Conference Paper

Research of Polymetallic Sulfide Industrial Waste Nitric Acid Treatment

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Abstract

Thermodynamic and kinetic features studies of polymetallic sulfide industrial waste nitric acid leaching were carried out. Elemental and phase composition of investigated raw material were studied with X-ray diffraction and electron microscopy methods. Calculations of the Gibbs energy change for the likely reactions of sulfide minerals with nitric acid were performed. In order to determine the most probable conditions of the sulfide industrial waste leaching in nitric acid, as well as the mutual influence of the produced pulp components on the performance of the process, the kinetics evaluation of multicomponent sulfide industrial waste in a nitric medium was studied using mathematical methods.

Keywords: nitric acid leaching, polymetallic sulfide industrial waste, Gibbs energy change, kinetic features

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1. Introduction

Processing of low-grade sulfide industrial waste by traditional methods leads to problems at stages of beneficiation and metallurgical processing. This leads to increased complexity of nonferrous metals extraction and loss of valuable components [1].

At polymetallic sulfide industrial waste flotation there are small amounts of refractory collective industrial products. The operation was carried out to improve the quality of the monometallic concentrates [2, 3].

The introduction of hydrometallurgical technologies which are more useful from an environmental and economic point of view compared to conventional processes is a promising method to solve the problem [4].

Nitric acid was used as a reagent for the sulfide industrial waste. This acid has a high chemical reactions heat and allows recycling of the exhaust gases with nitrous regeneration of nitric acid [5, 6].

The aim of this work was to perform calculations of the Gibbs energy change for the likely reactions of sulfide minerals with nitric acid and to study kinetic features

Cu	Zn	Fe	S	Pb	Ca	Na	Mg	As	Al	Au, ppm	Ag, ppm
6,37	9,21	33,57	46,3	1,18	1,72	1,66	0,24	0,21	0,1	11,5	81,3

Table 1: The chemical composition of investigated industrial waste, % mass.

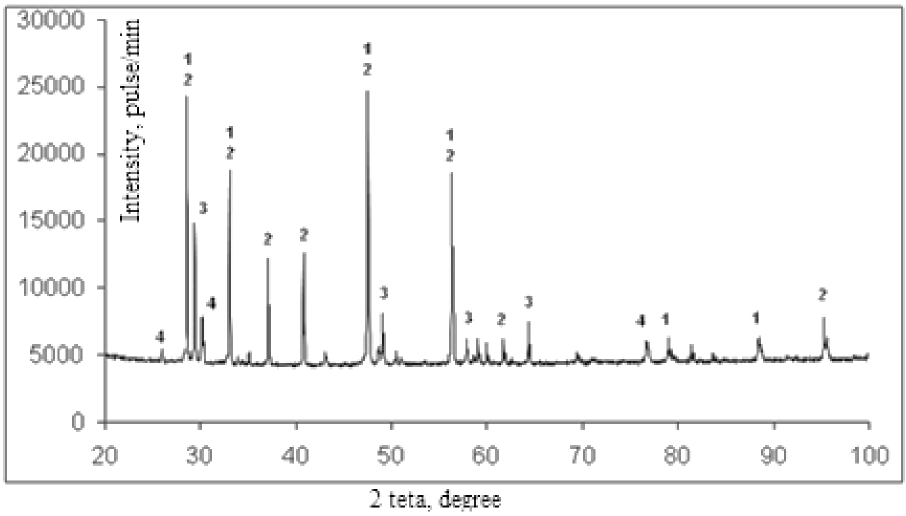

Figure 1: X-ray phase composition of the investigated industrial waste: 1 – ZnS; 2 – FeS_2; 3 –$CuFeS_2$; 4 – PbS.

of sulfide industrial waste nitric acid leaching reactions. This work is an extension of previous studies [7] in order to clarify, generalize and expand earlier results.

2. Experimental

Investigated raw material is an intractable part of the selective flotation multicomponent sulfurous materials. The chemical composition of industrial waste is presented in Table 1.

Figure 1 shows the phase composition of the investigated raw material obtained via X-ray diffraction analysis.

The X-ray diffraction analysis showed that sphalerite, pyrite, chalcopyrite and galena are the most common minerals represented in the raw material.

Electron microscopic studies were performed to determine fine structure of the material, phase composition, chemical composition of the individual phases and their crystallographic orientation of raw materials using a transmission electron microscope JEM 2100 prefix for microanalysis Oxford Inca. Figure 2 shows the results of solid sulfide grains industrial waste composition microanalysis study.

Comparison of data with the results of X-ray analysis confirmed the presence of ZnS, $CuFeS_2$, FeS_2, PbS.

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Element	Weight%	Atomic%
O K	6.03	15.46
Si K	0.50	0.74
S K	32.75	41.93
Ca K	1.12	1.15
Fe K	29.65	21.80
Cu K	12.19	7.87
Zn K	16.53	10.38
As L	1.23	0.67
Totals	100.00	

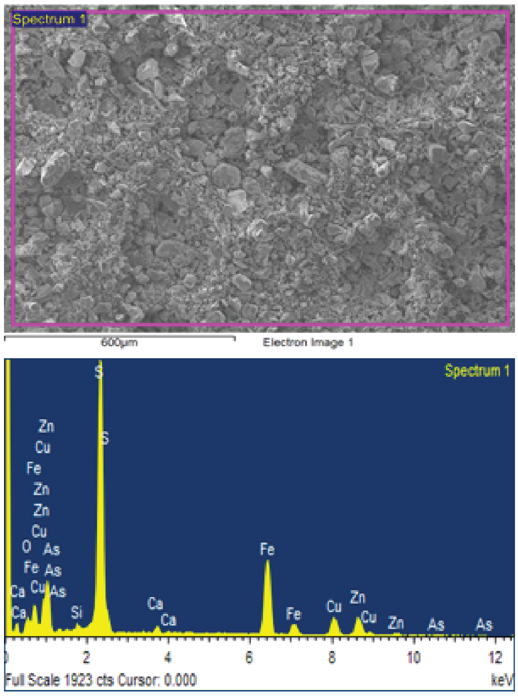

Figure 2: The results of solid sulfide grains industrial waste composition study.

№	Reaction	ΔG, [kJ]
1	$CuFeS_2 + 8HNO_3 = CuSO_4 + FeSO_4 + 4NO + 4NO_2 + 4H_2O$	-1071,04
2	$2FeS_2 + 8HNO_3 = Fe_2(SO_4)_3 + S^0 + 8NO + 4H_2O$	-1598,14
3	$ZnS + 8HNO_3 = ZnSO_4 + 8NO_2 + 4H_2O$	-587,827

Table 2: The results of the Gibbs energy change calculation for the reactions of interaction of ZnS, $CuFeS_2$, FeS_2 with nitric acid at 353 K.

Interaction of ZnS, $CuFeS_2$, FeS_2 with nitric acid can be represented by the following reactions [8] (Table 2).

In the reactions above it is conventionally accepted that as result of sulfides interaction with HNO_3 only NO is formed. However, apart from the nitrogen oxide (II), can form a variety of compounds: N_2O_4, N_2O_3, N_2O, N_2, NH_3. Nitrogen may have to change its oxidation state throughout the possible range and the degree of nitric acid reduction depends on its concentration and the activity of the reducing agent.

Gibbs energy change (ΔG) was used to determine direction of reactions (1-3) and to study the interaction of sulfide raw material with nitric acid. Value of Gibbs energy change was used to judge the feasibility of the process.

In order to determine the most probable conditions of the desired products formation during sulfide industrial waste leaching in nitric acid, as well as the mutual influence of the produced pulp components on the performance of the process, the kinetics evaluation of multicomponent sulfide industrial waste in a nitric medium was studied using mathematical methods [9].

To achieve optimal performance of the technological process applied the method of mathematical planning of the experiment in the form of a three-level model by three independent parameters.

The results of experiments processed in the computer program "Statistica 7.0" in the form of response surfaces, where the resulting functions are the values of extraction of copper, zinc and iron in solution.

For each surface were calculated values of coefficients of multiple correlation R, equations of the regression to identify the adequacy of the obtained results and determine the most important parameters of the process.

3. Results and Discussion

The calculations of the Gibbs energy change of possible reactions between nitric acid and metal sulfides show that there is high thermodynamic probability of their occurrence with the formation of elemental sulfur, water-soluble compounds of copper, zinc and iron, oxides of nitrogen.

Knowing relation between reacted substance amount and acid concentration, samples analysis experimental data numerical differentiation was used to calculate metal sulfides dissolution specific reaction velocity (Figure 3).

At nitric acid concentration 3,3 mol/dm^3 abrupt change in speed V dependence from concentration C_{acid} occurs along with reaction order change, indicating process mode change from kinetic to diffusional.

In concentration range between 3,5-4,5 mol/dm^3 reaction speed does not depend on acid concentration until certain point, after which rapid decrease in reaction speed is observed. It might be due to fact that reaction on initial stage is irreversible, while after reaching certain concentration process kinetics are affected by adjacency to equilibrium state or by midlings particles size decrease.

Having taken the logarithm from equation, reaction orders and reaction constants for metal sulfides dissolution in nitric acid were found using graphical method (Figure 4).

Values on graph can be adequately described by straights. Reaction order values obtained were close to 0,5. Reaction order value is typical for kinetic process mode. Close *n* values were expected because chalcopyrite, sphalerite and pyrite have

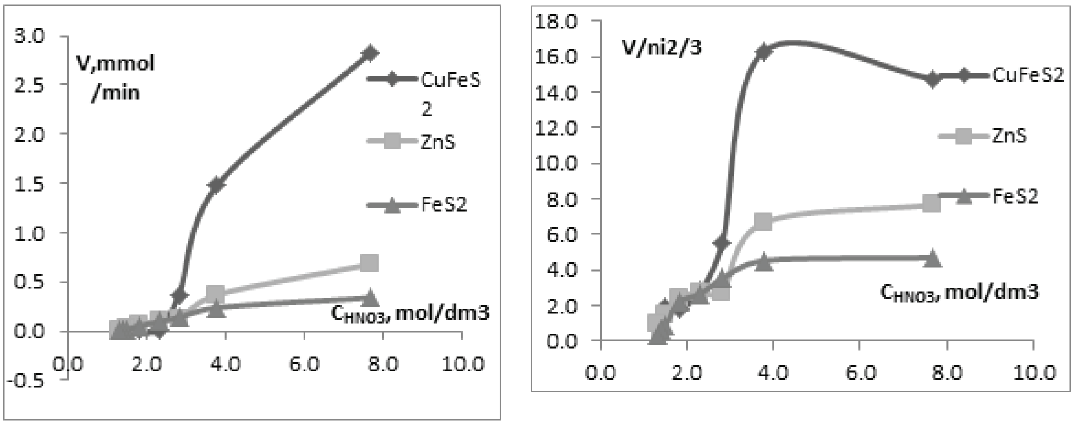

Figure 3: Dependence of reaction speed from nitric acid concentration.

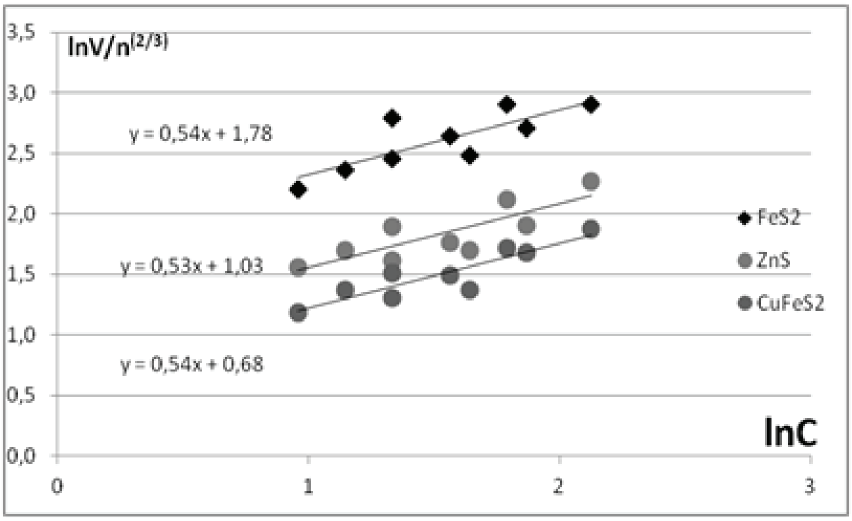

Figure 4: Dependence of specific speed logarithm from nitric acid concentration logarithm.

common properties and react with nitric acid alike. Reaction rate constant: k_{CuFeS2} = exp(0,68) = 2, k_{ZnS} = exp(1,03) = 2,8, k_{FeS2} = exp(1,78) = 5,9.

Using obtained *n* and *k* values, processes 1-3 virtual velocities were calculated using formal kinetic equation:

$$V_i = k_i \cdot C_{HNO_3}{}^{n_i} \quad (1)$$

Comparison between calculated and experimental data from Table 1 is shown on Figure 5 and confirms obtained results adequacy.

The interaction of metal sulfides with nitric acid leads to its degradation and the formation of nitrous gases. The resulting nitrogen oxides are oxidized to higher oxides in the absorption column to form a mixture of nitric and nitrous acids.

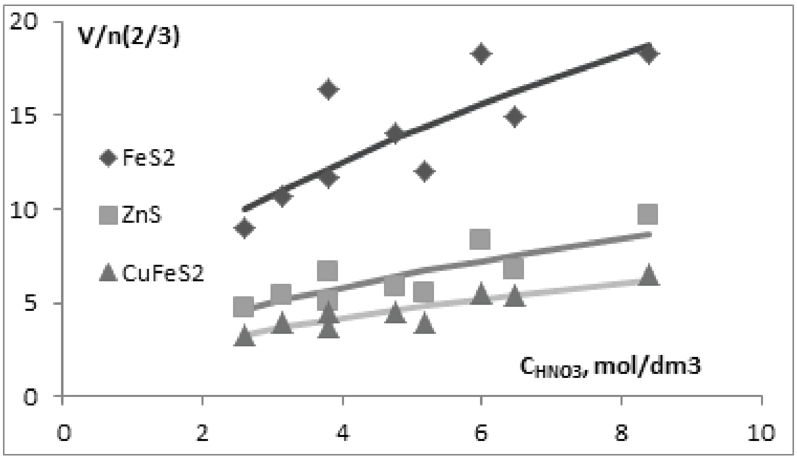

Figure 5: Specific rate dependence from nitric acid concentration. Points represent experimental data, lines – calculated data.

The obtained results of mathematical experiment planning in the form of polynomials allow us to estimate the contribution of each factor in the efficiency of the leaching process:

R_{Cu}= 91,5 %

Y_{Cu} = 119,83 - 11,185X_1 - 1,146X_2 + 0,623X_3 - 0,096X_1^2 + 0,004X_2^2 - 0,001X_3^2 + 0,119X_1X_2 + 0,250X_1X_3 - 0,029X_1X_3;

R_{Zn}= 96,7 %

Y_{Zn} = 101,545-6,286X_1 - 0,785X_2 + 0,565X_3 + 0,005X_2^2 - 0,001X_3^2 + 0,041X_1X_2 - 0,001X_2X_3 - 0,18X_1X_3;

R_{Fe} = 94,8 %

Y_{Fe} = 146,534 - 7,106X_1 - 1,243X_2 + 0,208X_3 - 0,405X_1^2 + 0,003X_2^2 + 0, 12X_1X_2 + 0,015X_1X_3.

All the coefficients of the given polynomials are significant; the obtained values of coefficients R indicate the adequacy of the models.

The adequacy of the equations is confirmed using the Fisher criterion.

4. Conclusions

1. The results of X-ray and electron microscopic studies of multicomponent sulfide industrial waste phase and mineralogical composition show that the major minerals in middlings are sphalerite, pyrite and chalcopyrite.

2. The calculations of the Gibbs energy change of possible reactions between nitric acid and metal sulfides displays large enough thermodynamic probability of their

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occurrence with the formation of elemental sulfur, water-soluble compounds of copper, zinc and iron, oxides of nitrogen.

3. Experimental data numerical differentiation allowed sulfide dissolution rate calculation. Dependence of total (dx/dt) and specific ($dx/(n^{2/3}*dt)$) from nitric acid concentration was shown.

4. Individual reaction orders for pyrite, chalcopyrite and sphalerite interactions with nitric acid were comparable. Their value was calculated as 0,5. Dissolution rate constants were found to be k_{FeS_2}= 5,9; k_{CuFeS_2}= 2,0; k_{ZnS}= 2,8. Basing on their values it can be said that process speed is limited by kinetics.

5. With the help of mathematical planning of the experiment the optimal parameters of conducting the process of the nitric acid leaching technogenic raw materials were chosen, which can ensure the maximum extraction of copper and zinc in a solution of 98 and 99 %, respectively. Analysis of response surfaces and mathematical models have shown that such parameters are: the ratio of S:L= 4; the concentration of nitric acid of 8,5 mol/dm^3; duration of the experiment 120 min.

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