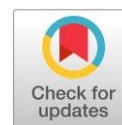# Kinetics of nitric acid leaching of bornite and chalcopyrite

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Abstract

The paper presents a study of the process of nitric acid dissolution of the natural minerals chalcopyrite and bornite. The influence of various parameters, including temperature, nitric acid concentration and particle sizes, on this process was examined. Based on the data obtained, the values of apparent activation energy (57.41 and 42.98 kJ/mol for chalcopyrite and bornite, respectively), empirical orders with respect to nitric acid (1.62 and 1.57 for chalcopyrite and bornite, respectively) and with respect to particle size (–1.16 and –2.53 for chalcopyrite and bornite, respectively) were calculated using the shrinking core model. Generalized kinetic equations for the dissolution process of both minerals were derived. Based on the calculations performed, it was suggested that the dissolution processes of chalcopyrite and bornite under these conditions are limited by internal diffusion.

Key findings

● The influence of temperature, nitric acid concentration, and particle size on the process of nitric acid dissolution of chalcopyrite and bornite was studied.

● Using the shrinking core model, the values of the apparent activation energy and the orders with respect to particle size and nitric acid concentration were calculated.

● It was suggested that the process of mineral dissolution is limited by internal diffusion.

1. Introduction

Sulfide ores are the main raw materials for copper production. However, the rich copper ore deposits have been depleted, so hard-to-open copper raw materials are increasingly being involved in processing. Chalcopyrite and bornite are the main minerals of such hard-to-process raw materials.

Nowadays, there are many technologies to process copper raw materials. Pyrometallurgical methods are the most widely used ones. They provide a high degree of copper extraction and high copper content in the matte [1]. But, depending on the type of smelting, they have the following disadvantages: the need for additional processing, high coke consumption, low thermal efficiency, complex and expensive repair, and copper-rich slags [2]. In this regard, hydrometallurgical technologies began to be actively integrated into the practice of processing copper raw materials. Among modern hydrometallurgical methods, chloride [3],

sulfate [4] and ammonia leaching processes [5] stand out. Bioleaching [6] and autoclave oxidation [7, 8] are considered to be the most promising processes.

The main disadvantages of bioleaching are the difficulty of maintaining the vital activity of the microorganisms used, the need to build large heated rooms, and the long duration of the process [9].

The main difficulties in implementing autoclave processes are associated with high energy demand and large capital investments [10].

To intensify hydrometallurgical leaching, various ultrafine grinding methods are used, Albion and Activox technologies being the most widely implemented among them [11]. The main difficulties of these technologies are associated with high capital costs for corrosion-resistant equipment and high energy costs associated with obtaining finely dispersed material for hydrometallurgical processing.

In the current situation, the development of novel effective methods for processing such hard-to-process sulfide raw materials seems relevant. Nitric acid leaching is one of the promising approaches in this field. Nitric acid has strong oxidizing properties (oxidation potential 0.957 V). It is capable of decomposing sulfide minerals, transferring copper, iron, zinc and other valuable components into solution [12–14]. The possibility of capturing the resulting nitrous gases with further nitric acid recovery is an advantage of this process. This reduces reagent costs.

The literature contains a limited number of works [15–17] devoted to studying the regularities of nitric acid leaching of copper sulfide minerals. These papers were aimed at studying the dissolution kinetics of certain concentrates. This indicates the need for additional research to deepen the previously obtained data regarding the natural copper sulfide minerals.

The purpose of this research was to study kinetics of the nitric acid dissolution of sulfide copper minerals.

2. Materials and methods

2.1. Materials and reagents

The main raw materials for our research were the minerals chalcopyrite from the Vorontsovskoye deposit and bornite from the Karabashskoye deposit. They were pre-crushed and sifted to obtain a certain size class.

2.2. Methods

Nitric acid leaching experiments were carried out in a setup consisting of a borosilicate glass reactor with an external jacket Lenz Minni-60 with a volume of 0.5 dm³. A constant temperature in the reactor was maintained with a Huber CC-205B thermostat-circulator. Mixing was performed using a Cat R-100C overhead mixer at 250 rpm to ensure slurry homogeneity. Before the start of each experiment, the solution was heated up to the required temperature and then a portion of the initial material was added. During each experiment, the samples were taken at certain times using a Sartorius Proline dispenser. At the end of the experiment, the leach pulp was sent for filtration, the solutions were analyzed using a PerkinElmer Elan 9000 inductively coupled plasma mass spectrometer, and the solid residue after leaching was washed with distilled water and dried at 75 °C until constant weight.

3. Results and Discussion

3.1. Influence of temperature

Figure 1 presents the effect of temperature on the dissolution of chalcopyrite and bornite at a nitric acid concentration of 5 mol/dm³, duration of 60 min, L:S (liquid-to-solid ratio) = 20:1, size class – 0.074 + 0.063 mm.
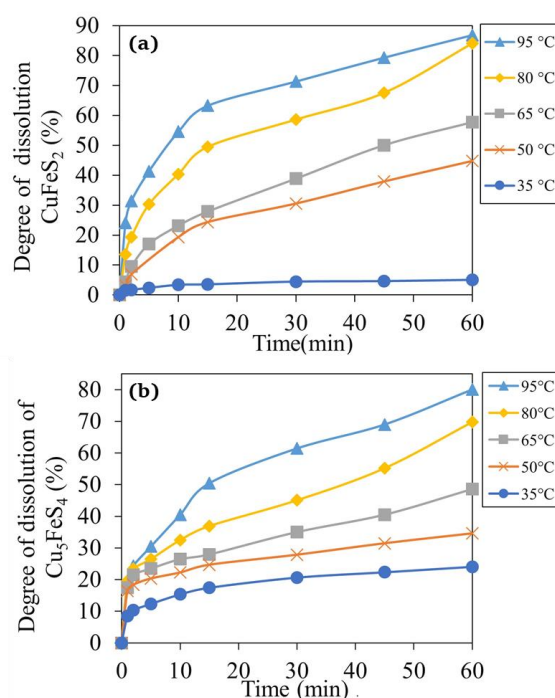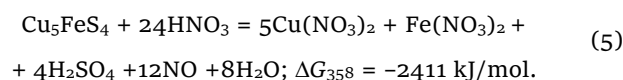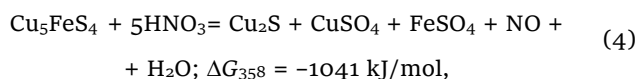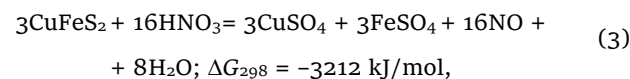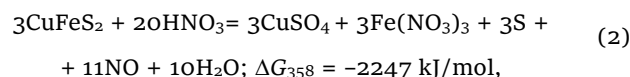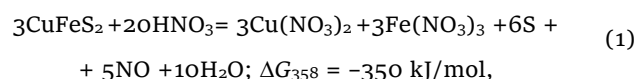

Figure 1 Dependence of the degree of dissolution on duration at several temperatures for chalcopyrite (a) and bornite (b).

According to Figure 1, an increase in temperature had a positive effect on the dissolution of chalcopyrite and bornite: the dissolution degree of chalcopyrite and bornite increased from 5.03 to 86.84% and from 24.07 to 80.06%, respectively. A slowdown in the course of the reaction with time was also observed; in addition, the presence of a clear inflection point in the curves suggests an intrafusion mechanism of interactions. The main cause for possible internal diffusion may be the formation of elemental sulfur on the surface of the minerals through the following reactions:

$$3CuFeS_2 + 20HNO_3 = 3Cu(NO_3)_2 + 3Fe(NO_3)_3 + 6S + \qquad (1)$$
$$+ 5NO + 10H_2O; \Delta G_{358} = -350 \text{ kJ/mol},$$

$$3CuFeS_2 + 20HNO_3 = 3CuSO_4 + 3Fe(NO_3)_3 + 3S + \qquad (2)$$
$$+ 11NO + 10H_2O; \Delta G_{358} = -2247 \text{ kJ/mol},$$

$$3CuFeS_2 + 16HNO_3 = 3CuSO_4 + 3FeSO_4 + 16NO + \qquad (3)$$
$$+ 8H_2O; \Delta G_{298} = -3212 \text{ kJ/mol},$$

$$Cu_5FeS_4 + 5HNO_3 = Cu_2S + CuSO_4 + FeSO_4 + NO + \qquad (4)$$
$$+ H_2O; \Delta G_{358} = -1041 \text{ kJ/mol},$$

$$Cu_5FeS_4 + 24HNO_3 = 5Cu(NO_3)_2 + Fe(NO_3)_2 + \qquad (5)$$
$$+ 4H_2SO_4 + 12NO + 8H_2O; \Delta G_{358} = -2411 \text{ kJ/mol}.$$

3.2. Influence of nitric acid concentration

The influence of nitric acid concentration on chalcopyrite and bornite dissolution at a temperature of 65 °C, duration of 60 min, L:S = 20:1, size class – 0.074 + 0.063 mm is shown in Figure 2.
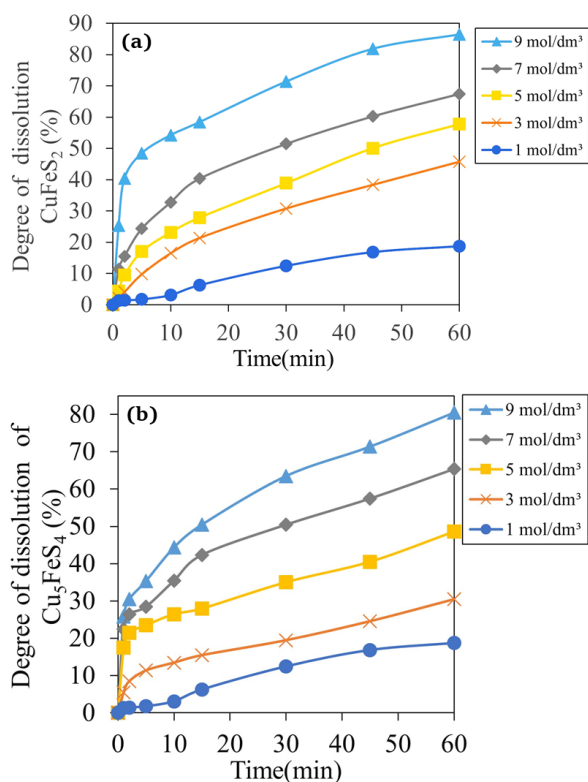
Figure 2 Dependence of the dissolution degree on duration at several concentrations of nitric acid for chalcopyrite (a) and bornite (b).

Figure 3 Dependence of the dissolution degree on duration at several particle sizes of chalcopyrite (a) and bornite (b).

According to Figure 2, an increase in the nitric acid concentration contributes to a significant increase in the dissolution degree of both chalcopyrite and bornite. The established significant effect of HNO_3 concentration on the reaction rate and the dissolution degree of minerals may also indicate that the reactions are controlled by diffusion through a product layer, where an increase in the HNO_3 concentration in the initial solution leads to acceleration of the S^o to SO_4^{2-} conversion.

3.3. Influence of particle size

Figure 3 presents the effect of particle size on the dissolution of chalcopyrite and bornite at a temperature of 65 °C, duration of 60 min, L:S = 20:1, and nitric acid concentration of 5 mol/dm³.

As expected, decreasing particle sizes had a positive effect on chalcopyrite and bornite dissolution: the dissolution degree of chalcopyrite and bornite increased from 42.05 to 51.57% and from 29.46 to 65.67%, respectively.

3.4. Calculation of kinetic characteristics

To determine the dissolution regime of chalcopyrite and bornite in nitric acid, a shrinking core model (SCM) was used. Table 1 presents the basic equations describing its stages.

Based on the results of R^2 calculations, the equation describing diffusion through a product layer (sp) had the highest value of the correlation coefficient within the entire temperature range considered for both minerals.
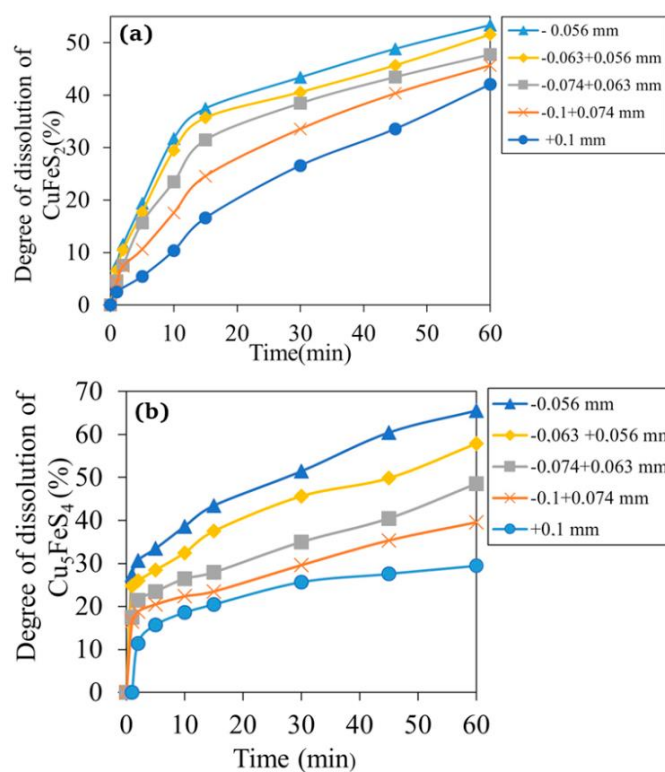
Table 1 Equations describing various limiting SCM stages.

Limiting stage	Equation
Diffusion through a product layer (sp)	$1-3(1-X)^{2/3} + 2(1-X)$
Diffusion through a product layer (pr)	X^2
Diffusion through a product layer (con)	$X + (1-X)\ln(1-X)$
Diffusion through a liquid film (sp)	X
Surface chemical reaction (con)	$1-(1-X)^{1/2}$
Surface chemical reaction (sp)	$1-(1-X)^{1/3}$

Particle shape: sp – spherical, pr – prismatic, con – conical.

The apparent activation energy values for chalcopyrite and bornite were calculated using $\ln k_c$ vs $1/T$ plots (Figure 5), where k_c is the slope estimated graphically (Figure 4). According to Equation 6 derived from the Arrhenius law, the apparent activation energy was calculated from the straight-line slope, which was 57.41 and 42.98 kJ/mol for chalcopyrite and bornite, respectively.

$$\ln k_C = \ln A - E_a/RT \qquad (6)$$

Also, using the $\ln k_c$ vs $\ln(C_{HNO_3})/\ln(r)$ plots, the empirical orders with respect to nitric acid concentration and particle size were calculated. The calculation results are presented in Table 2.

According to the data obtained, generalized kinetic equations were derived for the nitric acid dissolution of chalcopyrite and bornite:
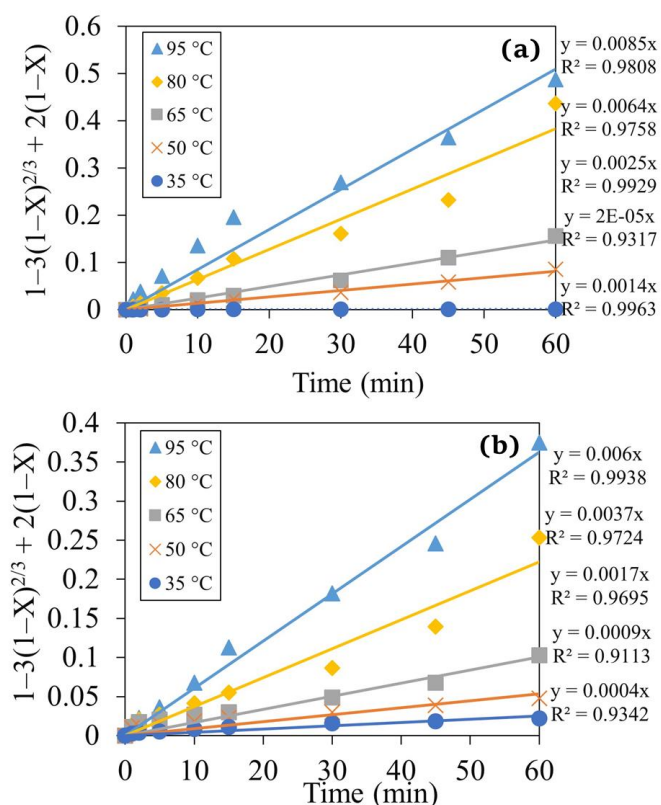
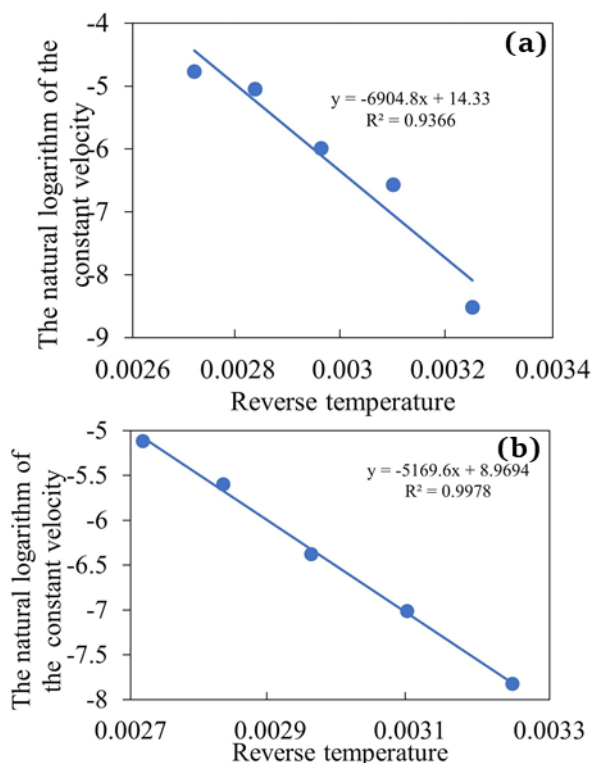**Figure 4** Determination of k_c for chalcopyrite (a) and bornite (b).

Figure 5 Dependence of $\ln k_c$ vs $1/T$ for chalcopyrite (a) and bornite (b).

Table 2 Calculation results of the empirical orders with respect to HNO$_3$ concentration and particle size for chalcopyrite and bornite.

Mineral	CuFeS$_2$	Cu$_5$FeS$_4$
HNO$_3$		
Empirical order	1.62	1.57
Particle size		
Empirical order	–1.16	–2.53

For CuFeS$_2$:

$$1 - 3(1-X)^{\frac{2}{3}} + 2(1-X) = 2488.2 \cdot C_{\text{HNO}_3}^{1.62} \cdot r^{-1.16} \cdot e^{\frac{-55410}{8.314\,T}} \tau \tag{7}$$

For Cu$_5$FeS$_4$:

$$1 - 3(1-X)^{\frac{2}{3}} + 2(1-X) = 793.8 \cdot C_{\text{HNO}_3}^{1.57} \cdot r^{-2.53} \cdot e^{\frac{-42980}{8.314\,T}} \tau. \tag{8}$$

4. Limitations

This study did not examine the mutual influence of minerals on each other. In the future, it is planned to conduct studies of nitric acid dissolution of a mixture of natural minerals and an industrial concentrate with the same mineralogical composition.

5. Conclusions

The process of nitric acid leaching of the natural minerals chalcopyrite and bornite was studied. As a result of the work, the following conclusions can be drawn:

1. It was established that the nitric acid concentration and temperature have the greatest positive effect on chalcopyrite and bornite dissolution, a decrease in particle sizes having a lesser effect.

2. The values of apparent activation energy were calculated according to SCM: 57.41 kJ/mol for chalcopyrite and 42.98 kJ/mol for bornite, respectively; the empirical orders for chalcopyrite and bornite were: 1.62 and 1.57 with respect to nitric acid concentration, respectively; –1.16 and –2.53 with respect to particle size, respectively.

3. Generalized kinetic equations for the dissolution process of both minerals were derived (see Equations 7 and 8).

4. According to the results obtained, it was suggested that under these process conditions, chalcopyrite and bornite dissolution is limited by internal diffusion associated with the formation of elemental sulfur films on their surface.

● Supplementary materials

No supplementary materials are available.

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● Conflict of interest

The authors declare no conflict of interest.

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