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OPTIMUM CONDITIONS FOR COPPER EXTRACTION FROM THE FLOTATION WASTE USING FACTORIAL EXPERIMENTAL DESIGN

Copper flotation waste, generated as a byproduct of pyrometallurgical copper production, contains a significant amount of Cu together with trace amounts of other toxic elements such as Fe, Sn, Sb, As, and Pb. It is usually disposed in uncovered tailing ponds in the vicinity of a copper smelter plant. Heavy metals released into the water and soil can cause a number of environmental problems. The amount of copper in copper flotation waste is high enough to be extracted economically using appropriate methods. In this study, the leaching characteristics of copper flotation waste from the Bor Copper Mine, Serbia, were investigated to assess the feasibility of copper extraction.

1. INTRODUCTION

Industrial solid waste containing toxic elements poses risks to human health and the environment, particularly when exposed to weathering, resulting with spontaneous leaching [1]. Products of leaching spill into a wide area of the waste yard and may enter groundwater, which may lead to larger ecological problems such as contamination of soil and groundwater in neighbouring countries [2]. Also it is a source of mineral dust which is dispersed in the form of PM_{10} and $PM_{2.5}$ [3, 4].

Copper is one of the most important materials in the development of civilization, being one of the oldest metals used. Copper is recovered from raw materials either by pyrometallurgy or hydrometallurgy. About 83% of the annual primary copper production is produced pyrometallurgically by smelting. The most important types of copper ores, for pyrometallurgical production, are sulfides. Before the smelting operation, copper ores are transformed into concentrates by flotation. Copper flotation waste

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(which refers to the remaining impurities), generally contains significant amounts of Cu together with trace elements of other toxic materials such as Fe, Sn, Sb, As, and Pb.

Copper flotation waste generated from copper industry is classified as hazardous waste according to European Union directive concerning integrated pollution prevention [5] as well as the Mining Waste Directive [6]. According to [7], for every ton of metal production ca. 2.2 ton of copper flotation waste is generated. Furthermore, approximately 24.6 million tons of copper flotation waste are generated each year from world copper production [8]. Because of this excess, copper flotation wastes are generally disposed of without any prior solid waste treatment in areas around the industry. Due to spontaneous leaching into water courses, disposed hazardous waste containing Cu and other toxic metals is highly dangerous pollutant affecting human health and the surrounding physical environment [1, 9].

Flotation is an important stage in transforming copper ore to copper concentrate, suitable for further smelting operation, and cannot be omitted. Ores used in modern Cu production generally have Cu contents of about 0.5%, thus requiring flotation concentration to obtain concentrates containing above 20% Cu [10]. To reduce transportation costs, flotation plants are usually located near the smelter. Accordingly, flotation tailings ponds are also located near copper smelter facility. This was also the case with the flotation tailing ponds in Bor copper mine (Serbia) which is located in close vicinity of the city, making a boundary between the urban and the industrial zone (Fig. 1). Mining production in Bor started more than one hundred years ago in 1903. The open pit facility was opened in 1912 and was active until 1986. The town of Bor was built, after the mining and metallurgical production started, in the vicinity of the mine and copper smelter plant. More than 40 000 people live in the town of Bor. An additional 20 000 inhabitants reside in the rural area around Bor.

Bearing in mind that waste was accumulated in earlier years without any processing, it is estimated that about 10^9 metric tones of waste have been stored at the Bor copper mine deposit [10]. Large areas covered with tailings are a source of mineral dust. The dust from this location, in the form of $PM_{2.5}$ and PM_{10}, is dispersed towards the urban area and the areas of fertile land depending on the wind rose and the time of the year.

In the wider area of the town of Bor, there are around 200 000 inhabitants whose health is imperilled by the soil and water contamination. This location is a very high-risk area per European standards [11, 12]. Research conducted by various authors [4, 11, 13] unmistakably shows that this area is the most polluted area in south-eastern Europe which forces the management of the company to take action aimed at global resolution of the problem.

On the other hand, complete remediation of the flotation tailings ponds requires huge investments. Many active mines in the world are affected by weathering of their tailing ponds [14–16]. This situation is worse after closure of the mine. Most often, flotation tailings ponds remain only partly stabilized, presenting a large environmental hazard [17, 18].

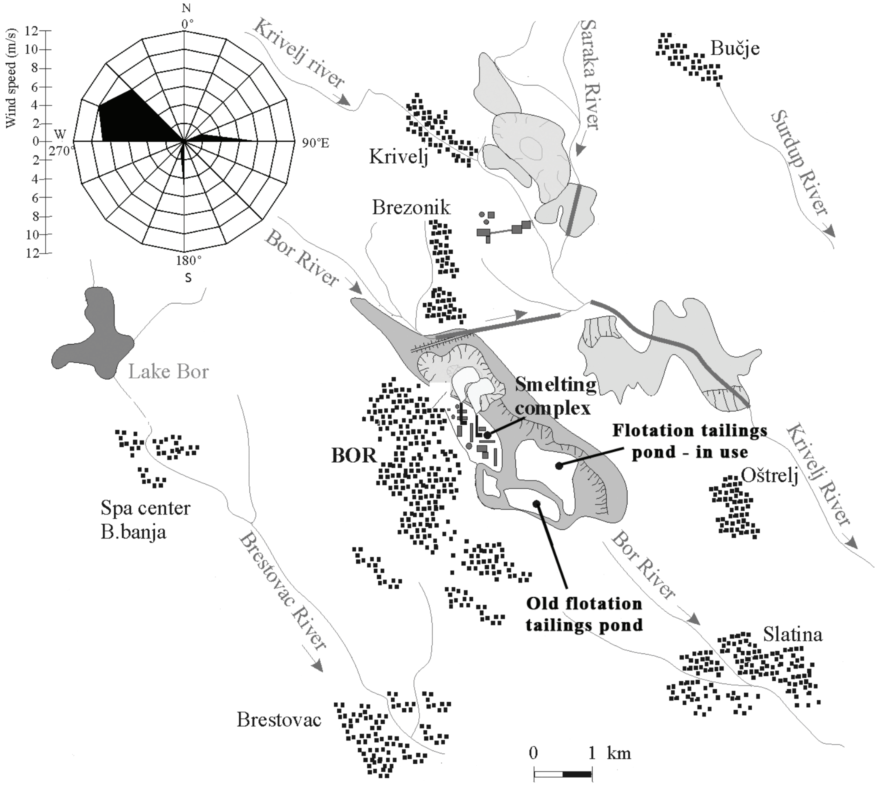

Fig. 1. Location of the flotation tailings ponds near the city of Bor

Several methods have been proposed to reduce or eliminate the problem arising from the flotation tailings ponds [10, 19–21]. One of the methods was based on acidic leaching of kaolinite from the flotation waste [10] which resulted with obtaining the kaolinitic concentrate containing 32% Al_2O_3. Other methods included vitrification of copper flotation waste [19], with possibility of subsequent leaching of vitrified product [20]. One of attempts was the immobilization of heavy metals in copper flotation waste using fly ash [21] followed with leaching in various leachants. The idea of the work presented in this paper is to investigate the possibility of copper utilization from the flotation waste collected from copper industry in Bor during the years of extraction. Having in mind high copper price at the Worlds market, this will generate additional income which could be partially used for remediation and safe disposal of the waste material remaining after copper extraction. This investigation is in continuance with the previous research [10] which revealed that the part of the flotation waste can also be safely removed in the form of the aluminate salt or alumina. In this previous research, the object of study was to obtain kaolinitic concentrate from the flotation waste and to investigate the possibility of its further processing with the aim of alumina extraction. Prior to leaching process, the influence of the thermal treatment on the starting kaolinite concentrate on fractional conversion during leaching was investigated. The heated samples were subsequently leached in sulfuric acid, nitric acid and hydrochloric acid. After determined the optimal conditions for Al_2O_3 removal from copper flotation waste, it was decided to investigate the possibility of utilization of copper from the same starting material. Results of investigations are presented in this paper.

Investigations on leaching methods to extract copper from the flotation tailings of the Bor Copper Mine were the subject of interest of many researchers in the past. Experiments were performed by a number of scientific and research institutions. Chemical compositions of the starting samples, potential experimental conditions as well as the results obtained in these investigations are presented elsewhere [1]. The investigations presented in the paper [1] included determining the influence of sulfuric acid concentration, pulp density (solid to liquid ratio), stirring speed, the time and the temperature on copper recovery from the starting material. The results showed that leaching with sulfuric acid resulted in relatively low copper dissolution values, which was a limiting factor for further treatment of tailings. Also, based on the results of the investigations presented in the reference [1], it is not possible to develop a model that could be used to predict the outcome of the leaching experiments and optimization of starting conditions of the process. This is because each of the experimental variables were analyzed separately (in combination of two factors) and not as a whole. For example, in one set of experiments, copper recovery was investigated in function of leaching time and the temperature. In other set of experiments, it was a function of leaching time and the sulfuric acid concentration, etc.

The approach undertaken in the current study was different. The method of factorial experimental design applied on obtaining the mathematical model which will include all experimental factors at the same time, is proposed in this study. The most important experimental factors and the possible range of each experimental variable values, as the starting point of the modelling procedure were based on literature review and previous research. For the purpose of modelling copper extraction dependence on various experimental factors in expanded range of values, we used the factorial experimental design method. As the result of this approach, it is possible to design the experimental setup with the optimum process conditions that might yield the highest copper utilization. The method and the results are further discussed in following sections of the paper.

2. EXPERIMENTAL

To obtain a reliable statistical model, prior knowledge of the procedure is generally required. Three steps used in the experimental design include statistical design of experiments, estimation of coefficients through a mathematical model with response prediction, and statistical analysis [22].

Today, the most widely used experimental design to estimate main effects as well as interaction effects is the 2^n factorial design, where each variable (X_i, $i = 1– n$) is investigated at minimum two levels [23, 24]. As the number of factors (n) increases, the number of runs for a complete replicate of the design also increases rapidly. Modelling can be performed using the first order model, defined by the equation:

$$y = b_0 + \sum_{i=1}^{n} b_i x_i + \sum_{i=1}^{n} \sum_{j>1}^{n} b_{ij} x_i x_j \tag{1}$$

or the second order model, which is:

$$y = b_0 + \sum_{i=1}^{n} b_i x_i + \sum_{i=1}^{n} b_{ii} \left(x_i^2 - \overline{x_i^2} \right) + \sum_{i=1}^{n} \sum_{j>1}^{n} b_{ij} x_i x_j \tag{2}$$

where:

$$\overline{x_i^2} = \frac{1}{N} \sum_{i=1}^{N} x_i^2 \tag{3}$$

where N is the total number of experiments, including the holdout cases.

This way, with following approximation:

$$b_0' = b_0 - \sum_{i=1}^{n} b_{ij} \overline{x_i^2} \tag{4}$$

the second order model can be presented as:

$$y = b_0' + \sum_{i=1}^{n} b_i x_i + \sum_{i=1}^{n} b_{ii} x_i^2 + \sum_{i=1}^{n} \sum_{j>1}^{n} b_{ij} x_i x_j \tag{5}$$

The estimation of the accuracy of developed model (both of the first or second order) can be assessed using the root means squared error (RMSE) calculation between the model predicted and experimentally obtained value of the output variable, applied on the holdout cases which are added to the experimental plan to estimate pure experimental errors.

$$\text{RMSE} = \sqrt{\frac{1}{m_0} \sum_{i=1}^{m_0} \left(y_i - y_i' \right)^2} \tag{6}$$

where y_i is model predicted and y_i' – the actual value of the output variable, m_0 is the number of holdout cases.

3. EXPERIMENTAL

Representative samples of the flotation waste were obtained from exploration borehole cores taken at the depth of 10 m. Sampling was organized by Mining and Metallurgical Institute (Bor, Serbia) during the summer of 2010. The samples were dried and subsequently homogenized. Homogenization of the samples was performed using the cone and quartering method. Particle size distribution in a sample was determined by the sieve analysis on a standard Tyler sieve series. The results of the granulometric analysis are presented in Fig. 2.

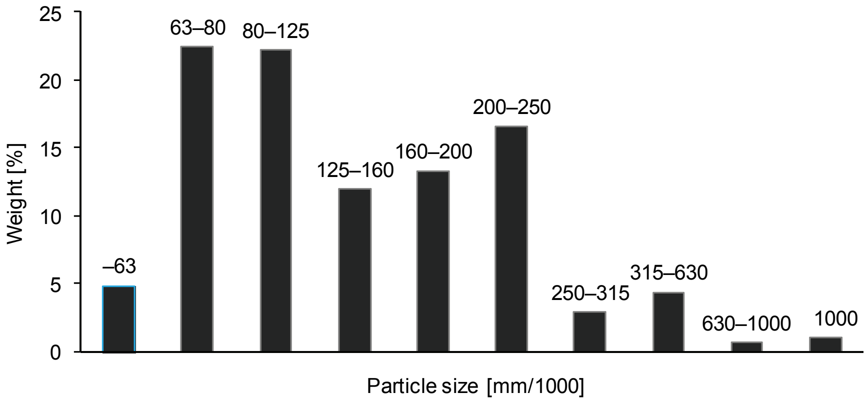

Fig. 2. Particle size distribution in a sample of flotation tailings

Table 1

Chemical characterization of the flotation tailings

Component	Concentration [wt. %]	Component	Concentration [wt. %]
Cu_{cum}	0.24	SiO_2	56.72
Cu_{ox}	0.05	Al_2O_3	12.64
Cu_{sulf}	0.235	Fe	8.65
S	10.56	Zn	0.005
As	0.026	Mn	0.011
Pb	0.003	CaO	0.95
Sn	0.0071	MgO	0.052
Sb	0.003	remaining	<10
Ba	0.0048	Au (g/t)	0.1
Sr	0.011	Ag (g/t)	1.1

Chemical composition of flotation tailing sample is given in Table 1. Chemical analyses included energy dispersive X-ray fluorescence (EDXRF) coupled with ICP

–AES. Energy dispersion X-ray fluorescence analysis was done on Canberra equipment with the radioisotopes: Cd 109 (22.1 keV) and Am 241 (59.5 keV). ICP–AES analysis was performed on an atomic emission spectrometer (model Plasma Vision 3410+ARL). Figure 3 shows the results of EDXRF analysis of investigated sample.

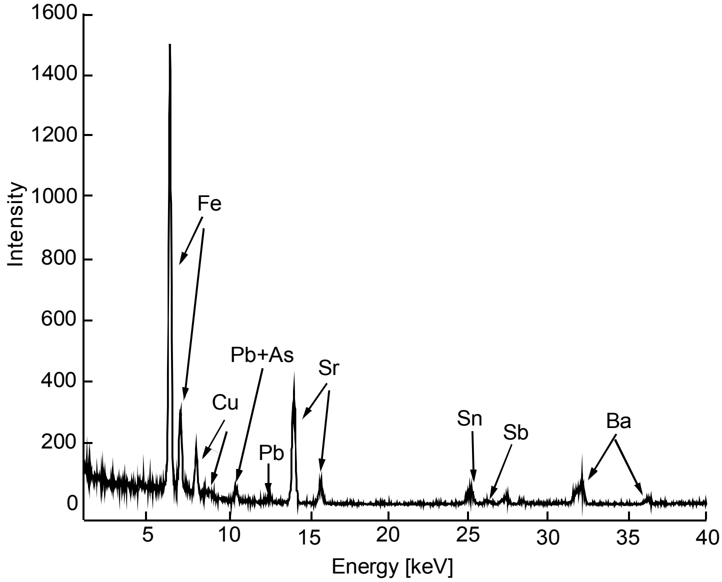

Fig. 3. EDXRF spectrum of the starting flotation waste sample: excitation source – ^{241}Am, measurement time – 1800 s, starting sample weight – 300.0 mg

Table 2

Factor levels

Factor	Level		
	high (+)	medium (0)	low (–)
Solid-to-liquid ratio during sulfatisation (X_1)	100 : 1	50 : 1	10 : 1
Sulfatisation temperature, °C (X_2)	250	150	25
Sulfatisation time, h (X_3)	12	6	1
Solid-to-liquid ratio during leaching (X_4)	1 : 1	1 : 2	1 : 4
Leaching temperature, °C (X_5)	80	50	25
Leaching time, min (X_6)	60	40	20
Stirring speed, rpm (X_7)	600	300	100
Sulfuric acid concentration, M (X_8)	1.5	1	0.4

Copper extraction from the samples was performed according to the following procedure. Flotation waste samples weighting 50 g were mixed with solution of sulfuric acid with different solid to liquid ratios and different H_2SO_4 concentrations as indicated in Table 2. A small amount of water (7 to 10 cm^3) was added to the sample forming a pulp. Prepared samples were then placed in ceramic crucibles and heated in the range 25–250 °C. The time intervals of sulfatisation varied according to the levels presented in Table 2. After sulfatisation, the samples were leached in water, in a 1000 cm^3 glass reactor equipped with an electromagnetic stirrer. Solid to liquid ratios, time intervals, leaching temperatures and agitation rates were in the ranges presented in Table 2.

4. RESULTS AND DISCUSSION

As indicated in the previous section, eight factors, namely, raw material to the sulfuric acid (solid to liquid) ratio (variable X_1), sulfatisation temperature (variable X_2), time period of sulfatisation (variable X_3), solid to liquid ratio during leaching (variable X_4), leaching temperature (variable X_5), leaching time interval (variable X_6), the rate of agitation (variable X_7) and the sulfuric acid molar concentration (variable X_8) were selected as characteristic process parameters. The high, medium and low levels of all factors are given in Table 2.

Table 3

Experimental design and copper leaching yield

No.	X_1	X_2	X_3	X_4	X_5	X_6	X_7	X_8	Leaching yield [%]	No.	X_1	X_2	X_3	X_4	X_5	X_6	X_7	X_8	Leaching yield [%]
1	–	0	+	–	0	+	+	+	6.30	18	+	0	–	0	–	0	+	0	2.87
2	0	+	+	–	+	–	–	0	13.04	19	–	0	–	+	–	+	–	–	4.87
3	+	+	0	+	–	0	–	+	5.17	20	+	–	0	–	0	–	+	–	2.39
4	–	–	+	+	–	–	–	0	2.43	21	–	+	–	+	+	0	+	0	2.61
5	+	0	0	0	+	+	0	0	2.61	22	–	+	+	–	+	+	0	+	89.57
6	+	–	+	–	–	0	0	–	7.51	23	–	–	–	0	0	+	–	–	2.96
7	–	0	–	–	–	–	0	+	5.61	24	+	+	–	–	+	+	–	–	2.39
8	0	+	+	–	–	+	0	0	4.35	25	–	+	0	0	–	–	+	–	1.74
9	0	0	0	+	+	–	+	–	2.52	26	–	0	–	+	0	–	0	+	2.87
10	–	0	0	–	+	0	–	+	3.91	27	+	+	+	+	0	0	0	–	3.13
11	–	+	–	–	0	0	+	0	64.17	28[a]	0	+	0	–	–	–	0	0	2.83
12	0	–	0	0	0	0	–	+	2.17	29[a]	–	+	–	0	–	–	+	0	23.48
13	0	–	–	0	+	–	0	+	2.26	30[a]	0	–	0	–	0	–	+	0	15.61
14	+	0	+	0	0	–	–	0	3.04	31[a]	0	–	–	–	+	+	0	0	62.39
15	–	–	0	+	0	+	0	0	2.43	32[a]	0	0	–	0	0	0	–	–	13.57
16	–	+	+	0	+	0	0	–	19.13	33[a]	0	–	+	–	+	0	+	+	22.83
17	0	–	+	0	–	+	+	+	8.61										

[a]Holdout case.

A first order model was used to fit the experimental data. With eight factors, and three factor levels, SPSS software (SPSS v. 18) suggested a factorial experimental design that requires 27 runs. Six holdout cases were added to the experimental plan to estimate pure experimental errors (Table 3). Experiments were run in random order to avoid systematic errors. After conducting all 33 experiments, results of copper extraction were included in the database as the output variable Y (Table 3). Experiments 31, 32 and 33, were repeated to asses the replicability of the experimental results obtained. Results of repeated experiments were in accordance with results presented in Table 3, with the error of ±0.5%. Using the multiple linear regression analysis (MLRA), on the results of the first 27 experiments, a first order model (Eq. (1)) was obtained. The values of the model coefficients which have statistical significance $p < 0.01$ are given in Table 4.

Table 4

First order model of the process of copper extraction from flotation waste

Model	*b* unstandardized	Standard error	Beta standardized	*t*	Significance (p)
Constant	–30.513	18.319		–3.29	0.004
X_1	–0.401	0.4	3.2	4.119	0.001
X_5	0.743	0.456	–2.226	–4.114	0.001
X_6	0.819	0.304	1.409	5.14	0.000
X_1X_2	–0.001	0.001	–1.509	–3.097	0.007
X_1X_5	–0.002	0.004	–1.125	–2.394	0.028
X_2X_4	–0.219	0.089	–1.772	–4.954	0.000
X_2X_5	0.004	0.002	2.718	5.457	0.000
X_2X_8	0.075	0.052	0.642	1.972	0.065
X_3X_4	5.215	2.209	2.075	5.01	0.000
X_3X_6	–0.108	0.062	–3.123	–4.264	0.001
X_3X_7	0.002	0.003	1.888	3.000	0.008
X_3X_8	0.793	1.162	–0.928	–2.544	0.021
X_5X_8	0.314	0.229	1.714	4.067	0.001

Based on these results, the following final model equation resulted from the regression analysis:

$$\begin{aligned} Y = &-30.513 - 0.401X_1 + 0.743X_5 + 0.819X_6 - 0.001X_1X_2 - 0.002X_1X_5 \\ &- 0.219X_2X_4 + 0.004X_2X_5 + 0.075X_2X_8 + 5.215X_3X_4 - 0.108X_3X_6 \\ &+ 0.002X_3X_7 - 0.793X_3X_8 + 0.314X_5X_8 \end{aligned} \tag{7}$$

According to the coefficients in the Eq. (7), it is possible to analyze the regression equation and to determine the effect of each factor. Accordingly, the regression equation shows the principal effects of the eight selected factors on copper yield. If observing only the unstandardized coefficients (b unstandardized in Table 4), the leaching time (X_6) has the strongest effect on the response since the corresponding coefficient ($b = 0.819$) is larger than the coefficients of the other investigated factors. The positive sign of this coefficient indicates that an increase in the leaching time improves copper extraction from the flotation waste. Another important factor is leaching temperature (X_5 with $b = 0.743$). This coefficient also has a positive sign indicating that increase of leaching temperature leads to better copper yield. On the other hand, solid to liquid ratio during sulfatisation (X_1) has a negative impact on copper extraction as expected ($b = 0.401$). The design of experiments for copper extraction, after leaching from flotation waste, also exhibits interactions between various factors studied, the strongest one being between the sulfatisation time (X_3) and the solid to liquid ratio during leaching (X_4), with $b = 5.215$. However, if analyzing the coefficient obtained after standardization of the input variables (beta standardized in Table 4), which removes the effect of magnitude of the value of different variables; the situation seems to be different. It can be concluded that the solid to liquid ratio during sulfatization (X_1) has the principal effect on the copper leaching yield. Accordingly, the interaction between the sulfatization time (X_3) and the leaching time (X_6) has the largest influence on copper extraction among all combined variables. However, according to the similar values of the t coefficients, for almost all investigated factors (Table 4), it can be concluded that all statistically significant variables do have influence on copper extraction from the flotation waste.

Internal validity of the obtained model was than tested using control tests made on six holdout cases presented in Table 3. After calculating the root means squared error (Eq. (6)) between the model predicted and experimentally obtained copper extraction for holdout cases, it was concluded that the data obtained experimentally and the model estimations are in good agreement. Reliability of the model was further tested using the ANOVA test. The results of ANOVA tests of developed model are presented in Table 5.

Table 5

Results of ANOVA test of finally obtained first order model

Source	Sum of squares	Degrees of freedom	Mean squares	F	Significance
Regression	11075.52	12	626.86	56.341	0.007
Residual	2268.67	15	219.41		
Uncorrected total	13 344.19	27			

Dependent variable: Y

Significant *F* statistics (Table 5) indicates that using the model is better than guessing the mean [25, 26]. Also, the significance value of the *F* statistic is lower than 0.05, which means that the variations explained by the model are not caused by chance. The ratio of regression to residual is 83:17, advocating that 83% of the dependent variable (*Y*) values are explained by the model. The coefficient of determination of the final model R^2 is 0.834, as shown in Fig. 4. Its large value indicates a strong relationship between observed and the model predicted values of the dependent variable. Also, standard error estimate (SEE) for the model was calculated, equalling 2.723. Thus the obtained first order model may be used to predict copper extraction from the flotation waste with satisfying accuracy. This way, development of the experimental plan for the second order model, was not necessary. Namely, second order model would require wider range of investigated experimental factors (independent process variables). Usually, design of experiments for the second order model requires five experimental levels instead of three being defined for the first order model (Table 2). Also, this would require additional number of experiments.

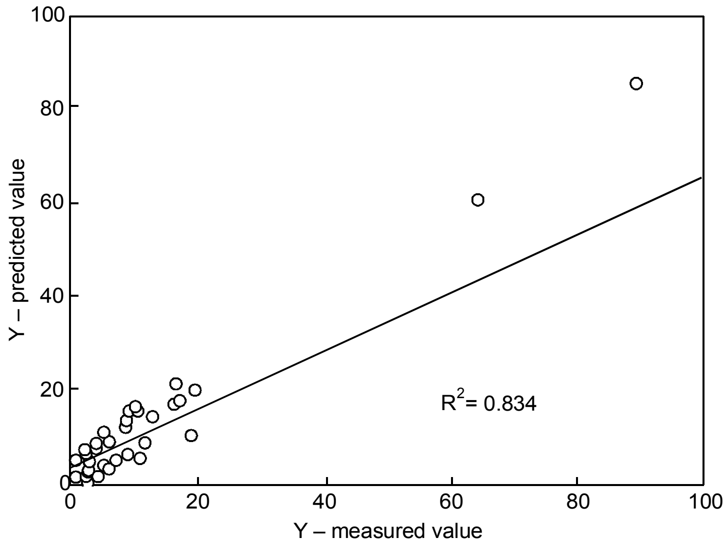

Fig. 4. Correlation between values experimentally determined and predicted by the model of copper extraction from the flotation waste (straight line – regression line, circles – values calculated using the final MLRA model)

Using the final model equation (Eq. (7)), which predicts the amount of copper extraction accurately enough (R^2 = 0.834), it is possible to determine optimum conditions for operations management of the process, since the model fits the experimental results well enough. Optimization consists of finding such a set of operational variables values which would result in optimum extraction yield of copper. The localization of the optimum set of operational variables can be obtained in various manners [22]. However, the layout of the surface contours plot is the easiest method to interpret based on a model equation.

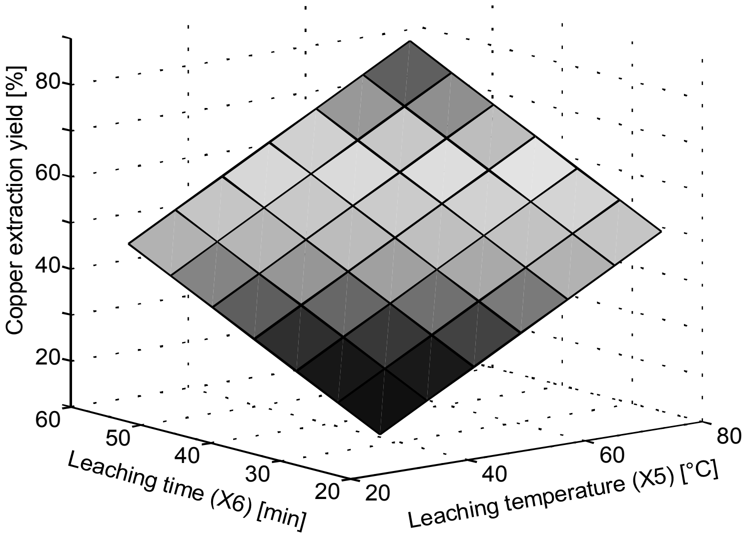

Fig. 5. Response surface for copper extraction in the plane leaching temperature or leaching time at optimum values of remaining variable (Exp. No. 22)

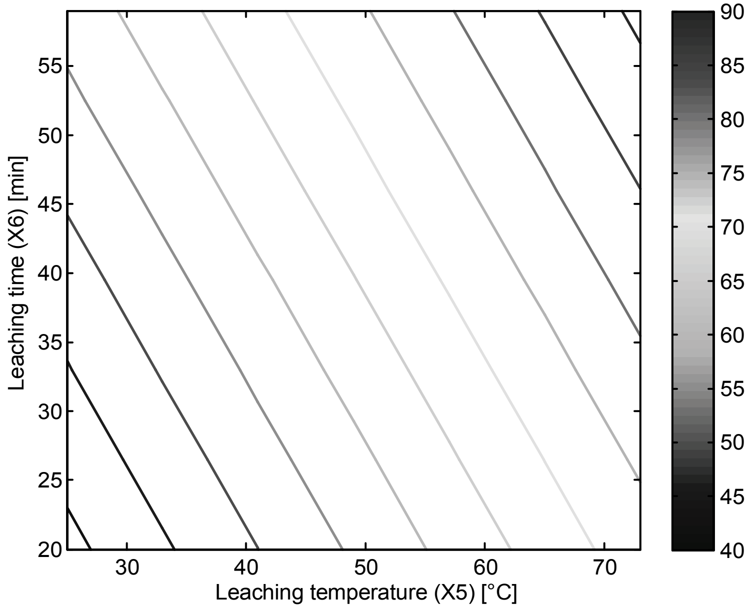

Fig. 6. Response contour for copper extraction in the plane leaching temperature or leaching time at optimum values of remaining variable (Exp. No. 22)

The surface contour plots were analyzed using Matlab 7.0 software [27] to determine the optimum solution. The response surface and contour plots given in Figs. 5 and 6 are drawn in the plane leaching temperature–leaching time when the remaining variables are kept at their optimum values responding to the experiment No. 22 (Table 3). These curves allow us to determine the region of the work domain where copper extraction from the flotation waste is optimum. Accordingly, if the solid to liquid ratio during sulfatization (X_1) is 10:1, sulfatization temperature (X_2) – 250 °C, sulfatization time (X_3) – 12 h, solid to liquid ratio during leaching (X_4) – 1:1, stirring speed (X_7) – 300 rpm and the sulfuric acid molar concentration (X_8) – 1.5 M, the copper extraction yield can reach 90% if leaching the flotation waste for 60 min above 70 °C. This way optimum copper yield predicted by the model is 90%, which agrees closely with the experimental copper yield of 89.77% in experimental run 22. The solution after the leaching process under these conditions contains 0.95 g/dm^3 of copper. The acidity level of the leachate is pH = 2.3. Concentration of copper being collected in the solution can be improved using solvent extraction [28].

5. CONCLUSIONS

The efficiency of copper extraction from flotation waste was found to be a function of: solid-to-liquid ratio during sulfatisation, sulfatisation temperature, sulfatisation time, solid-to-liquid ratio during leaching, leaching temperature, leaching time, stirring speed and sulfuric acid concentration. The obtained linear correlation dependence with R^2 = 0.834 was calculated using the experimental data acquisition, with experiments prepared according to the factorial experimental design method.

The proposed model can be used to determine the experimental conditions that can produce optimal copper extraction after sulfatisation leaching of copper flotation waste. Using the model equation could serve to further analyze the influence of each process variable on copper yield. Also, it can allow testing the possibility of extrapolating the values of process variables outside the ranges defined in this investigation. This would be the subject of our further investigations.

Utilization of copper flotation waste in copper production has both economical and ecological aspect. High copper price on the worlds market is making this project sustainable. Also, the finance accumulated after selling copper, can be used for remediation and safe disposal of the waste material, remaining after copper extraction from this flotation tailing pond located in the vicinity of the town of Bor.

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