl₄ was 70.1 % after one hour, and 99.2 % after six hours of leaching. In the presence of C₂Cl₄, zinc extraction reached 88.2 % after one hour, and 99.6 % after three hours of leaching. As a result, leaching rates significantly improved in the presence of C₂Cl₄. The rate of reaction was predominantly controlled by diffusion in the leaching process without C₂Cl₄.

The dissolution mechanism of sphalerite is based on three main kinetic models. These kinetic models are diffusion controlled, surface reaction controlled, and a mixed kinetic model containing diffusion and surface reaction components, which simultaneously take place.

In this paper, chemical, XRD, light microscopy, and SEM/EDX analysis were used to determine the characteristics of the samples of complex concentrate and leach residue. Also, the kinetics of sphalerite

leaching from complex concentrate by sodium nitrate in sulphuric acid was studied.

2. Experimental

2.1. Materials

The complex concentrate enriched through the flotation of a $\text{CuFeS}_2\text{-PbS-ZnS}$ complex ore in the "Rudnik" flotation plant (Rudnik – Serbia) was used in this study. It was wet sieved to obtain the particle size distribution. Sodium nitrate and sulphuric acid of analytical grade and distilled water was used to make up all required solutions. Analytical grade chemicals were used for analysis.

2.2. Leaching procedure

Leaching experiments were carried out in a closed glass reactor equipped with a Teflon stirrer, condenser, thermometer, glass funnel for adding the solid sample and a sampling device. This set-up provides stable hermetic conditions and allows heating at constant temperature. The 1.2 dm^3 of leaching solution ($\text{NaNO}_3 + \text{H}_2\text{SO}_4$) was added to the glass reactor and heated-up to the selected temperature. When the temperature was reached, the 20 g of solid concentrate was added. The stirring started and the reaction commenced. After selected time intervals, the solution samples were taken for chemical analysis, which was carried out by AAS (Perkin Elmer). The samples were chemically analyzed for the zinc content and degree of zinc extraction was calculated. The leach residues were filtered, washed with distilled water, and dried. The phase content of complex

concentrate and leach residue were determined by XRD using diffractometer (PHILIPS PW-1710), reflected light microscopic (Carl Zeiss-Jena, LENAPOL-U) and SEM-EDX (JEOL equipped with software package PAX). The leaching reaction was studied with the help of XRD, light microscopy and SEM-EDX.

3. Results and discussion

3.1. Characterization of complex concentrate

The particle size distribution and chemical analysis of the concentrate and each size fraction is shown in Table 1. The major amount (52.4%) of the concentrate was of very small particles ($-45 \mu\text{m}$), while the fraction $+75 \mu\text{m}$ was in minor amount (9.4%). The zinc, copper, lead and iron content in different fractions were similar.

Table 1. Chemical composition of different fractions of complex concentrate

Particle size (μm)	Fraction (wt.%)	Element (%)			
		Zn	Cu	Pb	Fe
Mixed particle	-	8.79	8.92	12.66	19.8
75	9.4	7.85	7.42	13.26	19.41
$-75 + 50$	16.4	8.93	9.18	10.75	19.96
$-50 + 37$	21.8	9.27	9.53	11.03	20.03
-37	52.4	8.83	8.99	12.56	19.78

The X-ray diffraction analysis of the concentrate sample (Figure 1) shows the presence of sphalerite, chalcopyrite, galena, pyrrhotite, and quartz.

The mineralogical qualitative and quantitative analysis of complex concentrate was realized using a reflected light

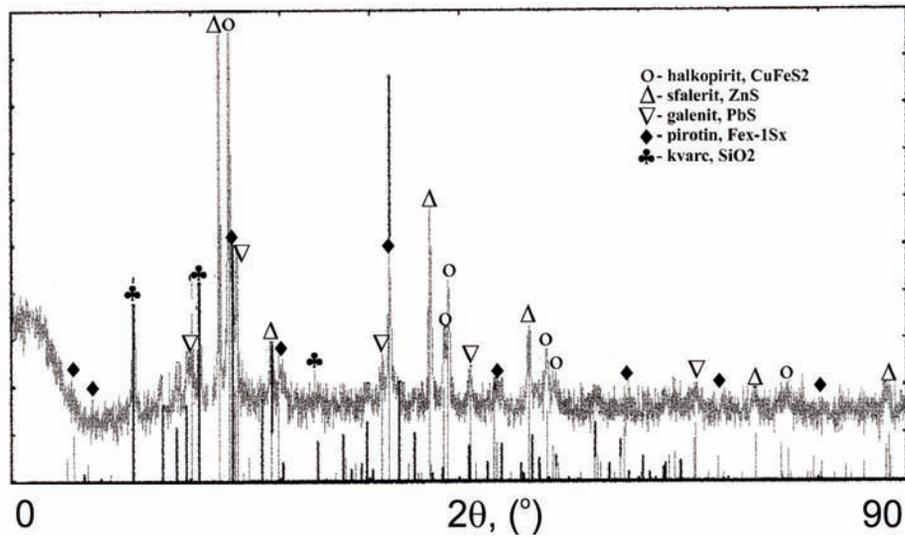


Figure 1. X-ray diffractogram of the complex concentrate

microscopy and was given in Table 2. The correction of quantitative mineralogical analysis was obtained through the chemical analysis of Cu, Zn and Pb. The sulphide volume content in whole sample is 69.5 %, in which 60.9 % are sulphide-liberated grains.

The main and most abundant zinc sulphide mineral is sphalerite (13.01 %). It

Table 2. Mineralogical composition of complex concentrate

Mineral	Wt. (%)
Chalcopyrite	25.62
Sphalerite	13.01
Galena	14.62
Pirrotite	15.7
Marcasite	0.25
Arsenopyrite	0.15
Sulfosalts Pb-Bi	0.07
Covellite	0.02
Native bismuth	0.04
Tetrahedrite	0.03
Limonite	0.03
Gangue minerals	30.47
Total:	100

appears in a form of liberated grains in some 59 %. The rest mineral grains of sphalerite are mostly in a form of concretions, simple and complex intergrowths.

The SEM image of complex concentrate is shown in Fig. 2. The EDX analysis of complex concentrate for marked area in SEM micrograph presented in Fig. 2 shows a presence of sphalerite grains with high content of iron (Zn – 55.49%, Fe – 11.43% and S – 33.08%).

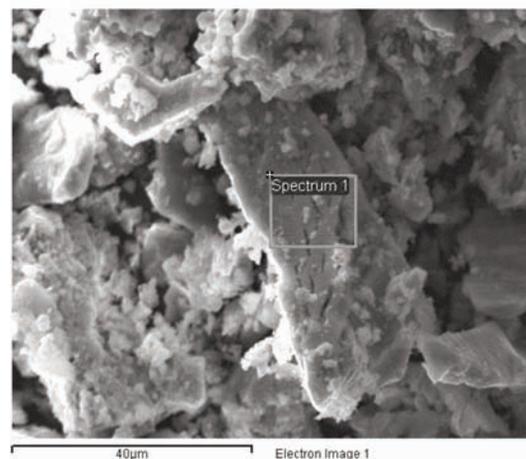


Figure 2. SEM micrograph of complex concentrate

3.2. Effect of temperature and time

The influence of the temperature and time on the dissolution rate of sphalerite in the temperature range of 60 to 90°C, and during the time intervals of 60 to 240 min, under optimal following conditions: stirring speed 300 rpm, particle size – 37 µm, 1.5 M H₂SO₄, 0.6 M NaNO₃, and phase ratio 20 g concentrate/1.2dm³, was presented in Figure 3. Leaching degrees were calculated based on the results of chemical analysis of the solutions and the leach residues.

The temperature and time has a significant influence on the leaching rate. As expected, zinc dissolution increases with increasing the temperature and time. By increasing the temperature from 60 to 90°C, the dissolution rate increases from 25.23% to 71.66% after 2 hours, i.e. from 59.40% to 99.83% after 4 hours of leaching. A significant slowing down on the leaching rate in the final stage of leaching was noted.

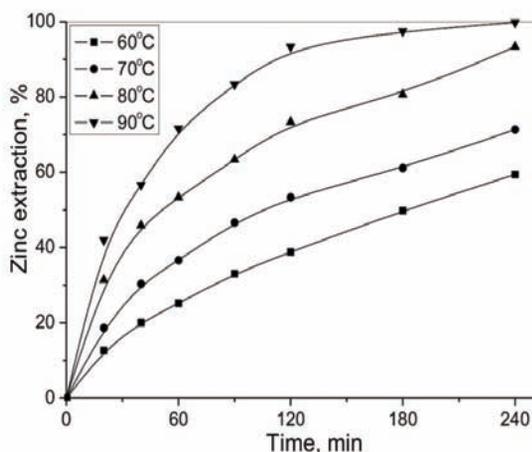


Figure 3. Effect of temperature and time on zinc extraction (stirring speed = 300 rpm, particle size – 37 µm, [H₂SO₄] = 1.5 M, [NaNO₃] = 0.6 M, phase ratio 20 g/1.2dm³)

The reason for this was elemental sulphur, formed during the process, precipitated at the particle surfaces.

3.3. Kinetic analysis

The process of zinc sulphide leaching by H₂SO₄ + NaNO₃ solution is a complex heterogeneous process. In order to determine the kinetic parameters and the rate-controlling step of the sphalerite leaching process, Sharps's method of reduced half time of reaction was used to select the kinetic models [25, 29-32]

$$F(x) = A \times (t/t_{0.5}) \quad (5)$$

where x is the degree of reaction, $t_{0.5}$ is the time to reach $x = 50\%$, and constant A depends on a function $F(x)$.

It is possible to determine values of the reaction half time and time for different degrees of leaching for each temperature, for the isotherms in Fig. 3. Therefore, the values of $(t/t_{0.5})$ for different kinetic models can be compared with the values of the experimental results to get the best kinetic function for linearization of the results [25, 31]. For the extraction of zinc, the experimental curve is closest to the function:

$$x^2 = k \cdot t \quad (6)$$

where k is the rate constant, t is the reaction time.

This kinetic model is used for a description of diffusion-controlled processes. The rate of reaction may be limited by diffusion of the reactants through the sulphur layer, precipitated on the particle surfaces.

In order to determine the activation energy, Eq. (6) was applied to the data

obtained from each temperature for zinc leaching in Fig. 3. The variation in $x^2 = k \cdot t$ with time at different temperatures is shown in Fig. 4. The activation energy of 55 kJ/mol was calculated using the Arrhenius equation $k = A \cdot e^{-Ea/RT}$ from the slopes of the straight lines in Fig. 4, as shown in Fig. 5.

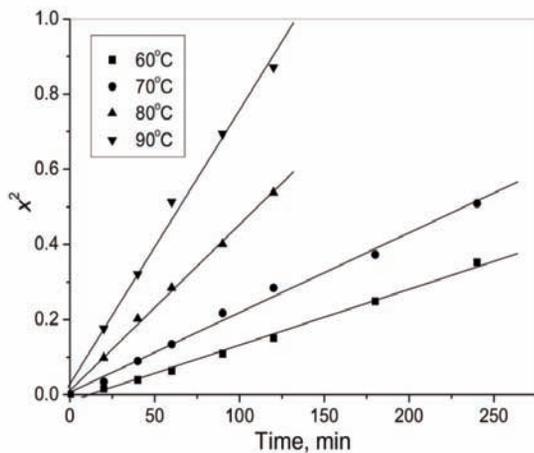


Figure 4. Plot of x^2 vs time for zinc extraction

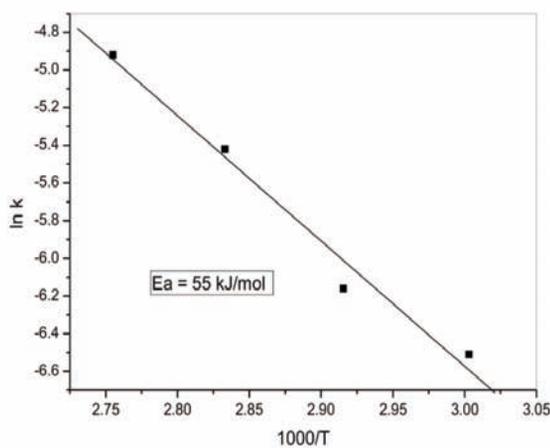


Figure 5. Arrhenius plot for zinc extraction

Various investigators were found the similar values of activation energy for the sphalerite leaching. Babu et al. [20] leached

sphalerite with ammonium persulphate in sulphuric acid media. The activation energy was 41 ± 2 kJ/mol in the temperature range $35\text{-}60^\circ\text{C}$, and the diffusion through the product layer was the rate-controlling step.

Lochmann and Pedlik [4] leached sphalerite concentrate with acidic ferric sulphate solution and found that the elemental sulphur layer controlled the dissolution rate.

Bobeck and Su [33] obtained the activation energy of 46.9 kJ/mol for sphalerite leaching in ferric chloride solution. During the initial stages of leaching the rate of reaction was chemically controlled and later, transport of ions across the product sulphur layer determined the reaction rate. Similar values of activation energy of 45.3 kJ/mol were determined Aydogan et al. [11], but they were found that the sphalerite dissolution in acidic ferric chloride solution controlled by the shrinking core model for reaction-controlled process. Aydogan [34], also investigated the kinetics of sphalerite leaching with hydrogen peroxide in sulphuric acid, and found that the leaching rate controlled by surface reaction. The value of activation energy was 43 kJ/mol.

3.4. Characterization of the leach residue

The leach residue, obtained at 80°C under the following conditions: stirring speed 300 rpm, 1.5 M H_2SO_4 , 0.6 M NaNO_3 , 20 g concentrate/ 1.2 dm^3 and 240 min, was chosen for chemical, X-ray, qualitative and quantitative mineralogical analyses and SEM/EDX analyses. A chemical analysis of the leach residue is shown in Table 3.

Table 3. Chemical composition of the leach residue

Mass of the leach residue (g)	Element (%)				
	Zn	Cu	Fe	Pb	Elemental S
11,78	1,96	3,57	10,75	19,75	17.02

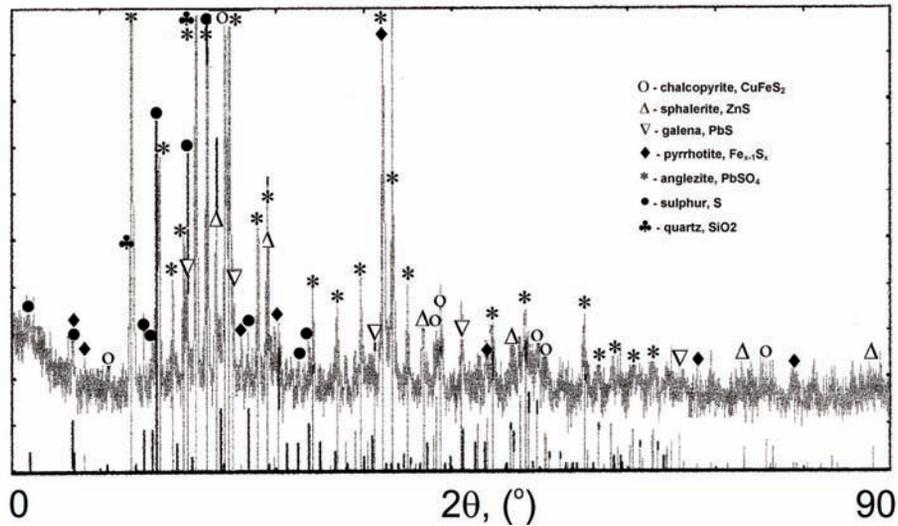


Figure 6. X-ray diffractogram of the leach residue: $T = 80^{\circ}\text{C}$, $t = 240 \text{ min}$, stirring speed = 300 rpm, $[\text{H}_2\text{SO}_4] = 1.5 \text{ M}$, $[\text{NaNO}_3] = 0.6 \text{ M}$, phase ratio 20 g/1.2dm³

The X-ray diffraction analysis of the leach residue is presented in Figure 6. Along with the unreacted minerals, the presence of elemental sulphur and anglesite were detected.

The qualitative and quantitative mineralogical analysis of the leach residue was realized using a reflected light microscopy and was given in Table 4. The main components in the residue are elemental sulphur and anglesite, while the content of sphalerite, chalcopyrite and galena are decrease. The elemental sulphur is the oxidized product of sulphide sulphur, precipitated on the surface of concentrate particles. In mineral grains, anglesite is present together with galena, in which the central parts filled with galena, while anglesite precipitated on the surface. The

sulphide volume content is 31.7 %, in which 37.9 % are sulphide-liberated grains. The sphalerite appears in a form of liberated grains in some 21.8 %. The rest mineral grains of sphalerite are mostly in a form of concretions, simple and complex intergrowths.

Table 4. Mineralogical composition of the leach residue.

Mineral	Wt. (%)
Chalcopyrite	10,32
Sphalerite	3,11
Galena	6,40
Pirrhote	11,86
Anglesite	20,86
Elemental sulphur	17,02
Gangue minerals	30,43
Total	100,00

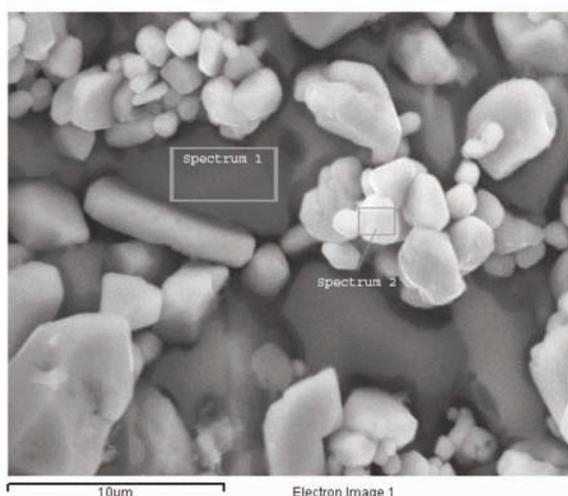


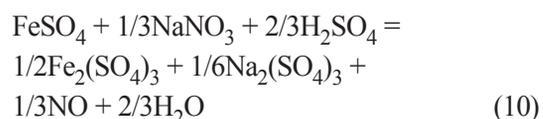
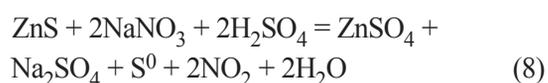
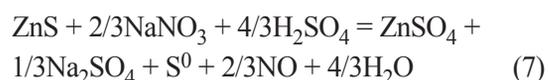
Figure 7. SEM micrograph of the leach residue: $T = 80^{\circ}\text{C}$, $t = 240$ min, stirring speed = 300 rpm, $[\text{H}_2\text{SO}_4] = 1.5$ M, $[\text{NaNO}_3] = 0.6$ M, phase ratio 20 g/1.2dm³

The SEM image of the leach residue is shown in Fig. 7. The EDX analysis of complex concentrate for marked areas on SEM micrograph presented in Fig. 2 show a presence of compact elemental sulphur (S – 100%) (area 1) and anglesite (Pb – 50.62%, S – 16.03%, O – 33.34%) (area 2) on the surface of sphalerite and other mineral particles, which inhibit their dissolution. The morphology of the leach residue implies that the sphalerite leaching proceeds by the diffusion of lixiviant through the sulphur reaction product.

3.5. Dissolution process

X-ray diffraction, qualitative and quantitative mineralogical analyses and SEM/EDX analyses of the residue indicates that the sulphur, which formed during the reaction, precipitated at the particle surfaces, and slowed down of the leaching rate in the

final stage of leaching. From these results and literature data it seems as if the dissolution process can be represented by one of the following chemical reactions:



The NO to NO₂ ratio in gaseous products and the elemental sulphur to sulphate ratio after leaching depend on the concentration of the nitrate ion [28]. NO gas that is produced is oxidized by the air into the NO₂, which dissolves in the solution and reacts with water to form HNO₃. Elemental sulphur is the main product of reaction, and a minor amount of sulphide sulphur is oxidized to sulphate during leaching. Iron is oxidized to form ferric sulphate in the high content of nitrates, which then acts as a leaching agent. A low concentration of nitrates does not result in noticeable acceleration of high temperature ferrous oxidation in a sulphuric acid solution [35].

4. Conclusion

The leaching kinetics and mechanism of sphalerite from complex concentrate, enriched through the flotation of a CuFeS₂-PbS-ZnS complex ore in the “Rudnik” flotation plant, by sulphuric acid and sodium nitrate was studied and discussed. It was determined that the leaching rate increased

with increasing temperature and time. A temperature increase from 60 to 90°C was accompanied by an increase in leaching degree from 25.23% to 71.66% after 2 hours, i.e. from 59.40% to 99.83% after 4 hours of leaching.

Experimental data, chemical, XRD, light microscopy and SEM/EDX analyses for the phases present in both the complex concentrate and leach residue were performed to determine the mechanism of the leaching process. The main phases in the leach residue are elemental sulphur, anglesite, unreacted pirrhotite, chalcopyrite, galena, and small amount of undissolved sphalerite.

The kinetic study showed that the leaching rate was controlled by diffusion of lixiviant through the sulphur layer, precipitated at the particle surfaces. The activation energy was calculated to be 55 kJ/mol.

The characterization of the leach residue with the help of XRD, light microscopy and SEM/EDX confirmed formation of elemental sulphur and diffusion-controlled leaching mechanism.

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