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Copper leaching from chalcopyrite concentrate by sodium nitrate in sulphuric acid solution – chemometric approach

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Hydrometallurgical processing of the copper concentrates is a promising alternative to the conventional pyrometallurgical production of copper due to significantly lower environmental impact, capital and operational costs. Development of the hydrometallurgical process for copper recovery from mineral concentrate requires extensive work in testing and optimization of operational parameters from laboratory to semi-industrial scale. Mathematical modelling of the copper leaching process can save human labour and time. Leaching of copper from chalcopyrite concentrate using sulphuric acid and sodium nitrate as an oxidant was tested, and the influence of temperature, particle size, stirring speed and concentrations of sulphuric acid and sodium nitrate were evaluated. Obtained results showed that increasing temperature and concentrations of sulphuric acid and sodium nitrate increase the leaching degree of copper, while increasing particle size and stirring speed reduce copper extraction. In this paper, second-order polynomial models (SOP) were applied to experimental data. Presented results show that mathematical models fit experimental data. The conclusion is that SOP models are a promising tool to be used for modelling leaching processes of metals.

Keywords: leaching, chalcopyrite, copper, influence of working parameters, mathematical modelling

INTRODUCTION

Although hydrometallurgy provides more environmentally friendly production of copper, and copper ores in the world's exploited deposits are being continually depleted, getting more complex, and grades of the valuable elements are constantly declining [1], approximately 80-85 % of the global annual copper production is still produced pyrometallurgically in smelters [2,3]. One of the main obstacles for wider application of hydrometallurgy are difficulties in copper leaching from the most abundant copper mineral, chalcopyrite, which accounts for approximately 70 % of the global copper reserves [3]. Chalcopyrite is one of the most reluctant copper minerals to leach and smelting it often provides better extraction of this metal from mineral concentrate [3,4]. Slow and incomplete leaching of chalcopyrite is a consequence of the formation of passivation layers on the mineral surface [3,5]. Passivation layers can be formed by sulphides, polysulphides, elemental sulphur [6,7], iron oxides, hydroxides, hydroxysulphates and jarosites [8,9]. Also, due to lower reaction temperatures, hydrometallurgical processes are significantly slower than pyrometallurgical ones. Effective leaching of chalcopyrite from mineral concentrate requires the application of oxidant, and/or high pressure [4,10]. Also, acidophilic microorganisms (bacteria and archaea) can be applied to catalyse leaching of copper from chalcopyrite [11-13]. Numerous research papers were published describing the application of various oxidants in order to enhance leaching of copper from chalcopyrite [2,3,14-18]. Optimization of the leaching process for the selected raw mineral material requires extensive work on testing the influence of various parameters on the leaching degree of copper. Development of a mathematical model that can be used to predict the leaching degree based on input data acquired by laboratory experiments.

This could significantly accelerate the optimization and development of leaching technology on the industrial scale. Second-order polynomial models (SOP) have a wide application in different areas of science and industry. These models allow prediction of the system's behaviour based on the input data collected during laboratory experiments. In the presented research, leaching of copper from chalcopyrite concentrate using sodium nitrate as an oxidant was tested and experimental results were used as input data for the development of a mathematical model. Sodium nitrate was selected because of its good performance as a leaching agent for chalcopyrite [17]. The aim of this work is to develop second-order polynomial models (SOP) for copper leaching and to test if experimental data collected during leaching

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experiments fits into the model. In a series of experiments the influence of leaching duration, temperature, stirring speed, sulphuric acid concentration and sodium nitrate concentration on the leaching degree of copper was measured. Obtained data fit into the SOP model, proving that this mathematical model can be applied for theoretical modelling of copper leaching from the chalcopyrite concentrate. Such models can significantly accelerate the development of industrial scale leaching technologies.

The main chemical reactions (1-9) for leaching of chalcopyrite using sodium nitrate in sulphuric acid were identified by computational thermodynamic analysis performed by HSC 6.1 software (Outotec Research Oy, Finland) and analysis of the reaction products [17]:

$CuFeS_2 + 4/3NaNO_3 + 8/3H_2SO_4 = CuSO_4 + FeSO_4 + 2/3Na_2SO_4 + 2S^0 + 4/3NO + 8/3H_2O$ (1)

$CuFeS_2 + 4NaNO_3 + 4H_2SO_4 = CuSO_4 + FeSO_4 + 2Na_2SO_4 + 2S^0 + 4NO_2 + 4H_2O$ (2)

$FeSO_4 + 1/3NaNO_3 + 2/3H_2SO_4 = 1/2Fe_2(SO_4)_3 + 1/6Na_2SO_4 + 1/3NO + 2/3H_2O$ (3)

$FeSO_4 + NaNO_3 + H_2SO_4 = 1/2Fe_2(SO_4)_3 + 1/2Na_2SO_4 + NO_2 + H_2O$ (4)

$CuFeS_2 + 5/3NaNO_3 + 10/3H_2SO_4 = CuSO_4 + 1/2 Fe_2(SO_4)_3 + 5/6Na_2SO_4 + 2S^0 + 5/3NO + 10/3H_2O$ (5)

$CuFeS_2 + 5NaNO_3 + 5H_2SO_4 = CuSO_4 + 1/2Fe_2(SO_4)_3 + 5/2Na_2SO_4 + 2S^0 + 5NO_2 + 5H_2O$ (6)

$CuFeS_2 + 2Fe_2(SO_4)_3 = CuSO_4 + 5FeSO_4 + 2S^0$ (7)

$NO + 2NaNO_3 + H_2SO_4 = 3NO_2 + Na_2SO_4 + H_2O$ (8)

$3NO_2 + H_2O = 2HNO_3 + NO$ (9)

The change in Gibbs free energy for chemical reactions 1-9 was calculated for temperatures from 25 °C to 90 °C and atmospheric pressure. The calculated negative values of Gibbs free energy for reactions 1-8 indicate that these reactions are thermodynamically feasible at the given conditions.

EXPERIMENTAL

Materials and methods

Chalcopyrite concentrate was obtained from the flotation plant of the „Rudnik“ mine in Serbia. Four particle size fractions were obtained by wet sieving. Mineralogical analysis of the concentrate was performed by chemical and X-ray diffraction analysis and qualitative and quantitative light microscopy.

Leaching experiments were performed in a 2L glass reactor equipped with a teflon stirrer, thermometer, glass funnel for adding solid samples, sampling device and condenser. The samples were collected at regular time intervals for chemical analysis by AAS (Perkin Elmer Aanalyst 300 Norwalk, USA). The phase content was determined by X-ray analysis using diffractometer (PHILIPS PW- 1710) and qualitative and quantitative light microscopy (Carl Zeiss-Jena, JENAPOL-U).

Experiments were conducted by varying one of the parameters important for copper leaching: temperatures from 20 to 90 °C, particle class -75, -75 +50, -50 +37 and -37 μm, sulphuric acid concentration from 0.6 to 2.0 M, sodium nitrate concentration from 0.15 to 0.90 M and stirring speed 100-400 rpm.

Temperature

A first set of experiments was conducted under following conditions: 1.5 M H_2SO_4, 0.6 M $NaNO_3$, stirring speed 300 rpm, solids concentration 20 g of concentrate in 1.2 dm^3 of the solution, duration of experiment 240 min. Temperature was set to 70 °C, 75 °C, 80 °C, 85 °C and 90 °C.

Particle size

Experimental conditions: T=80 °C, 1.5 M H_2SO_4, 0.6 M $NaNO_3$, stirring speed 300 rpm, solids concentration 20 g of concentrate in 1.2 dm^3 of the solution, duration of experiment 240 min. Particle class: -75, -75 +50, -50 +37 and -37 μm.

Stirring speed

Experimental conditions: T=80 °C, 1.5 M H_2SO_4, 0.6 M $NaNO_3$, stirring speed 300 rpm, solids concentration 20 g of concentrate in 1.2 dm^3 of the solution, duration of experiment 240 min. Stirring speed: 100, 200, 300 and 450 rpm.

Sulphuric acid concentration

Experimental conditions: T=80 °C, 0.6 M $NaNO_3$, stirring speed 300 rpm, solids concentration 20 g of concentrate in 1.2 dm^3 of the solution, duration of experiment 240 min. Concentrations of H_2SO_4: 0.6, 1.0, 1.5 and 2M.

Sodium nitrate concentration

Experimental conditions: T=80 °C, 1.5 M H_2SO_4, stirring speed 300 rpm, solids concentration 20 g of concentrate in 1.2 dm^3 of the solution, duration of experiment 240 min. Concentration of $NaNO_3$: 0.15, 0.20, 0.45, 0.60, 0.75 and 0.90 M.

Mathematical modelling and statistical analysis

The second-order polynomial (SOP) models were fitted to the observed experimental data. Five mathematical models of the following form were developed to relate leaching degree of copper (Y) and process variables [19,20]:

$$Y_k = \beta_{k0} + \sum_{i=1}^{2} \beta_{ki} \cdot X_i + \sum_{i=1}^{2} \beta_{kii} \cdot X_i^2 + \beta_{k12} \cdot X_1 \cdot X_2,$$

k=1-2, (10)

where: β_{k0}, β_{ki}, β_{kii}, β_{k12} are constant regression coefficients; Y_k is leaching degree of Cu, while X_1 is the duration of the process (t) and X_2 is one of the following parameters: temperature (T), particle class (Class), stirring speed (v), concentrations of sulphuric acid (C_{H2SO4}) or sodium nitrate (C_{NaNO3}). In this article, ANOVA was conducted to show the significant effects of independent variables on the responses, and to show which of the responses were significantly affected by the varying treatment combinations.

The adequacy of the developed models was tested using coefficient of determination (r^2), reduced chi-square (χ^2), mean bias error (MBE), root mean square error (RMSE), and mean percent error (MPE). These commonly used parameters can be calculated as follows [21]:

$$\chi^2 = \frac{\sum_{i=1}^{N}(y_{exp,i} - y_{pre,i})^2}{N - n},$$

$$RMSE = \left[\frac{1}{N} \times \sum_{i=1}^{N}(y_{pre,i} - y_{exp,i})^2\right]^{1/2},$$

$$MBE = \frac{1}{N} \times \sum_{i=1}^{N}(y_{pre,i} - y_{exp,i}),$$

$$MPE = \frac{100}{N} \times \sum_{i=1}^{N}\left(\frac{|y_{pre,i} - y_{exp,i}|}{y_{exp,i}}\right) \quad (11)$$

where: $y_{exp,i}$ stands for the experimental values and $y_{pre,i}$ are the predicted values obtained by calculating from the model for these measurements. N and n are the numbers of observations and constants, respectively.

RESULTS AND DISCUSSION

Characterization of chalcopyrite concentrate

The chalcopyrite concentrate was enriched during the flotation of a $CuFeS_2$–PbS–ZnS polymetallic ore in the "Rudnik" flotation plant (Rudnik–Serbia). Granulometric composition of the tailings was determined by wet sieving (37 μm sieve). Grain size of the residual fraction was determined by dry sieving using 50 μm and 75 μm sieves. Granulometric and chemical compositions of the tailings are presented in Table 1 [17]. Results of the chemical analysis show that grain size does not significantly affect the chemical composition of the concentrate.

Qualitative and quantitative mineralogical analysis revealed that the most abundant copper mineral in the concentrate was chalcopyrite (78.22 %), followed by sphalerite (6.29 %), galenite (2.63 %) and pyrrhotite (1.16 %). Dominant gangue minerals were quartz, silicates and carbonates [22]. Microscopic image of the concentrate sample is presented in Figure 1, showing liberated grains of chalcopyrite and one galenite grain.

Influence of particle size on the leaching degree of copper, Y_{Cu}(t, Class)

Copper extraction increased with decreasing particle size. Maximal copper extraction reached 69 % using -37 μm fraction. Smaller particles provided a larger contact surface for the chemical reactions with the oxidant. Particle size of -37 μm was used in the following experiments.

Table 1. Grain sizing and chemical composition of the chalcopyrite concentrate [17].

Particle size (μm)	Mass %	Element (%)			
		Cu	Fe	Zn	Pb
+ 75	7.32	23.38	22.25	3.43	4.08
- 75 + 50	21.15	26.55	24.43	4.28	1.70
- 50 + 37	5.18	26.95	24.75	4.36	1.85
- 37	66.35	27.08	25.12	4.15	2.28

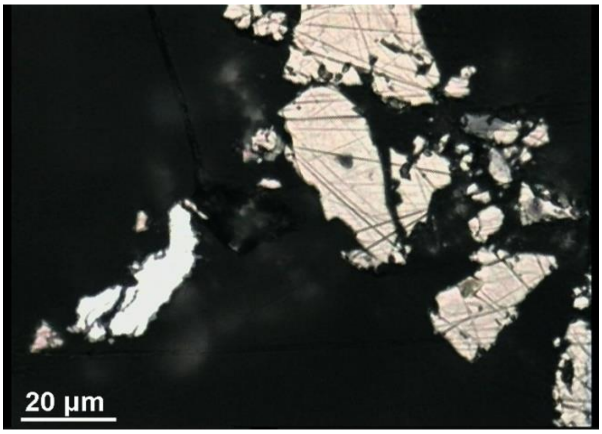

Figure 1. Liberated grain of chalcopyrite (yellow) and galenite (white). Reflected light, oil immersion, II N.

Influence of temperature on the leaching degree of copper, Y_{Cu} (t, T)

Copper extraction increased with increasing temperature. Maximal copper extraction was 75.5 % at 90 °C. The extraction of copper was rapid during the first 30 min of the experiment; after that period copper extraction was slower due to the formation of a sulphur passivation layer (chemical equations 3-5).

Influence of stirring speed on the leaching degree of copper, $Y_{Cu}(t, v)$

Stirring speed does not have a significant influence on copper extraction. Slight decrease in the leaching degree was observed at steering speeds higher than 100 rpm. Liquid turbulence created at higher steering speeds might interfere with the adsorption of oxidant on the surface of chalcopyrite.

Influence of sulphuric acid concentration on the leaching degree of copper, $Y_{Cu}(t, C_{H2SO4})$

Concentration of sulphuric acid has significant influence on copper extraction. The leaching degree increased from 47 % using 0.6 M H_2SO_4 to 75 % using 2.0 M H_2SO_4. This observed effect is explained by the fact that the oxidizing potential of NO_3^- ions increases with the increase in solution acidity [23].

Influence of sodium nitrate concentration on the leaching degree of copper, $Y_{Cu}(t, C_{NaNO3})$

As expected, increasing concentration of the oxidant $NaNO_3$ led to increased extraction of copper (Fig. 3e). Maximal copper extraction was 75 % after 240 min of leaching using 0.9M $NaNO_3$.

SOP models

Experimental results were fitted to the SOP models (Y_{Cu}(t, T); Y_{Cu}(t, Class); Y_{Cu}(t, v); Y_{Cu}(t, C_{H2SO4}), Y_{Cu}(t, C_{NaNO3})). As can be seen from the data in Figure 2, most of the terms in SOP models for prediction of the leaching degree of copper (Y_{Cu}) were statistically significant at $p<0.01$ level. The quadratic term *v* was statistically significant at $p<0.05$ level, while the quadratic term C_{H2SO4} was found statistically insignificant. The linear term *t* was the most influential one, no matter which other parameter was changed.

In the cases where interaction between factors was statistically significant, complete information regarding the effect of the factors on the responses can be perceived on the basis of the three-dimensional contour plots. The three-dimensional response surface plots (Figure 3) were plotted for experimental data visualization (experimental data are presented as white dots) and for the purpose of observation of the fitting of regression models to experimental data. The observed three-dimensional contour plot of Y_{Cu} surface showed a 'rising ridge' pattern. These graphics show a good correlation between experimental data and model results, as suggested by Madamba [24], which was also confirmed by the calculated coefficients of determination: 0.979; 0.991; 0.998; 0.994 and 0.981 for models: Y_{Cu}(t, T); Y_{Cu}(t, Class); Y_{Cu}(t, v); Y_{Cu}(t, C_{H2SO4}) and Y_{Cu}(t, C_{NaNO3}), respectively.

Experimental results have shown that temperature significantly affects copper extraction: the temperature increase is followed by an increase in the copper leaching degree [17]. Similar influence of temperature was obtained during leaching of chalcopyrite by potassium dichromate [25,26], and copper (I) sulphide by sodium nitrate and sulphuric acid [27]. At lower temperatures the molecules in the reaction system do not possess enough energy for chemical reactions. The dissolution of copper increased with increasing sulphuric acid and sodium nitrate concentrations, too. The oxidizing potential of NO_3^- ions increases with the increase of solution acidity, which contributes to the leaching of copper. Bredenhann and van Vuuren [28] and Vračar *et al.* [27] detected the same influence of $NaNO_3$ concentration during the leaching of nickel sulphide concentrate by sulphuric acid and sodium nitrate, while several other authors confirmed the similar effect of sulphuric acid concentration [25-27].

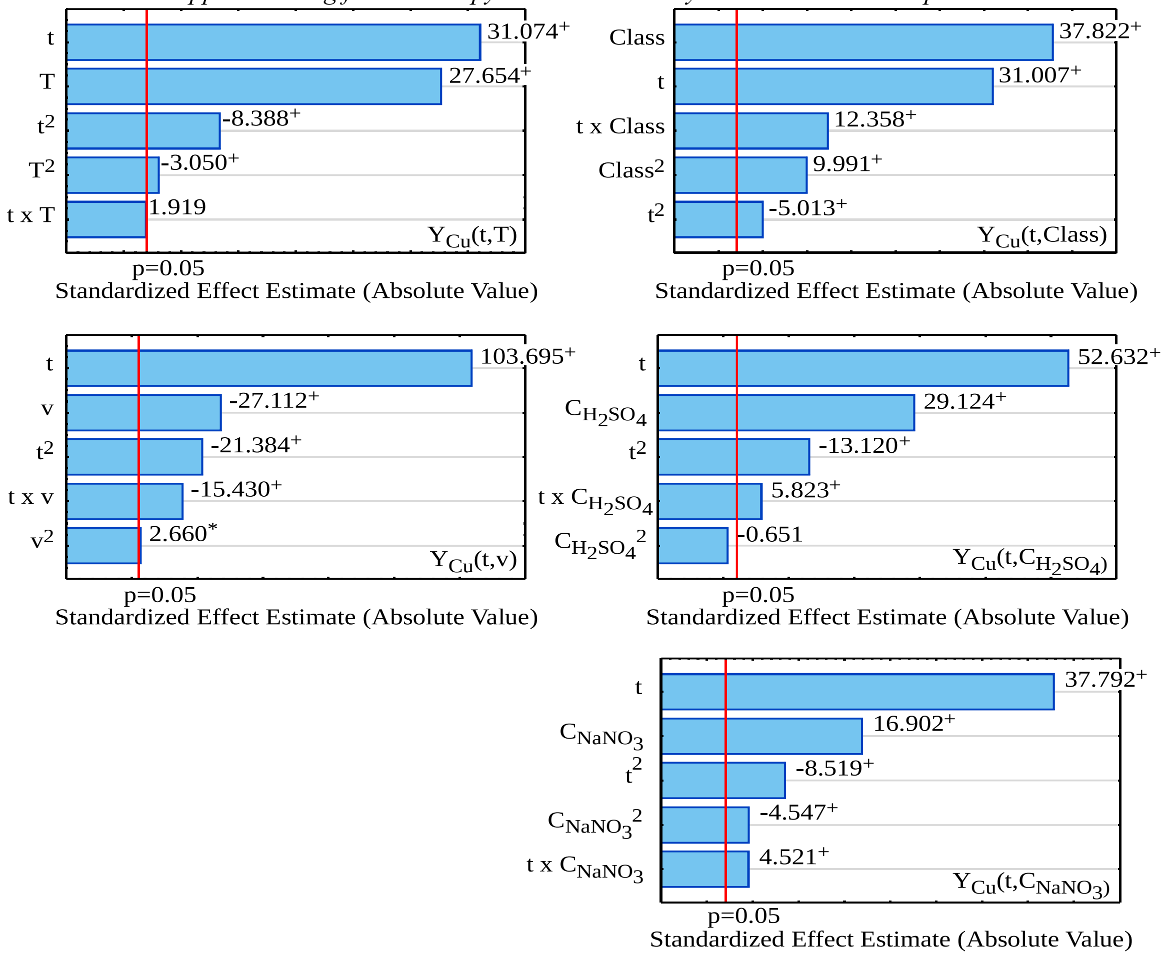

Figure 2. Pareto charts for Y_{Cu}(t, T); Y_{Cu}(t, Class); Y_{Cu}(t, v); Y_{Cu}(t, C_{H2SO4}) and Y_{Cu}(t, C_{NaNO3})

On the other hand, the reaction rate decreased with increasing particle size [17]. Smaller particles provided a larger contact surface between chalcopyrite and the oxidant [25,26,29].

The stirring speed did not significantly influence the rate of the chalcopyrite dissolution, but a slight decrease was observed, probably due to the poor adsorption capacity of chalcopyrite surface for nitrate ions. The same results were obtained during the leaching of chalcopyrite by hydrogen peroxide in the presence of ethylene glycol by Mahajan *et al.* [30]. Antonijević *et al.* [31] noticed that the rate of pyrite dissolution increased as the stirring speed decreased due to better contact between pyrite particles and peroxide. During the chalcopyrite leaching in the H_2SO_4+$K_2Cr_2O_7$ system, Aydogan *et al.* [26] noticed that chalcopyrite dissolution increased with increasing stirring speed up to 400 rpm, and thereafter the rate significantly declined.

Residual analysis

The quality of the model fit was tested in Table 1, the higher r^2 values, and the lower χ^2, RMSE, MBE, and MPE values show the better fit to the experimental results [21]. The residual analysis of the developed model was also performed. Skewness measures the deviation of the distribution from normal symmetry. If skewness is clearly different from 0, then the distribution is asymmetrical, while normal distributions are perfectly symmetrical. Kurtosis measures the 'peakedness' of a distribution. If kurtosis is clearly different from 0, then the distribution is either flatter or more peaked than normal; the kurtosis of the normal distribution is 0. The analysed mean values, standard deviations (SD), and the variance of the residuals are shown in Table 2. These results showed a good approximation to a normal distribution around zero with a probability of 95% (2 × SD), which means a good generalization ability of the developed model for the range of observed experimental data. SOP models had an insignificant lack of fit tests, which means that all the models represented the data satisfactorily.

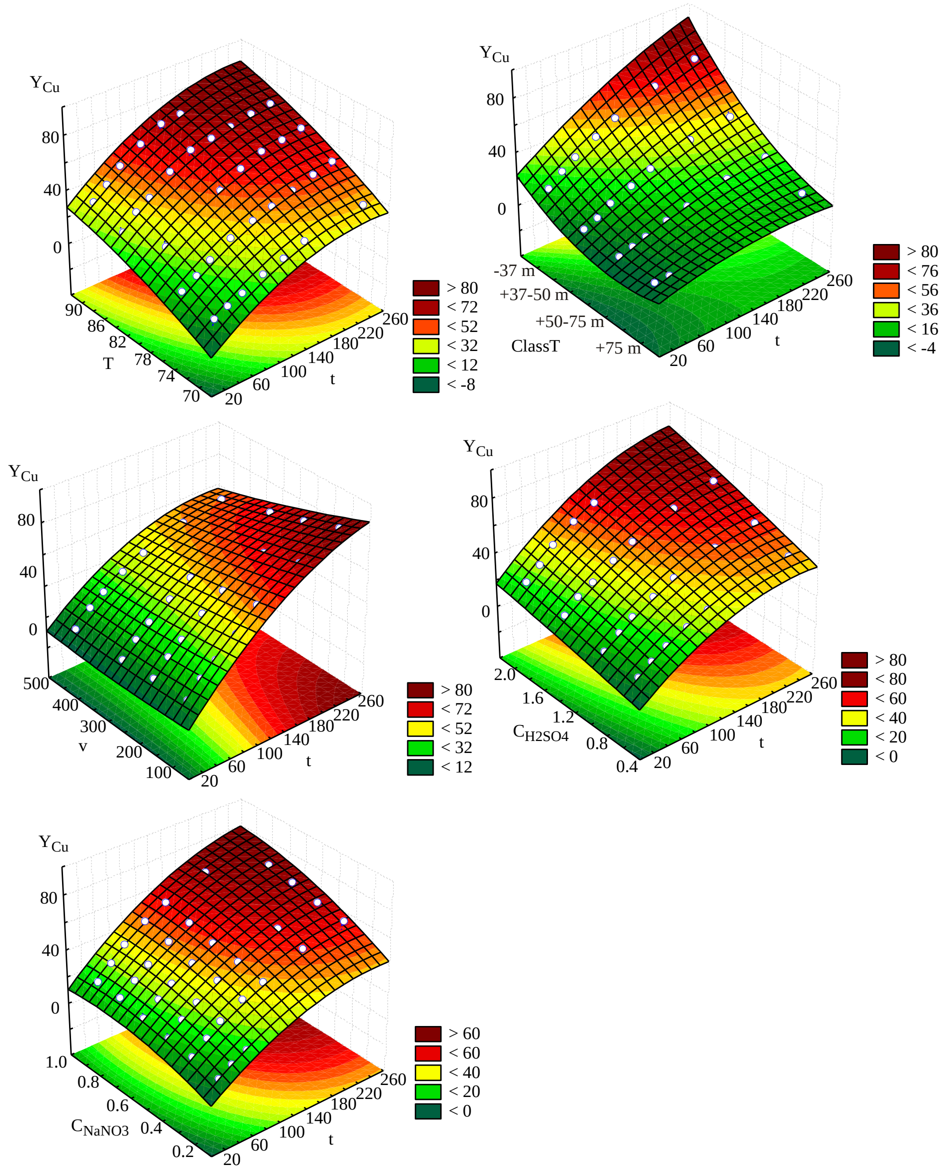

Figure 3. Three-dimensional contour plot of Y_{Cu} responses, affected by temperature (T), particle size (Class), steering speed (v), concentration of H_2SO_4 (C_{H2SO4}) and $NaNO_3$ (C_{NaNO3}).

Table 2. The 'goodness of fit' tests of the developed mathematical models

	χ^2	RMSE	MBE	MPE	r^2	Skew.	Kurt.	Mean	SD	Var.
Y_{Cu}(t, T)	8.6	2.9	-7.7E-14	7.4	0.979	0.254	-0.627	0.000	2.897	8.39
Y_{Cu}(t, Class)	3.0	1.7	2.3E-11	19.0	0.991	0.017	-1.105	0.000	1.688	2.85
Y_{Cu}(t, v)	0.7	0.8	-9.4E-15	2.0	0.998	-0.503	0.032	0.000	0.802	0.64
Y_{Cu}(t, C_{H2SO4})	2.0	1.4	-4.4E-15	3.5	0.994	0.369	-0.492	0.000	1.392	1.94
Y_{Cu}(t, C_{NaNO3})	6.7	2.5	-3.0E-15	6.0	0.981	0.259	0.434	0.000	2.560	6.55

CONCLUSION

The obtained relationship between the independent extrinsic factors (temperature, time, particle size, steering speed, concentration of H_2SO_4 and $NaNO_3$) and the dependent responses (targeted leaching degree of copper) could be a useful tool to assess and manage the optimal production parameters.

Results of laboratory experiments revealed that the leaching degree of copper from chalcopyrite concentrate increases with the increase in temperature, concentrations of H_2SO_4 and $NaNO_3$ and reduction of particle size, while462 the increase of steering speed slightly decreases the leaching degree of copper.

The responses predicted by the proposed model are in good agreement with the experimental data. Regardless of all the other raw materials and processing parameters the proposed models performed the prediction accurately within the range of observed set of values. The models tend to be universal and higher r^2 values and lower χ^2, MBE, RMSE and MPE values should be obtained. The developed SOP models were statistically significant as predicted and observed response variables correspond well.

The developed SOP models could be successfully implemented to optimize the copper leaching process from selected mineral raw materials.

Nomenclature:

T - temperature (°C)
t - time (min)
Class - particle class (μm)
v - stirring speed (rpm)
C_{H2SO4} - sulphuric acid concentration (M)
C_{NaNO3} - sodium nitrate concentration (M)
Y_{Cu} - copper leaching degree (%)

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