



## Investigation of leaching conditions of chalcopyrite by chlorine gas in aqueous medium

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### ABSTRACT

Generally, copper is obtained by pyrometallurgical methods from sulphide ores and SO<sub>2</sub>, a dangerous gas is emitted to environment. Hydrometallurgical processes is preferred over pyrometallurgical processes in recent years. The present work aims to optimize leaching of chalcopyrite with chlorine gas in aqueous medium by an experimental design using Taguchi method. Thus, both Cl<sub>2</sub>, a by-product of chlor-alkali industry, is removed using as a reagent, and emission of SO<sub>2</sub> from copper sulphide prometallurgy is prevented. In this study, experimental parameters and their values were 16-45°C for reaction temperature, 0.05-0.20 g ml<sup>-1</sup> for solid-to-liquid ratio, 30-120 min for reaction time, 0.027-0.4 mol l<sup>-1</sup> for [Fe<sup>3+</sup>] and 0.025-0.4 mol l<sup>-1</sup> for [Cu<sup>2+</sup>]. The optimum conditions were 45°C for reaction temperature, 0.05 g ml<sup>-1</sup> for solid-to-liquid ratio, 0.2 mol l<sup>-1</sup> for [Fe<sup>3+</sup>], 0.025 mol l<sup>-1</sup> for [Cu<sup>2+</sup>] and 120 min for reaction time. Under these conditions, 68.44% of copper in chalcopyrite dissolved.

**Keywords:** Chalcopyrite, optimization, Taguchi method, chlorine

### Sulu Ortamda Klor Gazıyla Kalkopirit Liçinginin İncelenmesi

#### ÖZ

Genellikle bakır, sülfürlü cevherlerden pirometallurjik yöntemlerle elde edilmekte ve çevreye tehlikeli bir gaz olan SO<sub>2</sub> salınmaktadır. Son yıllarda pirometallurjik prosesler yerine hidrometallurjik prosesler tercih edilmektedir. Mevcut çalışmada, Taguchi metodunu temel alan bir deneysel tasarımla sulu ortamda klor gazı ile kalkopirit çözünmesinin optimize edilmesi amaçlanmıştır. Böylece, hem klor-alkali sanayiinin yan ürünü olarak elde edilen Cl<sub>2</sub> bir reaktif olarak kullanılmak suretiyle bertaraf edilmekte ve hem de bakır sülfüre uygulanan pirometallurjik işlemlerden çıkan SO<sub>2</sub>'nin çevreye yayılması önlenmektedir. Bu çalışmada kullanılan deneysel parametrelerin aralıkları, reaksiyon sıcaklığı için 16-45°C, katı-sıvı oranı için 0,05-0,20 g.ml<sup>-1</sup>, reaksiyon süresi için 30-120 dk. [Fe<sup>3+</sup>] için 0,027-0,4 mol l<sup>-1</sup> ve [Cu<sup>2+</sup>] için 0,025-0,4 mol l<sup>-1</sup> dir. Optimum şartlar, reaksiyon sıcaklığı için 45°C, katı-sıvı oranı için; 0,05 g.ml<sup>-1</sup>, [Fe<sup>3+</sup>] için; 0,2 mol l<sup>-1</sup>, [Cu<sup>2+</sup>] için; 0,025 mol.L<sup>-1</sup> ve reaksiyon süresi için; 120 dk. olarak bulundu. Bu şartlar altında, kalkopirit içindeki bakırın % 68,44'ü çözüldü.

**Anahtar Kelimeler:** Kalkopirit, optimizasyon, Taguchi metodu, klor

### 1. INTRODUCTION

Recently, in production of copper and its compounds hydrometallurgical processes have taken the place of classical metallurgical processes.<sup>1</sup> In pyrometallurgical methods, chalcopyrite and other sulphides contained in complex ore form sulphur dioxide during roasting process and thus flue gases released to atmosphere pollute the environment. Because of this, new processes which are friendly to the environment must be developed.

Chlorine gas is effect on metal sulphides and it is candidate to be an important reagent for leaching in this area.<sup>2</sup> Chlorine gas, a by-product of chlor-alkali industry

which sodium hydroxide is produced is very toxic for being human, animals and plants. To preclude this damage, new use areas must be research to dispose of chlorine.

In recent years, the kinetics of the reaction of pyrite and chalcopyrite with chlorine gas in aqueous media have been investigated. In result, kinetic parameters and speed control mechanisms have been determined.<sup>1,3</sup> Groves and Smith<sup>4</sup> studied the reaction of copper sulfur minerals with chlorine gas in an aqueous medium and revealed reaction products.

FeCl<sub>3</sub>, CuCl<sub>2</sub> or mixtures thereof have been used as leaching reagents in the leaching of copper sulphide ores.<sup>5</sup> Lu and co-workers<sup>6</sup> investigated the effect of

chloride ions on the dissolution of chalcopyrite in solutions acidified with  $H_2SO_4$  and found that excellent dissolution kinetics existed for solutions containing chloride, while for solutions without chloride, the leaching was very slow. It was believed that the role of chloride was to promote the formation of a more porous sulphur product, thus permitting the dissolution reaction to proceed at a reasonable rate.

Bonan co-workers<sup>7</sup> studied chalcopyrite leaching by  $CuCl_2$  in NaCl solutions. They stated that increasing in  $Cu^{2+}/Cu^+$  ratio and chloride concentration increased copper leaching. Wilson and Fisher<sup>8</sup>, contrary to this result, claimed that  $Cu^{2+}$  and  $Cl^-$  concentrations did not influence the rate of chalcopyrite dissolution in chloride solutions.

Scrobian co-workers<sup>9</sup> studied the effect of NaCl concentration and particle size on chalcopyrite leaching in solutions acidified with HCl and found that while NaCl concentration had a definitely positive effect on the leaching rate, the effect of particle size was almost negligible.

Lunström co-workers<sup>10</sup> made an electrochemical study of the dissolution behavior of chalcopyrite in a concentrated sodium chloride solution ( $250\text{ g l}^{-1}$ ) with cupric ion concentrations varied in the range  $0.09\text{--}26.6\text{ g l}^{-1}$ . They found that increase in dissolution rate was observed to be proportional to the increase in the temperature and to bigger cupric ion concentration than  $9\text{ g l}^{-1}$ . Also, the results suggested that iron oxides, hydroxides and chlorides gathered on the chalcopyrite surface at higher pHs, chalcopyrite passivated and a sulphur-rich layer was detected on the surface.

Havlik co-workers<sup>11</sup> examined leaching of chalcopyrite with ferric chloride. Authors found that leaching rate increased with concentration of  $Fe^{3+}$  up to  $0.5\text{M}$  and does not depend on acidity of the solution within the range of  $0.25\text{--}1.0\text{ M}$  concentration of HCl.

Dutrizac<sup>12</sup> elucidated the formation of elemental sulphur during the  $FeCl_3$  leaching of chalcopyrite and found that more than 95% of sulphur converted to  $S^0$  and less than 5% of sulphur to  $SO_4^{2-}$  under studied conditions. Chalcopyrite has been leached with various leaching reagents such as HCl<sup>13</sup>,  $Cl^-/OCl^-$  media<sup>14</sup>,  $FeCl_3$ <sup>12,15</sup>, acidic  $Cl^-$  solutions<sup>6</sup>,  $CCl_4$  saturated with  $Cl_2$ <sup>16</sup> and  $H_2SO_4\text{--}NaCl\text{--}O_2$ <sup>17</sup>, by a lot of authors, too.

Determination of conditions of recovering metallic values from the ores by hydrometallurgical methods in industrial processes is important and many researches have been realized by various authors.<sup>18-30</sup>

In this study, the optimum conditions of chalcopyrite leaching by chlorine gas in aqueous media were investigated by using Taguchi method. Experimental parameters have been chosen as reaction temperature, solid-to-liquid ratio, reaction time,  $[Fe^{3+}]$ ,  $[Cu^{2+}]$  and  $[H^+]$ .

## 2. MATERIALS AND METHOTDS

$75\text{ }\mu\text{m}$ -chalcopyrite sample used in this study was prepared by sieving chalcopyrite concentrate ore from Çayeli-Rize, Turkey. The chemical analysis of ore gave a composition of 24.02% Cu, 29.36% Fe, 36.55% S, 2.19% Zn, 0.19% Pb, 0.1%  $Al_2O_3$ , 0.9% moisture and 6.69% other components. X-ray diffractogram of chalcopyrite concentrate is seen in Figure 1.

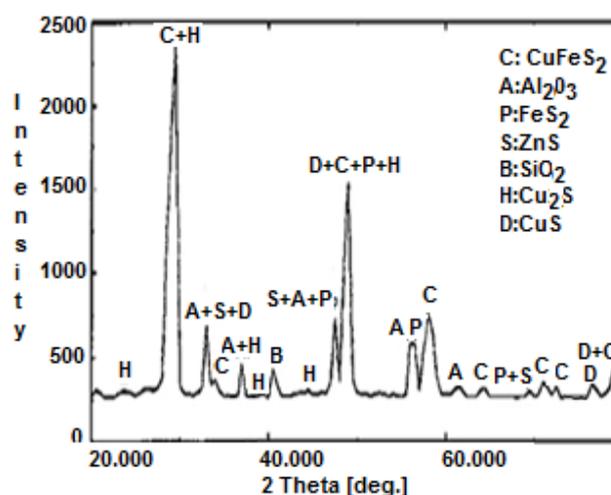


Figure 1. X-Ray diffractogram of the chalcopyrite concentrate.

As seen, the chalcopyrite concentrate contains  $CuFeS_2$ ,  $FeS_2$ ,  $ZnS$ ,  $Cu_2S$ ,  $CuS$  and very small amount of  $Al_2O_3$  and  $SiO_2$ . Also, SEM photogram of the concentrate is shown in Figure 2.



Figure 2. SEM photogram of the chalcopyrite concentrate.

In the experiments, temperature, solid-to-liquid ratio,  $[Fe^{3+}]$ ,  $[Cu^{2+}]$  and reaction time were parameters. Levels of parameters of the experiments designated according to Taguchi method are given in Table 1.

**Table 1.** Parameters and their values corresponding to their levels studied in experiments

| Parameters   | Levels |     |      |     |
|--|--------|-----|------|-----|
|  | 1      | 2   | 3    | 4   |
| <b>A</b> Reaction temperature (°C)                   | 16     | 25  | 35   | 45  |
| <b>B</b> Solid-to-liquid ratio (g ml <sup>-1</sup> ) | 0.05   | 0.1 | 0.15 | 0.2 |
| <b>C</b> [Fe <sup>3+</sup> ] (mol l <sup>-1</sup> )  | 0.027  | 0.1 | 0.2  | 0.4 |
| <b>D</b> [Cu <sup>2+</sup> ] (mol l <sup>-1</sup> )  | 0.025  | 0.1 | 0.2  | 0.4 |
| <b>E</b> Reaction time (min)                         | 30     | 60  | 90   | 120 |

In the first stage of dissolution experiments carried out in two stages, 7.0 g chalcopyrite was added to 200 ml of distilled water saturated with chlorine gas and the mixture was stirred at ambient temperature for two hours. In the second stage, 3.5 g chalcopyrite was added to 100 ml of the first stage filtrate, saturated with chlorine gas and the mixture was stirred under the same conditions of the first stage.

Leaching experiments were carried out in 250 mL a jacketed glass reactor equipped with a mechanical stirrer with tachometer, a constant temperature circulator and a condenser to prevent the volume reduction of the solution by the evaporation.

In the experiments, 100 ml-distilled water was saturated previously with Cl<sub>2</sub> at the desired experimental temperature. After the sample was added to the reactor, Cl<sub>2</sub> was passed through the reaction mixture during the desired experiment time while the mixture was stirring at a fixed speed. At the end of dissolution period, the amounts of Cu<sup>2+</sup> passing to the solution during the reaction were determined with the volumetric method.<sup>31</sup>

In this study, L<sub>16</sub> (5<sup>4</sup>) design, with five parameters each four values given in Table 2 was chosen as the most suitable experimental design.<sup>23</sup> Each experiment was repeated twice under the same conditions at different times, to determine the effects of noise sources on results.

In Taguchi method, performance characteristics chosen as the optimization 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 Equations (1) and (2).

$$\text{Larger-the-better } S_{NL} = -10 \text{Log}_{10} \left( \frac{1}{n} \sum_{i=1}^n \frac{1}{Y_i^2} \right) \quad (1)$$

$$\text{Smaller-the-better } S_{NS} = -10 \text{Log}_{10} \left( \frac{1}{n} \sum_{i=1}^n Y_i^2 \right) \quad (2)$$

where  $S_{NL}$  and  $S_{NS}$  are performance characteristics,  $n$  number of repetition done for an experimental combination, and  $Y_i$  performance value of  $i^{\text{th}}$  experiment.<sup>23</sup>

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 orthogonal array. For this purpose, an additive model can be used as follows.<sup>23</sup>

$$Y_i = \mu + X_i + e_i \quad (3)$$

Where,  $\mu$  is the overall mean of performance value,  $X_i$  the fixed effect of the parameter level combination used in  $i^{\text{th}}$  experiment, and  $e_i$  the random error in  $i^{\text{th}}$  experiment.

If experimental results are in percentage (%), before evaluating Eq. (3)  $\Omega$  transformations of percentage values should be applied first using the Eq. (4) by which values of interest are also later determined by carrying out reverse transformation by using the same equation:<sup>23</sup>

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

where  $\Omega(db)$  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 predictive error must be evaluated.<sup>21</sup> The predictive error is the difference between the observed  $Y_i$  and the predicted  $\hat{Y}_i$ . The confidence limits for the predictive error,  $S_e$ , is

$$S_e = \pm 2 \sqrt{\left[ \frac{1}{n_0} \right] \sigma_e^2 + \left[ \frac{1}{n_r} \right] \sigma_e^2} \quad (5)$$

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

$$\frac{1}{n_o} = \frac{1}{n} + \left[ \frac{1}{n_{A_i}} - \frac{1}{n} \right] + \left[ \frac{1}{n_{B_i}} - \frac{1}{n} \right] + \left[ \frac{1}{n_{C_i}} - \frac{1}{n} \right] \dots \quad (7)$$

where  $s_e$  is the two-standard-deviation confidence limit,  $n$  is the number of rows in the matrix experiment,  $n_r$  is the number of repetition in confirmation experiment

**Table 2.** L<sub>16</sub>(4<sup>5</sup>) experimental plan table and results of experiments

| Experiment No | Quantities and their levels |   |   |   |   | Conversion fraction of copper |                 |         |
|---------------|-----------------------------|---|---|---|---|-------------------------------|-----------------|---------|
|               | A                           | B | C | D | E | Experiment (I)                | Experiment (II) | Average |
|               |                             |   |   |   |   | Cu %                          | Cu %            | Cu %    |
| 1             | 1                           | 1 | 1 | 1 | 1 | 34.65                         | 39.88           | 37.27   |
| 2             | 1                           | 2 | 2 | 2 | 2 | 31.75                         | 23.01           | 27.38   |
| 3             | 1                           | 3 | 3 | 3 | 3 | 30.45                         | 25.73           | 28.09   |
| 4             | 1                           | 4 | 4 | 4 | 4 | 16.22                         | 20.17           | 18.20   |
| 5             | 2                           | 1 | 2 | 3 | 4 | 48.11                         | 41.70           | 44.91   |
| 6             | 2                           | 2 | 1 | 4 | 3 | 33.65                         | 36.33           | 34.99   |
| 7             | 2                           | 3 | 4 | 1 | 2 | 25.73                         | 22.12           | 23.93   |
| 8             | 2                           | 4 | 3 | 2 | 1 | 18.61                         | 23.33           | 20.97   |
| 9             | 3                           | 1 | 3 | 4 | 2 | 56.62                         | 54.23           | 55.43   |
| 10            | 3                           | 2 | 4 | 3 | 1 | 18.78                         | 20.18           | 19.48   |
| 11            | 3                           | 3 | 1 | 2 | 4 | 38.63                         | 37.09           | 37.86   |
| 12            | 3                           | 4 | 2 | 1 | 3 | 30.85                         | 34.65           | 32.75   |
| 13            | 4                           | 1 | 4 | 2 | 3 | 47.79                         | 43.14           | 45.47   |
| 14            | 4                           | 2 | 3 | 1 | 4 | 56.75                         | 49.62           | 53.19   |
| 15            | 4                           | 3 | 2 | 4 | 1 | 24.68                         | 29.38           | 27.03   |
| 16            | 4                           | 4 | 1 | 3 | 2 | 29.54                         | 26.52           | 28.03   |

and  $n_{A_i}, n_{B_i}, n_{C_i}, \dots$  are the replication number for parameter level  $A_i, B_i, C_i, \dots$ . If the predictive error is inside these limits, it can be accepted that the additive model is adequate. Otherwise, it cannot be accepted 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 matches the observed response, then it implies that the interactions are probably not important and that the additive model is a good approximation.<sup>32</sup>

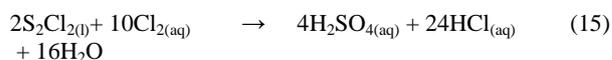
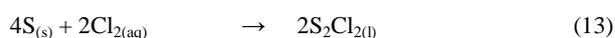
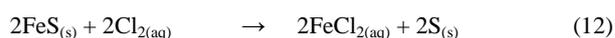
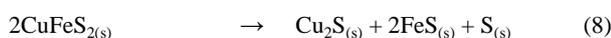
### 3. RESULTS AND DISCUSSION

#### 3.1. Dissolution

Dissolution carried out at two stages: At the end of the first stage experiment, it was seen that 17.99% of Fe and 13.66% of Cu in the ore passed to the filtrate. At the end of second stage, it was determined that 65% of Fe and 60% of Cu in the ore passed to the filtrate. This means that Cu<sup>2+</sup> and/or Fe<sup>3+</sup> are effective parameters in this dissolution system.

#### 3.2. Dissolution reactions

The reactions between chalcopyrite and chlorine gas in aqueous medium can be stated as follows



#### 3.3. Statistical analysis

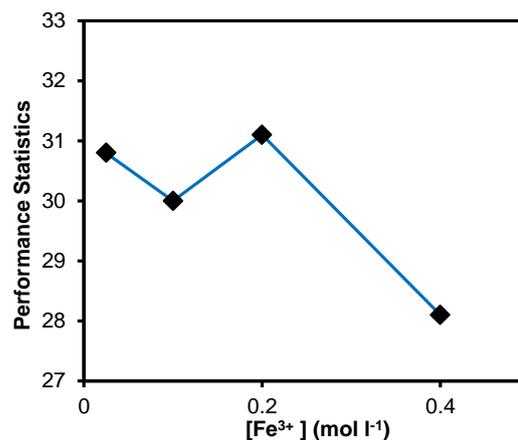
The data were evaluated according to Taguchi method.<sup>23</sup> Effective parameters and their levels on the leaching process were determined by analysis of variance. The results are shown in Table 3.

Likewise, the effects of the parameters on the performance characteristic are graphically shown in Figures 3-7. It had been determined that the temperature was 45°C in Figure 3, solid / liquid ratio, 0.05 g l<sup>-1</sup> in Figure 4, [Fe<sup>3+</sup>], 0.2 mmol l<sup>-1</sup> in Figure 5, [Cu<sup>2+</sup>], 0.025 mol l<sup>-1</sup> in Figure 6 and the reaction time, 120 min in Figure 7 as optimum conditions for Cu<sup>2+</sup> leaching. Any experiment corresponding to the optimum conditions is not available in the experimental plan in Table 2.

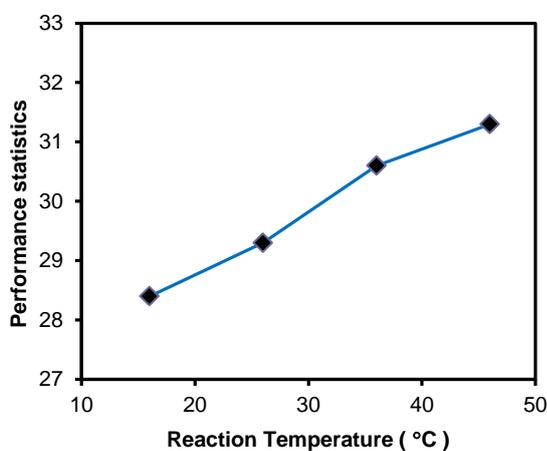
Using optimum conditions and Equations (3) and (4), the predicted result and the confidence interval are calculated.

**Table 3.** Results of the analysis of variance for the chlorination of chalcopyrite concentrate

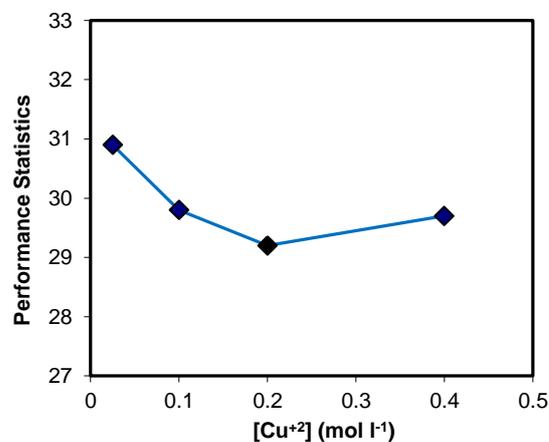
| Parameters                                    | Degrees of freedom | Sum of squares | Mean of squares | F     |
|---|--------------------|----------------|-----------------|-------|
| A Reaction temperature (°C)                   | 3                  | 568.9250       | 189.641         | 17.17 |
| B Solid-to-liquid ratio (g.mL <sup>-1</sup> ) | 3                  | 1929.829       | 643.276         | 58.26 |
| C [Fe <sup>3+</sup> ] (mol l <sup>-1</sup> )  | 3                  | 653.2051       | 217.735         | 19.72 |
| D [Cu <sup>2+</sup> ] (mol l <sup>-1</sup> )  | 3                  | 181.0988       | 60.3663         | 5.470 |
| E Reaction time (min)                         | 3                  | 657.5962       | 219.198         | 19.85 |
| Error   | 16                 | 176.6779       | 11.0424         |       |



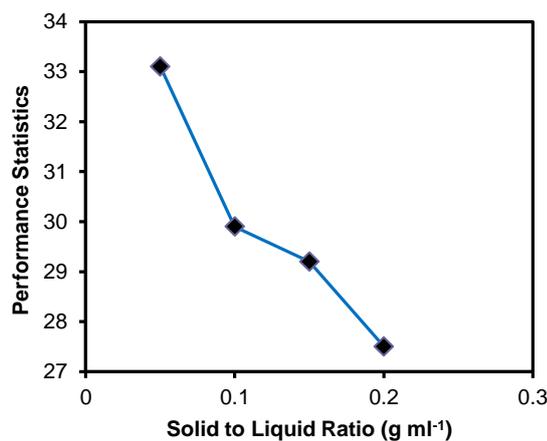
**Figure 5.** The effect of [Fe<sup>3+</sup>] on performance statistics.



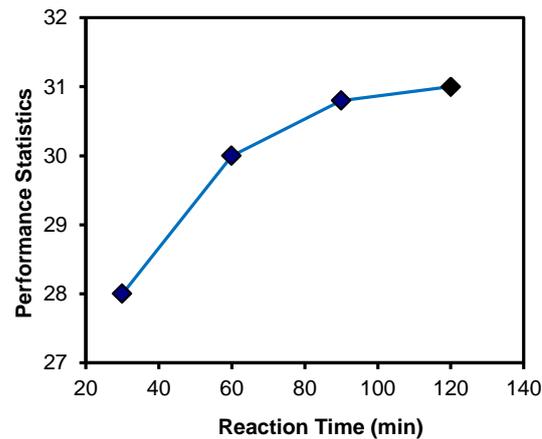
**Figure 3.** The effect of reaction temperature on performance statistics.



**Figure 6.** The effect of [Cu<sup>2+</sup>] on performance statistics.



**Figure 4.** The effect of solid-to-liquid ratio on performance statistics



**Figure 7.** The effect of reaction time on performance statistics.

In addition, two validation tests were performed under optimal conditions to test this predictor. The results are given in Table 4. Confirmation of test results show that the experimental plan and the results obtained are appropriate.

**Table 4.** Optimum working conditions and alternative working conditions for two different experimental conditions, observed and predicted dissolved quantities of Cu

| Parameters   | Value       | Level |
|--|-------------|-------|
| <b>A</b> Reaction temperature (°C)                   | 45          | 4     |
| <b>B</b> Solid-to-liquid ratio (g ml <sup>-1</sup> ) | 0.05        | 1     |
| <b>C</b> [Fe <sup>3+</sup> ] (mol l <sup>-1</sup> )  | 0.2         | 3     |
| <b>D</b> [Cu <sup>2+</sup> ] (mol l <sup>-1</sup> )  | 0.025       | 1     |
| <b>E</b> Reaction time (min)                         | 120         | 4     |
| Observed dissolved quantity for Cu (%)               | 67.86       |       |
| Predicted dissolved quantity for Cu (%)              | 65.19       |       |
| Confidence limits of prediction for Cu (%)           | 60.21-70.17 |       |

#### 4. CONCLUSIONS

The results obtained from the realized study are:

1. The most effective parameter in leaching of chalcopyrite with chlorine gas in aqueous medium are solid-to-liquid ratio.
2. Under optimal conditions given in Table 4, 68.44% Cu can be leached.
3. The additive model is suitable to define dependence of chalcopyrite leaching on studied parameters.
4. The obtained results may be used for industrial application due to characteristics of Taguchi method.

#### Conflict of interest

Authors declare that there is no a conflict of interest with any person, institute, and company, etc.

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