Synthetic Sulfide Concentrate Dissolution Kinetics in HNO\textsubscript{3} Media

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Abstract: The nature of tennantite (Cu\textsubscript{12}As\textsubscript{4}S\textsubscript{13}), chalcopyrite (CuFeS\textsubscript{2}) and sphalerite (ZnS) particles’ mixture dissolution in nitric acid (HNO\textsubscript{3}) media was investigated in this study. The effects of temperature (323–368 K), HNO\textsubscript{3} (1–8 mol/L) and Fe\textsuperscript{3+} (0.009–0.036 mol/L) concentrations, reaction time (0–60 min) and pyrite (FeS\textsubscript{2}) additive (0.5/1–2/1; FeS\textsubscript{2}/sulf.conc.) on the conversion of the minerals were evaluated. It has been experimentally shown that the dissolution of the mixture under optimal conditions (>353 K; 6 mol/L HNO\textsubscript{3}; FeS\textsubscript{2}/synt. conc = 1/1) allows Cu\textsubscript{12}As\textsubscript{4}S\textsubscript{13}, CuFeS\textsubscript{2} and ZnS conversion to exceed 90%. The shrinking core model (SCM) was applied for describing the kinetics of the conversion processes. The values of \(E_a\) were calculated as 28.8, 33.7 and 53.7 kJ/mol, respectively, for Cu\textsubscript{12}As\textsubscript{4}S\textsubscript{13}, CuFeS\textsubscript{2} and ZnS. Orders of the reactions with respect to each reactant were calculated and the kinetic equations were derived to describe the dissolution rate of the minerals. It was found that the interaction between HNO\textsubscript{3} solution and Cu\textsubscript{12}As\textsubscript{4}S\textsubscript{13}, CuFeS\textsubscript{2} and ZnS under the conditions investigated in this study are of a diffusion-controlled nature. Additionally, the roles of Fe(III) in the initial solution and FeS\textsubscript{2} in the initial pulp as catalysts were studied. The results indicated that the increase in Fe\textsuperscript{3+} concentration significantly accelerates the dissolution of the mixture, while the addition of FeS\textsubscript{2} forms a galvanic coupling between FeS\textsubscript{2} and Cu\textsubscript{12}As\textsubscript{4}S\textsubscript{13} and CuFeS\textsubscript{2}, which also accelerates the reaction rate. The results of the study are considered useful in developing a hydrometallurgical process for polymetallic sulfide raw materials treatment.

Keywords: leaching; nitric acid; tennantite; chalcopyrite; sphalerite; pyrite; sulfide minerals; kinetics; ion concentration; catalyst; galvanic coupling; mechanism

1. Introduction

Intensive exploitation of the primary raw materials in the non-ferrous metals industry resulted in the depletion of the rich deposits as a consequence of seeking alternative sources of raw materials. In view of the current trend in decreasing the metal content in the ore, smelters adapt to lower grade and technogenic raw materials [1]. One of the most specific raw material types are arsenic-containing ores and concentrates since their treatment is associated with additional environmental risks and technological complexity. Thus, along with the familiar minerals in copper industry such as chalcopyrite (CuFeS\textsubscript{2}), covellite (CuS), chalcocite (Cu\textsubscript{2}S), bornite (Cu\textsubscript{5}FeS\textsubscript{4}) and sphalerite (ZnS), sulfide ores occasionally contain minerals of the Fachlor group, such as tennantite (Cu\textsubscript{12}As\textsubscript{4}S\textsubscript{13}) and tetrahedrite (Cu\textsubscript{12}Sb\textsubscript{4}S\textsubscript{13}), which complicates the processing of the obtained ore/concentrates using typical approaches [2].

Pyrometallurgical processing of the arsenic-containing raw materials admits releasing arsenic dust and other waste into the atmosphere, which poses a significant danger to humans and the environment [3–12]. Therefore, pyrometallurgical processing of such materials is considered unacceptable today, and hence, undergoes strict government regulation in the most countries.
As an alternative to conventional smelting, various hydrometallurgical approaches are currently being researched, including the following: acid [13–15] and ammonia leaching [16], alkaline [17–19] and autoclave approaches [20–22], bioleaching [23,24], etc. Although autoclave approaches have been known since the middle of the last century and have found success and wide application for gold–silver sulfide raw materials treatment [25], atmospheric systems are also of great interest in hydrometallurgy [26].

One of the most promising approaches in this direction is an application of nitric acid (HNO$_3$) as a reactant for atmospheric leaching, since HNO$_3$ allows the most complete decomposition of the sulfide matrix [27,28]. Thus, HNO$_3$ leaching under optimal conditions could provide both the transference of valuable metals into solution and arsenic and other toxic elements into stable and environmentally friendly compounds [29–33].

This study is aimed at evaluating the fundamental effectiveness of sulfide low-grade raw-materials treatment using HNO$_3$ as the reactant for atmospheric leaching and also at evaluating the kinetic characteristics of the dissolution processes. High-purity specimens of Cu$_{12}$As$_4$S$_{13}$, CuFeS$_2$ and ZnS were used in this study to create the mixture of sulfides (synthetic concentrate), which was subjected dissolution in HNO$_3$ media. The choice of these minerals was for the purpose of creating the most refractory raw materials through hydrometallurgical treatment.

The shrinking core model (SCM) was applied for describing the kinetics of the dissolution processes. The effects of temperature, reaction time and HNO$_3$ concentration on the conversion of the minerals were evaluated. We also evaluated the effect of the pyrite (FeS$_2$) additive and the Fe$^{3+}$ concentration in the initial solution, since a number of studies reported [34–44] using the mentioned reactants as catalysts.

The results of the study are considered useful in developing hydrometallurgical processes for polymetallic sulfide raw-materials treatment.

2. Materials and Methods

2.1. Materials

High-purity specimens of Cu$_{12}$As$_4$S$_{13}$, CuFeS$_2$, ZnS and FeS$_2$ originating from the Uchalinskii deposit (Sverdlovsk region, Russia), the Vorontsovskii deposit (North Ural region, Russia), the Karabashskii deposit (South Ural region, Russia) and the Berezovskii deposit (Sverdlovsk region, Russia), respectively, were used in this study (Figure 1A–D). The samples for experiments were obtained from the ground crystals by wet sieving (20–40 µm), following the mixing of Cu$_{12}$As$_4$S$_{13}$, CuFeS$_2$ and ZnS in the proportion of 1/0.36/0.17 (by weight). The obtained mixture represented the sulfide concentrate of the complex composition (Table 1). The established ratio of the minerals in synthetic concentrate is typical for the industrial Cu-As concentrate of the Uchalinskii deposit [44]. An additive of FeS$_2$ into the leaching pulp was used in the study to evaluate the galvanic effect between FeS$_2$, Cu$_{12}$As$_4$S$_{13}$ and CuFeS$_2$.

2.2. Experimental Procedure

The dissolution of the synthetic concentrate in HNO$_3$ solution was conducted in a 500 mL round-bottom borosilicate glass reaction vessel (Lenz Laborglas GmbH & Co. KG, Wertheim, Germany) with a thermostatic jacket, which was thermostated using a Huber KISS-205B circulator (Huber Kältemaschinenbau AG, Offenburg, Germany). The reactor is equipped with an IKA EUROSTAR 20 digital overhead stirrer (IKA®-Werke GmbH & Co. KG, Staufen, Germany).

The values of the change in the Gibbs energy were calculated using the HSC Chemistry Software v. 9.9 (Metso Outotec Finland Oy, Tampere, Finland).
were determined based on wave dispersive spectrometry (ARL Advant’X 4200, Thermo Fisher Scientific, Waltham, MA, USA), X-ray diffraction “XRD” (XRD-7000, Shimadzu, Kyoto, Japan), scanning electron microscopy “SEM” (JSM-6390LV, Jeol, Tokyo, Japan) with a JED 2300 Energy Dispersive X-ray Analyzer (EDX) (Jeol, Tokyo, Japan), wet analysis and characterization. The solution samples received during the experiments as well as solutions at a temperature of 274 K at least for 1 h, weighed, and analyzed further for the residue characterization. The solution samples received during the experiments as well as solutions after filtration of the final pulp were subjected to volume measuring and analysis for Cu, Fe, As and Zn. The received data was used in calculating the fraction reacted (X) and the conversion (E, %) of the minerals with the following equations:

\[
X = \frac{m_s}{m_i} \quad (1)
\]

\[
E = \frac{m_s}{m_i} \times 100\% \quad (2)
\]

where \(m_s\) and \(m_i\) are the mass of As, Cu and Zn in solution after the treatment and the mass of As, Cu, Zn in the initial synthetic concentrate, respectively.

2.3. Analysis

The mineralogical and chemical compositions of the minerals and solid residues were determined based on wave dispersive spectrometry (ARL Advant’X 4200, Thermo Fisher Scientific, Waltham, MA, USA), X-ray diffraction “XRD” (XRD-7000, Shimadzu, Kyoto, Japan), scanning electron microscopy “SEM” (JSM-6390LV, Jeol, Tokyo, Japan) with a JED 2300 Energy Dispersive X-ray Analyzer (EDX) (Jeol, Tokyo, Japan), wet analysis
using inductively coupled plasma mass-spectrometry “ICP-MS” (Elan 9000, PerkinElmer, Waltham, MA, USA) and laser diffraction (Helos/BR, Sympatec, Clausthal-Zellerfeld, Germany). The solid materials were ground in a planetary mill (Pulverisette 6, Fritsch GmbH & Co. KG, Welden Germany) and dissolved in an aqua regia before ICP-MS analysis. The sulfur content was analyzed using a carbon/sulfur analyzer (CS 230, LECO, St. Joseph, MI, USA). Solution samples were analyzed by ICP-MS.

3. Results and Discussion

3.1. Effect of Temperature

Temperature range under investigation in this study was taken as 323–368 K, since previously published works [45] show a low conversion of sulfide minerals at ambient temperature. Thus, the chosen temperature range is of primary interest for the atmospheric leaching processes investigation.

Increasing the temperature seemed to have a significant effect on the conversion of Cu$_{12}$As$_4$S$_{13}$ (Figure 2a), CuFeS$_2$ (Figure 2b) and ZnS (Figure 2c). To illustrate, at 323 K for 60 min, only 65% of Cu$_{12}$As$_4$S$_{13}$, 45% of CuFeS$_2$ and 53% of ZnS were reacted, while at 368 K conversion increased to 96, 75 and 98%, respectively for Cu$_{12}$As$_4$S$_{13}$, CuFeS$_2$ and ZnS.

\[
E = \frac{m_s}{m_i} \times 100\% \quad (2)
\]

where $m_s$ and $m_i$ are the mass of As, Cu and Zn in solution after the treatment and the mass of As, Cu, Zn in the initial synthetic concentrate, respectively.

According to the conversion profiles, the progress of the reaction was observed to slow down with time. Additionally, the presence of a clear inflection line in curves allowed us to suggest an internal diffusion mechanism of the interactions. The possible internal diffusion

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Figure 2. Effect of temperature on the conversion of Cu$_{12}$As$_4$S$_{13}$ (a), CuFeS$_2$ (b), ZnS (c). (300 rpm; 6 mol/L HNO$_3$; 0.018 mol/L Fe (III); FeS$_2$/synt. conc. = 1/1).
may cause elemental sulfur formation during the processing of the synthetic concentrate by the following reactions:

\[
\begin{align*}
\text{CuFeS}_2 + 16\text{HNO}_3 &= \text{FeSO}_4 + \text{CuSO}_4 + 16\text{NO}_2 + 8\text{H}_2\text{O}; \Delta G^{0\text{353}} = -1187 \text{ kJ/mol}, \\
\text{CuFeS}_2 + 10\text{HNO}_3 &= \text{Fe(NO}_3)_3 + \text{Cu(NO}_3)_2 + 2\text{S}_0 + 5\text{NO}_2 + 5\text{H}_2\text{O}; \Delta G^{0\text{353}} = -438 \text{ kJ/mol}, \\
\text{Cu}_{12}\text{As}_4\text{S}_{13} + 64\text{HNO}_3 &= 12\text{Cu(NO}_3)_2 + 4\text{H}_3\text{AsO}_4 + 13\text{H}_2\text{SO}_4 + 40\text{NO} + 13\text{H}_2\text{O}; \Delta G^{0\text{353}} = -1866 \text{ kJ/mol}, \\
\text{Cu}_{12}\text{As}_4\text{S}_{13} + 38\text{HNO}_3 &= 12\text{Cu(NO}_3)_2 + 4\text{H}_3\text{AsO}_4 + 13\text{S}_0 + 14\text{NO} + 13\text{H}_2\text{O}; \Delta G^{0\text{353}} = -762 \text{ kJ/mol}, \\
\text{ZnS} + 8\text{HNO}_3 &= \text{ZnSO}_4 + \text{H}_2\text{SO}_4 + 8\text{NO}_2 + 4\text{H}_2\text{O}; \Delta G^{0\text{353}} = -640 \text{ kJ/mol}
\end{align*}
\]

3.2. Effect of HNO\textsubscript{3} Concentration

Figure 3 illustrates the effect of increasing the initial concentration of HNO\textsubscript{3} ranging from 1 to 8 mol/L on the conversion of Cu\textsubscript{12}As\textsubscript{4}S\textsubscript{13}, CuFeS\textsubscript{2} and ZnS. The increase in HNO\textsubscript{3} concentration seemed to also improve the rate and extent of the sulfides conversion. Over the reaction period, the conversion of Cu\textsubscript{12}As\textsubscript{4}S\textsubscript{13} (Figure 3a), CuFeS\textsubscript{2} (Figure 3b) and ZnS (Figure 3c) significantly increased from 35, 24 and 67%, respectively, at 1 mol/L HNO\textsubscript{3} in solution to 94, 81 and 98% at 8 mol/L HNO\textsubscript{3}.

![Figure 3](https://via.placeholder.com/150)

**Figure 3.** Effect of HNO\textsubscript{3} concentration on the conversion of Cu\textsubscript{12}As\textsubscript{4}S\textsubscript{13} (a), CuFeS\textsubscript{2} (b) and ZnS (c) (300 rpm; 353 K; 0.018 mol/L Fe (III); FeS\textsubscript{2}/synt. conc = 1/1).

The significant effect of HNO\textsubscript{3} concentration on the reaction rate and conversion extent may also indicate that the reactions are controlled by diffusion through the product layer, where the increasing HNO\textsubscript{3} concentration in the initial solution leads to acceleration of
3.3. Effect of Fe(III) Concentration

The effect of Fe (III) concentration ranging from 0.009 to 0.036 mol/L on the conversion of Cu$_{12}$As$_4$S$_{13}$, CuFeS$_2$ and ZnS was investigated. The results in Figure 4 show a moderate increase in the reaction rate by increasing the Fe (III) concentration. After 60 min of reaction at 0.009 mol/L Fe (III), 79, 65 and 91% of Cu$_{12}$As$_4$S$_{13}$ (Figure 4a), CuFeS$_2$ (Figure 4b) and ZnS (Figure 4c), respectively, were converted, compared with 90, 96 and 98% conversions, respectively at 0.036 mol/L. The interaction of main minerals in synthetic concentrate with Fe(III) are supposed to proceed according to the following reactions:

\[
\text{CuFeS}_2 + 2\text{Fe}_2(\text{SO}_4)_3 = \text{CuSO}_4 + 5\text{FeSO}_4 + 2\text{S}_0; \quad \Delta G^0_{353} = -65 \text{ kJ/mol}, \quad (8)
\]

\[
\text{ZnS} + \text{Fe}_2(\text{SO}_4)_3 = \text{ZnSO}_4 + 2\text{FeSO}_4 + \text{S}_0; \quad \Delta G^0_{353} = -56 \text{ kJ/mol} \quad (9)
\]

\[
\text{Cu}_{12}\text{As}_4\text{S}_{13} + 13.5\text{Fe}_2(\text{SO}_4)_3 + 6\text{H}_2\text{O} = 12\text{CuSO}_4 + 27\text{FeSO}_4 + 14.5\text{S}_0 + 4\text{H}_3\text{AsO}_3; \quad \Delta G^0_{353} = -28 \text{ kJ/mol} \quad (10)
\]
3.4. Effect of FeS$_2$ Additive

Four different mass ratios of FeS$_2$ to synthetic concentrate (0.5/1, 1/1, 1.5/1, 2/1, which is equal to 2.5, 5, 7.5 and 10 g of FeS$_2$ adding) were used in the experiments to examine the effect of galvanic coupling. The results are shown in Figure 5.

As expected, increasing the mass of additive resulted in moderately improved conversion [35]. The obtained results indicate that the oxidation of Cu$_{12}$As$_4$S$_{13}$ and CuFeS$_2$ (Equations (4) and (6)) may proceed with the formation of S$^0$, which passivates the surface of the minerals. At the same time, FeS$_2$ may act as an alternative catalytic surface for these minerals. The latter provides the reduction of HNO$_3$ on FeS$_2$ surface and decomposition of other sulfide minerals [45].

In the experiments with 0.5/1 mass ratio, the conversion of Cu$_{12}$As$_4$S$_{13}$ (Figure 5a), CuFeS$_2$ (Figure 5b) and ZnS (Figure 5c) appeared to be limited to 64, 58 and 89%, respectively. Usage of the higher mass ratio (2/1) resulted in increased conversion of the minerals to be 83, 83 and 98%, respectively for Cu$_{12}$As$_4$S$_{13}$, CuFeS$_2$ and ZnS.

4. Characterization of Residues

Characteristics of the Received Cakes

Figure 6 shows the SEM images (Figure 6a,b) and EDX-mapping of the residue (Figure 6c–f) after leaching the synthetic concentrate in HNO$_3$ solution. EDX-mapping images confirm the formation of S$^0$ layer on the surface of unreacted synthetic concentrate...
particles. Thus, the dark layer over the muted points of Fe (Figure 6c) and Cu (Figure 6d) as well as bright green points on the image of joint EDX-mapping (Figure 6f) over all other components allow us to confirm the \( S^\circ \) presence. Thus, the mentioned conditions suggest proceeding interactions by Equations (4) and (6).

![SEM images of synthetic concentrate-leaching residue (a,b) and EDX-mapping of the residue for Fe (c), Cu (d), S (e) and combined (f). (300 rpm; 353 K; 6 mol/L H\(_2\)SO\(_4\); 0.018 mol/L Fe (III); 60 min; no FeS\(_2\) additive).](image)

The \( S^\circ \) content in the residue was observed to be 56% and the conversion of sulfide sulfur to \( S^\circ \) appeared to be about 38%. Under these conditions, the conversion of \( \text{Cu}_{12}\text{As}_4\text{S}_{13} \), CuFeS\(_2\), and ZnS was 59, 60 and 84%, respectively.

In contrast to the experiment without the FeS\(_2\) additive (Figure 6), the results with the additive (FeS\(_2\)/synt. conc = 1/1) showed a lesser \( S^\circ \) content.

The Fe and Cu points indicated in one component EDX-mapping images (Figure 7c,d, respectively) became brighter. According to Figure 7a,b, the residue has a heterogeneous surface resembling conglomerates, while the experiment without FeS\(_2\) additive shows a more homogeneous structure due to the covering of the particles by \( S^\circ \). The green zones in Figure 7f correspond to the distribution of \( S^\circ \), while the mixture of red and blue zones are copper minerals (\( \text{Cu}_{12}\text{As}_4\text{S}_{13} \) and CuFeS\(_2\)) and FeS\(_2\).

Therefore, \( S^\circ \) covers the surface of the synthetic concentrate in lesser extent, which confirms by the SEM-EDX residue investigation as well as the chemical composition of the residue—sulfide sulfur to \( S^\circ \) transformation decreased to 23%, while the \( S^\circ \) content in the solid residue decreased to 14%. Under these conditions of dissolution, the conversion of \( \text{Cu}_{12}\text{As}_4\text{S}_{13} \), CuFeS\(_2\), and ZnS was 87, 91 and 98%, respectively.

Figure 8 shows the XRD patterns of the solid residues after the dissolution of synthetic concentrate in HNO\(_3\) solution. The obtained data additionally confirms that the presence of FeS\(_2\) allows to limit the formation of \( S^\circ \).
Figure 7. SEM images of synthetic concentrate-leaching residue (a, b) and EDX-mapping of the residue for Fe (c), Cu (d), S (e) and combined (f). (300 rpm; 353 K; 6 mol/L H₂SO₄; 0.018 mol/L Fe (III); 60 min; FeS₂/syn. conc = 1/1).

Figure 8. XRD patterns after synthetic concentrate dissolution in HNO₃ solution without (A) and with (B) the additive of FeS₂. (300 rpm; 353 K; 6 mol/L H₂SO₄; 0.018 mol/L Fe (III); 60 min).

SEM images (Figure 9) of the material after dissolution for 15 min (bend point in Figure 5 for Cu₁₂As₄S₁₃ and CuFeS₂) coupled with EDX analysis (Table 2) suggest that most of the S⁺ was formed towards the end of this period and the subsequent dissolution of the material occurs at its coating by S⁺.
Figure 9. SEM images of the solid residue after synthetic concentrate dissolution in HNO$_3$ solution. (300 rpm; 353 K; 6 mol/L H$_2$SO$_4$; 0.018 mol/L Fe (III); 15 min).

Table 2. Normalized EDX analysis results.

| Element | Fe  | Cu | As | S$_{sulfide}$ | S$^0$ | Total |
|---------|-----|----|----|---------------|------|-------|
| Point 001 | 40.2 | 4.2 | 1.1 | 54.5          | 6.8  | 100.0 |
| Point 002 | 43.8 | 2.3 | 0.8 | 53.1          | 2.0  | 100.0 |
| Point 003 | 11.3 | 22.1 | 4.6 | 62.0          | 42.7 | 100.0 |
| Point 004 | 23.4 | 21.7 | 1.6 | 53.3          | 24.3 | 100.0 |
| Point 005 | 7.6  | 14.3 | 3.3 | 74.8          | 61.5 | 100.0 |
| Point 006 | 29.4 | 11.9 | 2.3 | 56.2          | 19.1 | 100.0 |
| Point 007 | 44.4 | 2.1  | 0.9 | 52.6          | 0.5  | 100.0 |
| Point 008 | 45.3 | 1.5  | 0.3 | 52.9          | 0.6  | 100.0 |
| Point 009 | 9.1  | 23.1 | 8.6 | 59.2          | 36.8 | 100.0 |
| Point 010 | 9.5  | 30.4 | 10.4 | 49.7          | 24.4 | 100.0 |

Therefore, it is appropriate to conclude that the diffusion in the system is the result of S$^0$ formation during the first 10–20 min of the experiment. After that, the dissolution process shifts to diffusion control.

5. Kinetics Analysis

As it was shown, the conversion of sulfides is significantly affected by temperature, HNO$_3$ concentration and the presence of FeS$_2$ in the system; that could mean possible control of the reactions by both chemical reaction and diffusion. To determine the limiting stage of the processes, the most commonly used kinetic equations of SCM describing liquid-solid reactions [46] were used to fit into the experimental data (Table 3). According to the results present in Figures 2–5, the higher conversion degree during the initial period of reaction was observed for ZnS, therefore, kinetic analysis of the mineral was carried out in the period from 0 to 2 min, while for Cu$_{12}$As$_4$S$_{13}$ and CuFeS$_2$, from 0 to 60 min.

Table 3. Typical SCM kinetic equations applied for systems with spherical particles.

| №  | Limiting Stage                        | Formula                  |
|-----|---------------------------------------|--------------------------|
| 1   | Diffusion through the product layer (sp) | $1 - 3(1 - X)^{2/3} + 2(1 - X)$ |
| 2   | Surface chemical reaction (sp)         | $1 - (1 - X)^{1/3}$      |
As shown in Figure 10, the SCM equation typically applied for diffusion kinetic system (Table 4, Equation (1)) can be used to describe the conversion processes with high values of the determination coefficient ($R^2$).

![Figure 10](image)

**Figure 10.** The linear relationship between $1 - 3(1 - X) ^ {2/3} + 2(1 - X) = k \cdot \tau$ and treatment time of Cu$_{12}$As$_4$S$_{13}$ (a), CuFeS$_2$ (b) and ZnS (c) at various temperatures.

Table 4. The reaction orders with respect to HNO$_3$ concentration, Fe (III) ions concentration and the amount of FeS$_2$ additive at Cu$_{12}$As$_4$S$_{13}$, CuFeS$_2$ and ZnS treatment.

|            | Cu$_{12}$As$_4$S$_{13}$ | CuFeS$_2$ | ZnS |
|------------|-------------------------|-----------|-----|
| HNO$_3$ concentration | 1.2 | 1.4 | 1.6 |
| Fe(III) ions concentration | 0.34 | 0.82 | 0.62 |
| Amount of FeS$_2$ | 0.47 | 0.69 | 0.59 |

The activation energy values ($E_a$) were calculated using the Arrhenius law (Figure 11). Thus, $E_a$ was determined as 28.8 kJ/mol for Cu$_{12}$As$_4$S$_{13}$ and 33.7 kJ/mol for CuFeS$_2$, values that are typical for inner-diffusion processes [46]. The activation energy values for ZnS treatment were determined as 53.7 kJ/mol, which is more typical for kinetically controlled processes. However, according to the literature [47–52], a high $E_a$ value is not always allowed to make the final decision on the process nature.
The reaction order with respect to HNO$_3$ concentration, Fe (III) ions concentration and amount of FeS$_2$ additive were calculated using the graphical method (Table 4). The fractional order of reaction with respect to HNO$_3$ concentration and amount of FeS$_2$ additive at Cu$_{12}$As$_4$S$_{13}$, CuFeS$_2$ and ZnS treatment suggests that the nature of the processes is diffusion controlled. At the same time, the reaction order with respect to HNO$_3$ concentration at Cu$_{12}$As$_4$S$_{13}$, CuFeS$_2$ and ZnS treatment is more typical for chemical reaction control. The latter could be a result of aggressive impact on the S° layer that allows it to overcome the effect of passivation.

As a result, the research data were generalized and the general kinetic equations were established separately for Cu$_{12}$As$_4$S$_{13}$, CuFeS$_2$ and ZnS treatment, which consider the influence of temperature, concentration of reagents and duration of the experiments. As it shown in Figure 12, the relationship between the equations $1 - 3(1-X)^{2/3} + 2(1-X)$ and $C_{HNO_3} C_{Fe(III)} C_{FeS_2} \exp[-E_a/(R-T)] \tau 10^5$ for all experimental data was established, and the data points were evenly distributed along straight lines with a high $R^2$.

The kinetic equations for treatment of Cu$_{12}$As$_4$S$_{13}$, CuFeS$_2$ and ZnS can be written as follows (11)–(13), respectively:

$$
Cu_{12}As_4S_{13}: 1 - 3(1 - X)^{2/3} + 2(1 - X) = 38820C_{HNO_3}^{1.2}C_{Fe(III)}^{0.34}C_{FeS_2}^{0.47}e^{-28858/RT}t \tag{11}
$$

$$
CuFeS_2: 1 - 3(1 - X)^{2/3} + 2(1 - X) = 74070C_{HNO_3}^{1.42}C_{Fe(III)}^{0.82}C_{FeS_2}^{0.69}e^{-33708/RT}t \tag{12}
$$

$$
ZnS: 1 - 3(1 - X)^{2/3} + 2(1 - X) = 4.2C_{HNO_3}^{1.52}C_{Fe(III)}^{0.62}C_{FeS_2}^{0.59}e^{-53723/RT}t \tag{13}
$$

Thus, the processes of sulfide minerals dissolution under investigated conditions are limited by internal diffusion [53]. The assessment was based on the obtained $E_a$ values, orders of the reactions with respect to the reactants, SCM equations fitting and SEM-EDS.
investigation of the samples. Pyrite was proved as an effective catalytic surface for the reduction of nitrate ions and iron (III) with empirical order less than 1.

Figure 11. Arrhenius plots for Cu$_{12}$As$_4$S$_{13}$ (a), CuFeS$_2$ (b) and ZnS (c).

Figure 12. Relationship between SCM equation and $C_{\text{HNO}_3}$ $C_{\text{Fe(III)}}$ $C_{\text{FeS}_2}$ $\exp[-E_a/(R \cdot T)] \cdot t \cdot 10^3$ for the treatment of Cu$_{12}$As$_4$S$_{13}$ (a), CuFeS$_2$(b) and ZnS (c).

6. Conclusions

The current work was undertaken to deepen the understanding of the nature of the dissolution process for sulfides Cu$_{12}$As$_4$S$_{13}$, CuFeS$_2$ and ZnS in HNO$_3$ media with application FeS$_2$ and Fe (III) ions as catalysts.

It was observed that HNO$_3$ concentration and temperature have the most significant influence on the conversion degree of Cu$_{12}$As$_4$S$_{13}$, CuFeS$_2$ and ZnS. The values of $E_a$ were calculated as 28.8, 33.7 and 53.7 kJ/mol, respectively for Cu$_{12}$As$_4$S$_{13}$, CuFeS$_2$ and ZnS.

SEM-EDS scanning of the solid residues showed a presence of S° layer covering the surface of the minerals. The latter combined with $E_a$ values and orders of the reactions with respect to the reactants obtained as well as SCM equations fitting allowed us to propose that the dissolution processes are of a diffusion nature.

It was additionally demonstrated that the presence of FeS$_2$ in the system accelerates the conversion process due to galvanic coupling between minerals.

The results obtained can be used in predicting hydrometallurgical processes for sulfide materials such as copper–arsenic ores and concentrates treatment in HNO$_3$ media.

Further detailed kinetic studies on the dissolution of sulfide minerals in HNO$_3$ media such as Cu$_3$AsS$_4$, Cu$_{12}$Sb$_2$S$_{13}$, Sb$_2$S$_3$, Cu$_5$FeS$_4$ are of great interest. Furthermore, the complex processing of the low-grade sulfide raw materials in HNO$_3$ media is associated with the extraction of arsenic into the solution, which necessitates the following neutralization of nitrous gases as well as the arsenic utilization in the form of environmentally
friendly compounds. These studies are of high relevance in terms of creating industrial hydrometallurgical technology.

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**Nomenclature**

| № | Abbreviation/Symbol | Description |
|---|---------------------|-------------|
| 1 | $E_a$ | Activation energy |
| 2 | SCM | Shrinking core model |
| 3 | XRD | X-ray diffraction |
| 4 | SEM-EDS (or EDX) | Scanning electron microscopy/energy dispersive X-ray spectrometry |
| 5 | EDS-mapping (or EDX-mapping) | X-ray characterization technique that allows extremely rapid elemental concentrations to be gathered and collected as map |
| 6 | ICP-MS | Inductively coupled plasma mass spectrometry |
| 7 | X | Fraction reacted (decimal share) |
| 8 | E | Conversion (%) |
| 9 | Synt. conc | Synthetic concentrate |
| 10 | FeS$_2$/synt. conc | Mass ratio of pyrite to synthetic concentrate in a sample of material before the start of the experiment run |
| 11 | HNO$_3$ | Nitric acid |
| 12 | Cu$_{12}$As$_3$S$_{13}$ | Tennantite |
| 13 | CuFeS$_2$ | Chalcopyrite |
| 14 | ZnS | Sphalerite |
| 15 | FeS$_2$ | Pyrite |
| 16 | FeAsS | Arsenopyrite |
| 17 | S$^0$ | Elemental sulphur |

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