A STUDY on the OPTIMUM CONDITIONS of the CEMENTATION of COPPER in CHLORINATION SOLUTION of CHALCOPYRITE CONCENTRATE by IRON SCRAPS

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Abstract

Present study aims an experimental design based on the approach of Taguchi method to optimize of cementation of copper in chlorination solutions of chalcopyrite concentrate neutralized with oxidized copper ore by iron scraps. The concentrations of Fe^{3+}, Cu^{2+}, H^{+}, SO_4^{2-} and Cl^{-} ions in the chlorination solution obtained under predetermined optimum conditions were 14.6, 4.0, 2.6, 2.2 and 124.3 gmL^{-1}, respectively.
The ranges of experimental parameters were between 20-40 ^oC for reaction temperature, C/5-C/15 $g.L^{-1}$ for concentration of leach solution, 300-600 rpm for stirring speed and 20-60 min for reaction time. Where, C is the concentration of the original chlorination solution.
After pH of the chlorination solution was set to 1.5 by adding oxidized copper ore, the cementation was carried out with iron scraps and the optimum conditions were found to be as follows: reaction temperature 40 ^oC, concentration of leach solution C/5 $g.L^{-1}$, stirring speed 450 rpm; and reaction time 40 min. Under these conditions, the percentage of copper obtained by cementation from aqueous solution was 98.35 %.

Keywords: Taguchi Method, chalcopyrite, copper, cementation.

KALKOPİRİT KONSANTRESİNİN KLORİNASYONU İLE ELDE EDİLEN ÇÖZELTİDEKİ BAKIRIN DEMİR TALAŞI İLE SEMENTASYONUNA AİT OPTİMUM ŞARTLARIN BELİRLENMESİ ÜZERİNE BİR ÇALIŞMA

Özet

Bu çalışma oksitli bakır cevheri ile nötürleştirilmiş kalkopirit konsantresinin klorinasyon çözeltisindeki bakırın demir talaşı ile semantasyonunu optimize etmek için Taguchi yaklaşımına dayalı bir deneysel tasarımı amaçlamaktadır. Daha önceden belirlenen optimum şartlar altında elde edilen klorinasyon çözeltisindeki Fe^{3+}, Cu^{2+}, H^{+}, SO_4^{2-} ve Cl^{-} iyonlarının konsantrasyonları sırası ile 14.6, 4.0, 2.6, 2.2 and 124.3 $g.L^{-1}$ şeklindedir. Deneysel parametrelerin aralığı 20-40 ^oC reaksiyon sıcaklığı, C/5-C/15 klorinasyon çözeltisi konsantrasyonu, 300-600 devir/dakika karıştırma hızı ve 20-60 dakika reaksiyon süresi aralığındadır. Burada C orijinal klorinasyon çözeltisinin konsantrasyonudur.
Klorinasyon çözeltisinin pH'sı oksitli bakır cevheri ilave edilerek 1,5'e ayarlandıktan sonra demir talaşı ile semantasyon gerçekleştirildi ve optimum şartlar reaksiyon sıcaklığı 40 ^oC, liç çözeltisinin konsantrasyonu C/5 g/L^{-1}, karıştırma hızı 450 devir/dakika ve reaksiyon süresi 40 dakika olarak bulundu.Bu şartlar altında semantasyonla sulu çözeltiden elde edilen bakır yüzdesi % 98,35 oldu.

Anahtar Kelimeler: Taguchi Metodu, kalkopirit, bakır, sementasyon

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1. INTRODUCTION

During last forty years, it has been seen important innovation, development and growth in the field of hydrometallurgical methods. The precipitation reaction of a more noble metal from the solution of its salts by a less noble one is called as cementation, and the general reaction for a cementation process is given by: $mN^{n+}_{(aq)} + nM_{(s)} \Leftrightarrow nM^{m+}_{(aq)} + mN_{(s)}$ where N represents the noble metal and M less noble or the reductant metal(1,2). The cementation reaction is widely used in industry for the recovery of metals and purification of electrolyte solutions.

There are so many studies on cementation and cementation kinetics of copper in literature. Dönmez et al.(1) carried out a kinetic study of the cementation of copper from sulphate solutions onto a rotating aluminum disc and determined that the diffusion of the reactants through fluid layer was the rate controlling step with an activation energy of 14.1 $kJ.mol^{-1}$. Sahoo and Rath(3) examined recovery of lead from complex sulphide leach residue by cementation with iron and found that the rate of cementation of lead by metallic iron proceeded in two stages with activation energies of 40 and 60 $kJmol^{-1}$.In a study carried out by Annamlai and Murr(4), the kinetics of copper cementation on pure iron substrates were studied using a rotating disc geometry. The authors found the optimum values of each parameter for maximum cementation rate as well. Copper recovery by the cementation method was also studied by Stefanowicz et al.(5) and they showed that copper ions can be effectively removed from sulphate type copper electroplating waste solutions by using scrap iron. The cementation method has been widely investigated in different studies such as cementation of copper by iron(6), gold onto zinc(7), cobalt, nickel and cadmium by zinc metal(8), cobalt from an industrial zinc electrolyte in the presence of Cu, Cd, Pb, Sb and Sn additives(9), copper from cyanide liquors using zinc(10), silver ions onto copper from acidic sulphate solutions(11), lead from ammonium sulphate solution(12) and copper from complex sulphide leach liquor(13). There are several studies also dealt with the effect of chlorine gas to chalcopyrite (14, 15).

The optimization of leaching conditions of the ores is important in industrial processes, and some researchers have been interested in these topics by using various techniques (1, 16-22). As a technique, Taguchi's Orthogonal Array (OA) analysis is used to produce the best parameters for the optimum design process, with the least number of experiments. In recent years, Taguchi method has been used to determine optimum parameters because of its advantages. The main advantages of this method over other statistical experimental design methods are that the parameters affecting an experiment can be investigated as controlling and not controlling, and that the method can be applied to experimental design involving a large number of design factors (21).

The present study aims an experimental design based on the approach of Taguchi method to optimize of cementation of copper with iron scraps in solutions obtained with chlorination of chalcopyrite concentrate in aqueous media. The cementation temperature, concentration of leach solution, stirring speed and cementation time were chosen as parameters.

2. MATERIALS AND METHODS

The chalcopyrite concentrate used in this study was provided as powder from Çayeli, Rize in Turkey and sieved by using a 75 µm ASTM standard sieve. Chemical analysis of concentrate was given in Table 1. X-ray diffractogram of chalcopyrite concentrate obtained by Rigaku DMAX 2000 Series X-ray diffractometer is given in Figure 1. It is seen that the

Table 1. Composition of the chalcopyrite concentrate.

Constituents	Percent by weight
Cu	24.02
Fe	29.36
S	36.55
Zn	2.19
Pb	0.19
Al_2O_3	0.1
moisture	0.9
other components	6.69

Table 2. Composition of the malachite ore

Constituents	Percent by weight
CuO	15.94
Fe2O3	6.20
Al2O3	0.48
Mn2O3	1.2
CaO	4.24
MgO	0.34
SiO2	49.8
ZnO	7.61
Heating loss	13.16
Other components	1.03

concentrate contains $CuFeS_2$, FeS_2, ZnS, Cu_2S, CuS and very small amount of Al_2O_3 and SiO_2. Enough chlorination solution was obtained by adding enough amount of chalcopyrite concentrate to certain volume water saturated with chlorine gas under the predetermined optimum conditions which temperature, solid to liquid ratio, (Fe^{3+}), (Cu^{2+}) and reaction time were 45°C, 0.05 g.mL^{-1}, 0.2 g.mL^{-1}, 0.025 g.mL^{-1} and 120 min. respectively(23). The concentrations of Fe^{3+}, Cu^{2+}, H^+, SO_4^{2-} and Cl^- ions in the chlorination solution obtained under these conditions were 14.6, 4.0, 2.6, 2.2 and 124.3 gmL^{-1}, respectively. The oxidized copper ore used in this study was provided from Maden, Elazığ in Turkey, ground and sieved by using a 150µm ASTM standard sieve. Chemical analysis of oxidized copper ore was given in Table 2. Dissolution experiments were carried out in a 250 mL jacketed glass reactor at atmospheric pressure. The reactor contents were mixed by a mechanical stirrer with tachometer and its temperature was controlled by a constant temperature circulator.

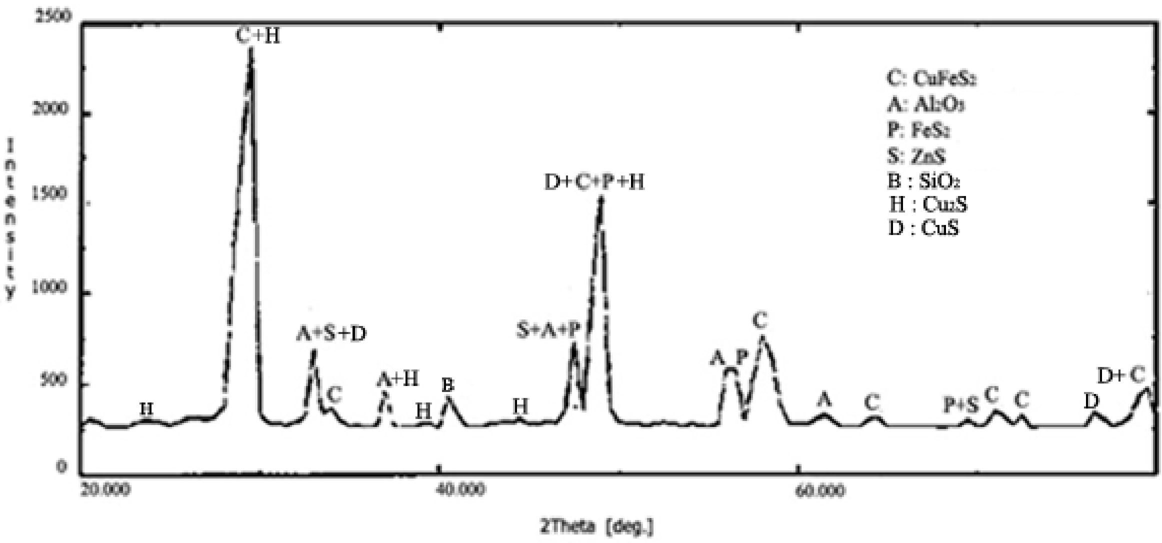

Figure 1. X-Ray diffractogram of the chalcopyrite concentrate

The reactor was fitted with a cooler to prevent the volume reduction of the solution by the evaporation. A diluted part of the chlorination solution (whose concentration was specified by C) was used to dissolve the oxidized copper ore. Therefore, a certain volume of this acidic solution was diluted with distilled water according to desired concentration, put to the reactor and then added the oxidized ore upon it till the pH value was 1.5. When the pH value was above 1.6, it was seen that the Fe^{3+} ions in the solution began to precipitate as $Fe(OH)_3$. Since $Fe(OH)_3$ precipitation caused some separation problems during the period of recovering copper by cementation, the factor determining amount of added oxidized copper ore was pH value of medium. According to examined leaching concentration, the required amounts of oxidized copper ore to bring the pH value to 1.5 were given in Table 3. After the added

Table 3. The amount of oxidized copper ore added to solution to bring the pH value to 1.5.(C is concentration of the original stock solution obtained by dissolution of chalcopyrite concentrate)

The concentration of leach solution ($g.L^{-1}$)	The amount of oxidized copper ore added to solution to bring the pH value to 1.5, g (50 mL for stock solution)
C/5	15.55
C/10	7.60
C/15	5.14

oxidized copper ore dissolved (at that time pH value was almost 1.5), the remained solid waste that contains mostly SiO_2 was removed from the reactor by filtration. An X-ray diffractogram of that solid waste is shown Figure 2. The filtrate taken to the reactor was heated to the desired cementation temperature and iron scraps weighted 1.5 times as much as

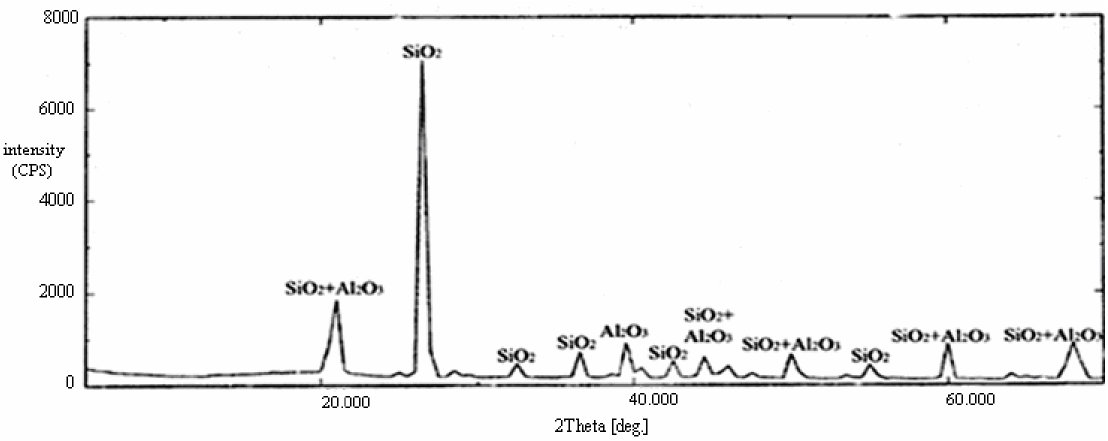

Figure 2. The X-ray diffractogram of the residue obtained by dissolution of oxidized copper ore in the leaching solution

theoretical needed amount were added to the heated filtrate. When the reaction period was ended, the reactor content consists of cemented copper and undissolved scrap iron was filtrated and the amount of copper remained without cementing was determined by volumetric methods(24), and then to obtain amount of the cemented copper from the solution was determined by subtracting cupric ion concentration remained in the solution from initial copper quantity.

The application of Taguchi Method to optimize of process by using with multiple performance characteristics includes eight steps, which make up Robust Design cycle view of planning and performing the experiments and analysing and verifying the experimental results(25):

-identify the main function, side effects, and failure modes,
-identify noise factors and the testing conditions for evaluating the quality loss,
-identify the quality characteristics to be observed and the objective function to be optimized,
-identify the control factors and their alternate levels,
-design the matrix experiment and define the data analysis procedure,
-conduct the matrix experiment,
-analyze the data, determine optimum levels for the control factors, and predict performance under these levels,
-conduct the verification(also called confirmation)experiment and plan future action.

Experimental parameters used in this study and their levels are seen in Table 4. The orthogonal array (OA) was chosen as the most suitable to make up the experimental

Table 4. Parameters and their values corresponding to their levels studied in experiments.

Parameters		Levels		
		1	2	3
A	Reaction temperature (^oC)	20	30	40
B	The concentration of leach reactive ($g.L^{-1}$)	(C/5)*	(C/10)*	(C/15)*
D	Stirring speed (rpm)	300	450	600
E	Reaction time (min)	20	40	60

*C: Concentration of original solution obtained with chlorination of chalcopyrite concentrate in aqueous media

design, $L_9(3^4)$, with four parameters each with three values given Table 5. Each experiment was repeated twice under the same conditions at different times in order to determine the effects of noise sources on process. Performance characteristics chosen as the optimization

Table 5. $L_9(3^4)$Experimental plan table and results of experiments

Experiment No	Conversion fraction of copper						
	A	B	D	E	Experiment(I) Cu %	Experiment(II) Cu %	Average Cu %
1	1	1	1	1	79.16	80.48	79.82
2	1	2	2	2	87.21	88.82	88.02
3	1	3	3	3	90.59	87.13	88.86
4	2	1	2	3	92.72	91.36	92.04
5	2	2	3	1	79.49	79.64	79.57
6	2	3	1	2	92.87	91.38	92.13
7	3	1	3	2	96.36	95.68	96.02
8	3	2	1	3	92.80	91.25	92.03
9	3	3	2	1	87.31	83.76	85.54

criteria are divided by three categories, the larger-the-better, the smaller-the-better and the nominal-the-best. The first two of them were calculated by using Equation 1 and 2 (25).

$$\text{Larger-the-better } SNL = -10 Log_{10}\left(\frac{1}{n}\sum_{i=1}^{n}\frac{1}{Y_i^2}\right) \tag{1}$$

$$\text{Smaller-the-better } SNS = -10 Log_{10}\left(\frac{1}{n}\sum_{i=1}^{n} Y_i^2\right) \tag{2}$$

where *SNL* and *SNS* are performance characteristics, *n* number of repetition done for an experimental combination, and Y_i performance value of i^{th} experiment.

In Taguchi method, the experiment corresponding to optimum working conditions might not be found in randomized experimental plan table. In such cases; the performance value for optimum conditions can be predicted by using the balanced characteristic of OA. For this purpose; an additive model can be used as follows(26).

$$Y_i = \mu + X_i + e_i \tag{3}$$

where μ is the overall mean of performance value, X_i the fixed effect of the parameter level combination used in i^{th} experiment, and e_i the random error in i^{th} experiment.

If experimental results are in percentage (%), before evaluating Equation 3 Ω transformation of percentage values should be applied first using the Equation 4 by which values of interest are also later determined by carrying out reverse transformation by using the same equation(27):

$$\Omega(db) = -10Log\left(\frac{1}{P} - 1\right) \tag{4}$$

Where *Ω(db)* is the decibel value of percentage value subject to omega transformation and *P* the percentage of the product obtained experimentally. Because Eq. 3 is a point estimation, which is calculated by using experimental data in order to determine whether the additive model is adequate or not, the confidence limits for the prediction error must be evaluated(25). The prediction error is the difference between the observed Y_i and the predicted Y_i. The confidence limits for the prediction error, *Se*, is

$$Se = \pm 2\sqrt{\left[\frac{1}{n_0}\right]\sigma_e^2 + \left[\frac{1}{n_r}\right]\sigma_e^2} \tag{5}$$

$$\sigma_e^2 = \frac{\text{sum of squares due to error}}{\text{degrees of freedom for error}} \tag{6}$$

$$\frac{1}{n_o} = \frac{1}{n} + \left[\frac{1}{n_{A_i}} - \frac{1}{n}\right] + \left[\frac{1}{n_{B_i}} - \frac{1}{n}\right] + \left[\frac{1}{n_{C_i}} - \frac{1}{n}\right] \ldots\ldots \tag{7}$$

where *Se* is the two-standard-deviation confidence limit, *n* the number of rows in the matrix experiment, n_r the number of repetition in confirmation experiment and $n_{A_i}, n_{B_i}, n_{C_i}, \ldots$ are the replication number for parameter level $A_i, B_i, C_i, \ldots$ If the prediction error is outside these limits, it should be suspected of the possibility that the additive model is not adequate. Otherwise, it can be considered that the additive model to be adequate. A verification experiment is a powerful tool for detecting the presence of interactions among the control parameters. If the predicted response under the optimum conditions does not match the observed response, then it implies that the interactions are important. If the predicted response matches the observed response, then it implies that the interactions are probably not important and that the additive model is a good approximation(25).

The order of the experiments was obtained by inserting parameters into columns of OA, $L_9(3^4)$, chosen as the experimental plan given in Table 5. But the order of experiments was made random in order to avoid noise sources which had not been considered initially and which could take place during an experiment and affect results in a negative way.

3. RESULTS AND DISCUSSION

3.1. Reaction of cementation

The cementation of copper from aqueous solution is described by the reaction:

$$Fe^{o}_{(\text{steel scrap})} + Cu^{2+}_{(aq)} \rightarrow Cu^{o}_{(\text{cemented metallic copper})} + Fe^{2+}_{(aq)} \tag{8}$$

Other metals besides iron, such as aluminum or zinc could be used for cementation but at considerably greater expense. Hence, iron (scrap steel) is the only practical cementation agent. As practiced in the copper industry, the pregnant leach solution is made to flow through a pile of scrap steel and the copper precipitates on the iron surface. The copper precipitate detaches in flake or powder form under the influence of the solution flow, and it is invariably contaminated with the iron upon which it precipitates (typical analysis: 85-90 % Cu, 0.2-2 % Fe, 0.5 % $SiO_2 + Al_2O_3$, remainder oxygen)(28).

3.2. Statistical analysis

In order to see effective parameters and their confidence levels on cementation process, the analysis of variance was performed. A statistical analysis of variance (ANOVA) was performed to see whether process parameters are statistically significant or not. F-test is a tool to see which process parameters have a significant effect on the cementation value. The F value for each process parameter is simply a ratio of mean of the squared deviations to the mean of squared error. Usually, the larger the F value, the greater the effect on the cementation value due to the change of the process parameter. With the performance characteristics and ANOVA analyses, the optimal combination of process parameters can be predicted(21). The results of variance analysis were given in Table 6.

Table 6. Results of the analysis of variance for the cementation of copper

Parameters		Degrees of freedom	Sum of squares	Mean of squares	F
A	Reaction temperature (^{o}C)	2	95.915	47.957	24.07
B	The concentration of leach solution ($g.L^{-1}$)	2	26.254	13.127	6.59
D	Stirring speed (rpm)	2	0.925	0.462	0.23
E	Reaction time (min)	2	393.485	196.743	98.74
	Error	9	17.933	1.993	

In order to obtain optimal cementation performance, the larger–the-better performance characteristic (Eq. 1) has been taken for cementation of Cu.

The order of graphs in Figure 3-6 is according to the degrees of the influences of parameters on the performance characteristics. The optimal level of a process parameter is the level with the highest SN value calculated by Eq.1. At first sight it can be difficult and complicated to deduce the experimental conditions for the graphs given in Figure 3-6. We’ll try to explain it with an example.

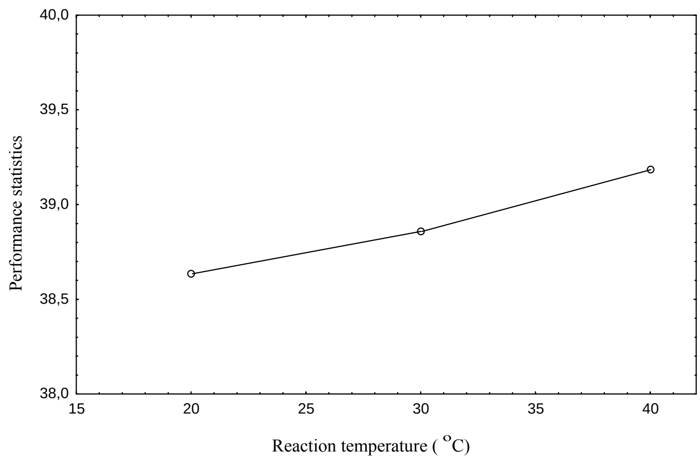

Figure 3. The effect of reaction temperature on performance statistics

Let’s see how Figure 5 is obtained. Figure 5 shows the variation of performance characteristics with stirring speed. Let’s try to determine the experimental conditions for the first datum point. The level 1 is 300 rpm for this parameter in this point. Now, let’s go to

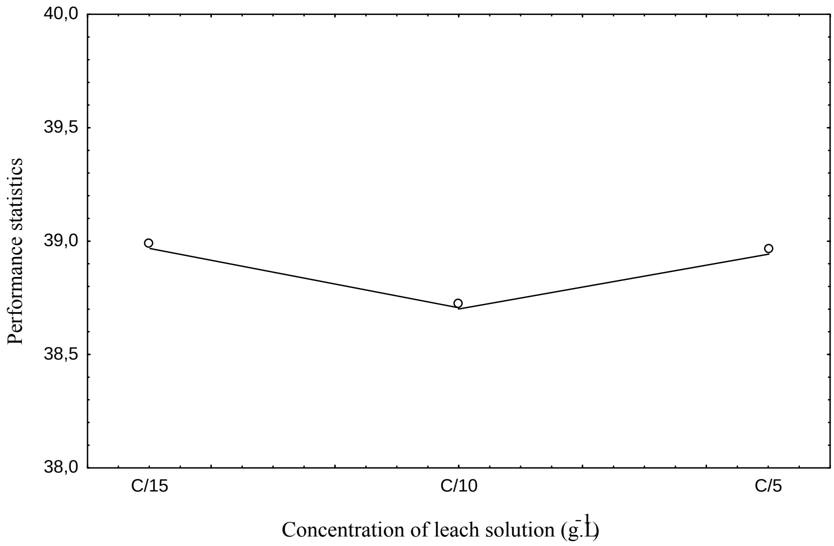

Figure 4. The effect of concentration of leach solution on performance statistics

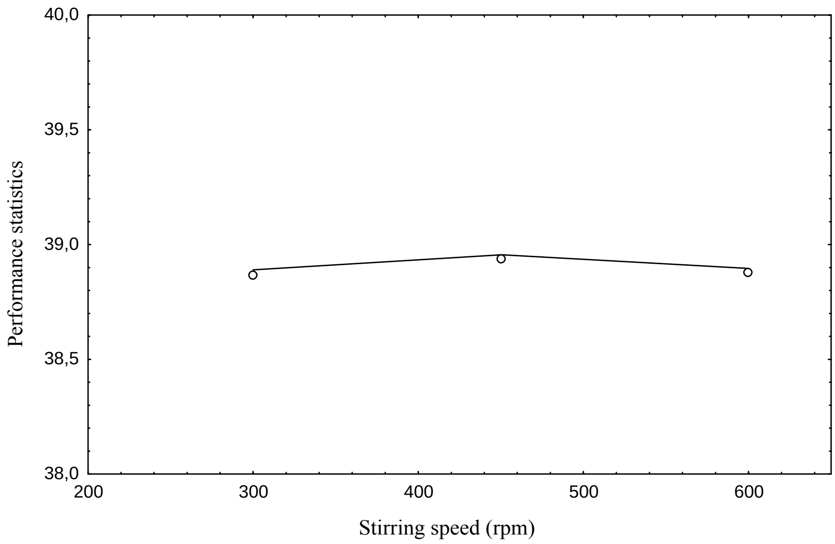

Figure 5. The effect of stirring speed on performance statistics

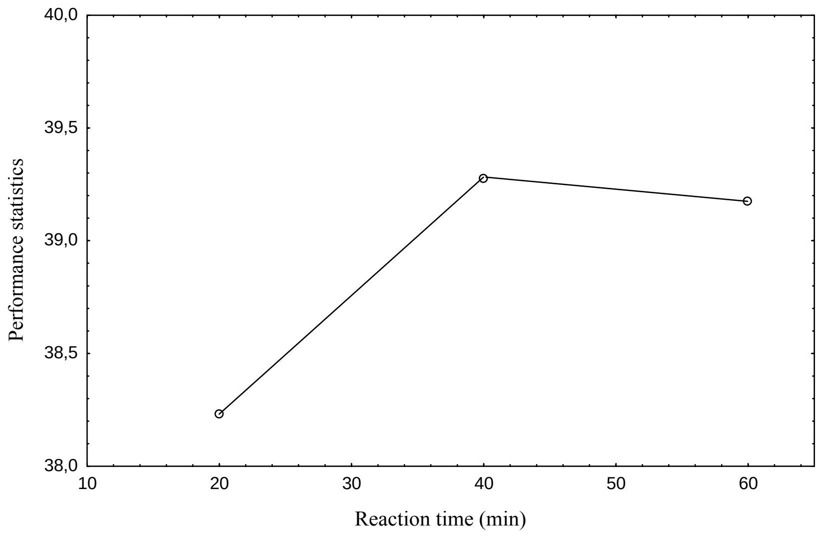

Figure 6. The effect of reaction time on performance statistics

Table 3 and find the experiments for which the level in the column D is 1. It is seen in Table 5 that the level is 1 for the experiment with 1, 6 and 8 numbers. The first datum point in Figure 6 is arithmetical average of performance characteristics for these experiments. All the points in Figure 6 graph and other graphs are established by the same way. In each graph, the numerical value of maximum point is corresponding to the best value for that parameter.

These values are seen to be A_3(40 ^oC), B_1(C/5 $g.L^{-1}$), D_2(450 rpm) and E_2(40 min). Therefore, for this process A_3, B_1, D_2 and E_2 conditions were taken as optimum cementation conditions and the cementation fraction under these conditions was found to be 98.35 %.

If the experimental plan given in Table 4 is studied carefully together with parameter values given as A_3(40^oC), B_1(C/5 $g.L^{-1}$), D_2(450 rpm) and E_2(40 min), it can be seen that experiments corresponding to optimum conditions A_3(40 ^oC), B_1(C/5 $g.L^{-1}$), D_2(450 rpm) and E_2(40 min) have not been carried out during the experimental work. Thus it should be noted that the cementation percentages in Table 7 are predicted results obtained by using Eqs. 3-4 and observed results for same conditions. Also, the results in Table 7 are confidence limits of predictions. In order to test the predicted results, confirmation experiments were carried out twice at the same working conditions. The fact that the cementation percentages from confirmation experiments are within the calculated confidence intervals calculated from Eqs.5-7 (see Table 7) shows that the experimental results are within ± 5 % in error. This case states that there is a good agreement between the predicted values and experimental values, and the interactive effects of the parameters are indeed negligible. It may be concluded that the additive model is adequate for describing the dependence of this cementation process on the various parameters (21).

Table 7. Optimum working conditions and alternative working conditions for two different experimental conditions, observed and predicted dissolved quantities of Cu

Parameters		Value	Level
A	Reaction temperature (^oC)	40	3
B	The concentration of leach solution ($g.L^{-1}$)	C/5	1
D	Stirring speed (rpm)	450	2
E	Reaction time (min)	40	2
Observed dissolved quantity for Cu (%)		98.35	
Predicted dissolved quantity for Cu (%)		95.95	
Confidence limits of prediction for Cu (%)		91.79-100	

CONCLUSIONS

The major conclusions from the present work are:

1-The effective parameters on study of the optimum conditions of the cementation of copper in solutions obtained with chlorination of chalcopyrite concentrate in aqueous media are reaction time, reaction temperature, concentration of leach solution and stirring speed, respectively.

2-The optimum conditions are 40 ^oC for reaction temperature, C/5 $g.L^{-1}$ for concentration of leach solution, 40 min. for reaction time and 450 rpm for stirring speed. Under these conditions, it can be seen in Table 4 that the cementation of 98.35 % is just for Cu.

3-The predicted and observed cementation values are very close to each other, it may be concluded that the additive model is adequate for describing the dependence of the cementation process on the various parameters.

4-Since optimum conditions determined by Taguchi method in laboratory environment is reproducible in real production environments as well, the findings of the present study may be useful for processing in industrial scale.

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