

An Optimization Study of Dissolution of Zn and Cu in ZnS Concentrate with HNO₃ Solutions

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The Taguchi method was used to determine optimum conditions for the dissolution of Zn, Cu and Fe in Zinc sulphide concentrate in HNO₃ solutions. The ranges of experimental quantities were between 12–55 °C for reaction temperature, 0.1–0.38 for solid-to-liquid ratio, 4–7 mol dm⁻³ for acid concentration, 15–120 min for reaction time, and 300–900 min⁻¹ for stirring speed. The optimum conditions for these quantities were found to be 55 °C, 0.1, 7 mol dm⁻³, 120 min and 700 min⁻¹, respectively. Under these conditions, the dissolution mass fraction of Zn, Cu and Fe in Zinc sulphide concentrate in HNO₃ solutions were $w = 96.32\%$, 62.55% and 29.5% , respectively.

Keyword:

Optimisation, nitric acid, zinc sulphide, Taguchi method

Introduction

Zinc is mostly found around the world disposed in the forms of ZnCO₃, ZnS etc. Traces of zinc are present in almost all the volcanic rocks. It is estimated that Zn forms 0.13 % of earth's crust.¹ About 6 tg y⁻¹ of zinc production originates from the treatment of sulphide concentrates containing sphalerite (ZnS) as the predominant zinc mineral.² The mineral deposits of the Black Sea region in Turkey have complex sulphide minerals containing mainly lead-zinc-copper. The ore contains sphalerite (ZnS), galena (PbS), chalcopyrite (CuFeS₂), pyrite (FeS₂), and tetrahedrite (Cu,Fe)₁₂(Sb,As)₄S₁₃. For example, Rize-Çayeli deposit has great importance due to its high amount of Cu and Zn.³

Over 80 % of the total world output is from the roast-leach-electrolysis process². Direct leaching of the concentrate eliminates the roasting step from the classical method which has been applied for many years. Thus, it has some such advantages that elemental sulphur is produced rather than sulphur dioxide, high extractions of zinc may be achieved as insoluble zinc ferrite is not formed.⁴ Chlorine gas-saturated water has been used as leaching agent for sulphurous ores.^{4–6} Acidic FeCl₃ and Fe₂(SO₄)₃ solutions have been used as leaching reagents for direct leaching of zinc from sulphurous ores.⁷ Some researchers were interested in the optimization of the best leaching conditions of the ores.^{8–12}

The acids such as HCl and H₂SO₄ as leaching reagents are not effective in dissolving ZnS concentrate containing CuFeS₂ and FeS₂ in moderate conditions. Nitric acid is a good lixivant for extraction of copper from chalcopyrite, because of its powerful oxidizing effect.¹³ Nitric oxide gas from the leaching is captured

by absorption in the aqueous solutions and reconverted to nitric acid by oxidation with air.^{13,14}

It is expected that when ZnS concentrate is dissolved in HNO₃ solution, Zn²⁺, Cu²⁺ and Fe³⁺ will pass into the solution, and Pb²⁺, available in small amounts in the concentrate, will precipitate in the form of PbSO₄, which can be separated easily by solid/liquid separation techniques. After this treatment, Fe³⁺ in the solution can be precipitated by adjusting pH about to 4. Cu²⁺ and Zn²⁺ can be converted to their metallic forms by cementation with Zn processes and electrowinning, respectively.

Dissolution of sphalerite, chalcopyrite, pyrite and galena in acidic FeCl₃ solutions have been investigated by other researchers, and it has been found that sulphide reacts with Fe³⁺ in two stages. In the first stage, sulphide is converted to S⁰ and in the second stage S⁰ to SO₄²⁻.^{7,15–18} On the other hand, the kinetics of pyrite oxidation with nitric acid solutions has been studied by *Kadioglu et al.*; the authors have determined that pyrite oxidation takes place in two stages. In the first stage, elemental sulphur is formed and in the second stage the elemental sulphur is converted to SO₄²⁻. They have expressed that the elemental concentration of sulphur increased with increasing acid concentration and temperature.¹⁹

Taguchi's Orthogonal Array (OA) analysis is used to produce the best quantities for the optimum design process, with the least number of experiments. In recent years, Taguchi method has been used to determine optimum quantities because of its advantages^{20,21}. The main advantages of this method over other statistical experimental design methods are, that the quantities 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.

In this study, the zinc sulphide concentrate was dissolved in HNO₃ solutions, and Taguchi experimental design method was employed to determine optimum leaching conditions.

Materials and methods

The zinc sulphide concentrate used in the experiments was provided from Rize-Çayeli region in Turkey. The concentrate was sieved by using a 200 mesh ASTM standard sieve. It was determined by X-ray diffractometer that the concentrate contained mainly ZnS, FeS₂ and CuFeS₂. X-ray diffractogram of the concentrate is given in Figure 1. The chemical composition of the concentrate was determined by volumetric and gravimetric methods^{22,23}. Trace elements were analyzed by using atomic absorption spectrometric method (Shimadzu AA-670) and given the result is in Table 1.

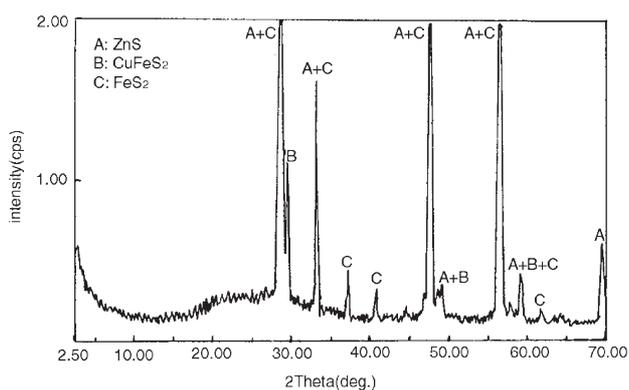


Fig. 1 – X-ray diffractogram of the original ZnS concentrate

Table 1 – The chemical composition of zinc sulphide concentrate

Mass fraction	Zn	Cu	Fe	Pb	Ag	Au	Moisture
w / %	49.50	2.80	8.58	0.67	1.33×10^{-2}	1.1×10^{-4}	8.70

The dissolution experiments were carried out in a 250 mL glass reactor equipped with a mechanical stirrer having a digital controller unit and timer, a thermostat and a cooler. The temperature of the reaction medium could be controlled within ± 0.5 °C. First 100 mL nitric acid of known concentration was introduced into the reactor. After the desired reaction temperature was reached, a predetermined amount of the zinc sulphide concentrate was added into the solution while the content of the vessel was stirred at a certain speed. At the end of the experiment, the contents of the vessel was filtered by a filter paper of Filtrak 391 and the filtrate solu-

tion was then analysed volumetrically for Zn, Cu and Fe.^{22,23}

The use of the quantity design in the Taguchi method to optimize a process with multiple performance characteristics includes the following steps (a) to identify the performance characteristics and select process quantities to be evaluated; (b) to determine the number of quantity levels for the process and possible interaction between the process quantities; (c) to select the appropriate orthogonal array and assignment of process quantities to the orthogonal array; (d) to conduct the experiments based on the arrangement of the orthogonal array; (e) calculate the performance characteristics; (f) to analyze the experimental result using the performance characteristic and ANOVA; (g) to select the optimal levels of process quantities; and (h) to verify the optimal process quantities through the confirmation experiment.^{20,24}

Experimental quantities and their levels, determined in the light of preliminary tests, are given in Table 2. The orthogonal array (OA) experimental design was chosen as the most suitable method to determine experimental plan, $L_{25}(5^5)$ (Table 3), five quantities each with five values.²⁴ In order to observe the effects of noise sources on the dissolution process, each experiment was repeated twice under the same conditions at different times. The performance characteristics were chosen as the optimization criteria. There are three categories of performance characteristics, the larger-the-better, the smaller-the-better and the nominal-the-better. The two performance characteristics were evaluated by using Eq. 1 and 2^{24, 25}

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

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

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

Table 2 – Quantities and their values corresponding to their levels to be studied in experiments

Quantities	LEVELS				
	1	2	3	4	5
A Reaction temperature, °C	12	25	35	45	55
B Dissolution mass concentration	0.10	0.17	0.24	0.31	0.38
C Acid concentration, mol dm ⁻³	3	4	5	6	7
D Stirring speed, min ⁻¹	300	500	600	700	900
E Reaction time, min.	15	30	60	90	120

Table 3 – $L_{25} (5^5)$ randomize experimental plan table

Experiment No	Quantities and their levels				
	A	B	C	D	E
1	1	1	2	1	1
2	2	5	2	2	3
3	3	2	3	1	3
4	2	1	4	3	4
5	4	1	3	2	5
6	1	3	1	3	3
7	3	5	4	4	1
8	4	5	1	1	4
9	4	4	4	5	3
10	2	3	3	5	1
11	2	4	5	1	2
12	2	2	1	4	5
13	4	3	2	4	2
14	1	4	3	4	4
15	1	5	5	5	5
16	5	3	4	1	5
17	5	2	2	5	4
18	3	1	1	5	2
19	3	4	2	3	5
20	5	1	5	4	3
21	4	2	5	3	1
22	1	2	4	2	2
23	5	4	1	2	1
24	3	3	5	2	4
25	5	5	3	3	2

periment. In Taguchi method the experiment corresponding to optimum working conditions might not been done during the whole period of the experimental stage. In such cases the performance value corresponding to optimum working conditions can be predicted by utilizing the balanced characteristic of OA. For this the following additive model may be used ²⁶

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

where μ is the overall mean of performance value, X_i the fixed effect of the quantity 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 Eq 3 Ω transformation 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 equation²⁷:

$$\Omega = -10 \log \left(\frac{1}{\eta} - 1 \right) \quad (4)$$

Where Ω (dB) is the decibel value of percentage value subject to omega transformation and η 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.²⁴ 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

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

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

$$\frac{1}{n_0} = \frac{1}{n} + \left[\frac{1}{n_{A_i}} - \frac{1}{n} \right] + \left[\frac{1}{n_{B_i}} - \frac{1}{n} \right] + \left[\frac{1}{n_{C_i}} - \frac{1}{n} \right] \dots \quad (7)$$

where s_e is the two-standard-deviation confidence limit, n 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} , ... are the replication number for variables quantity level A_i , B_i , C_i , ... 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 the additive model to be adequate.

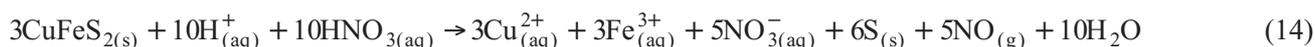
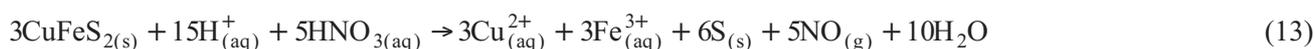
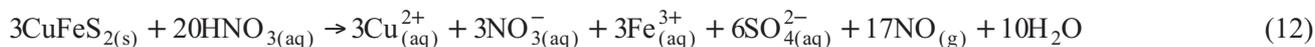
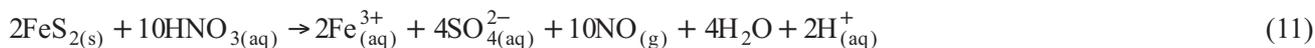
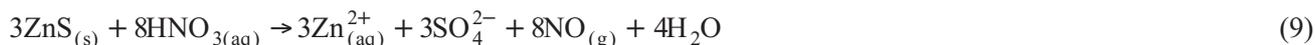
A verification experiment is a powerful tool for detecting the presence of interactions among the control quantities. If the predicted response under the optimum conditions does not match the observed response, then it implies that the interactions are important. If the predicted response matches the observed response, then it implies that the interactions are probably not important and that the additive model is a good approximation.²⁴

The order of the experiments was obtained by inserting quantities into columns of OA, $L_{25} (5^5)$, chosen as the experimental plan given in Table 3. 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.

Results and discussion

Dissolution reactions

According to the works cited in the Introduction section, when ZnS concentrate is added into the nitric acid solution, the reactions taking place in the medium can be expressed by Eqs 8–15:^{7,15–19}



Statistical analysis

The collected data were analyzed by an IBM compatible PC. In order to see effective parameters and their confidence levels on dissolution 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 quantities have a significant effect on the dissolution 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 dissolution 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.²⁰ The results of variance analysis were given in Table 4–6. To obtain optimal dissolution performance, the higher-the-better performance characteristic (Eq. 1) has been taken for dissolution of Zn and Cu, and the smaller-the-better performance characteristic (Eq. 2) for dissolution of Fe. The order of graphs in Figs. 2–4 is according to the degrees of the influences of quantities on the performance char-

acteristics. The optimal level of a process quantity is the level with the highest SN value calculated by Eq.1 or 2. At first sight it can be difficult and complicated to deduce experimental conditions for graphs given in Fig. 2–4. We'll try to explain it with an example. Let's take Fig.2A, it shows the variation of the performance characteristics with temperature

Table 5 – Results of the analysis of variance for the dissolution values of Cu

Quantities	Sum of squares	Degrees of freedom	Mean squares	F
Reaction temperature, °C	2035.809	4	508.95	7.05
Dissolution mass concentration	528.780	4	132.20	1.83
Acid concentration, mol dm ⁻³	1665.254	4	416.31	5.77
Stirring speed, min ⁻¹	64.047	4	16.012	0.22
Reaction time, min.	573.61	4	143.40	1.99
Error	288.810	4	72.20 (σ_e^2)	

Table 4 – Results of the analysis of variance for the dissolution values of Zn

Quantities	Sum of squares	Degrees of freedom	Mean squares	F
Reaction temperature, °C	3117.96	4	779.49	21.73
Dissolution mass concentration	1213.19	4	303.30	8.46
Acid concentration, mol dm ⁻³	2865.61	4	716.40	19.98
Stirring speed, min ⁻¹	378.54	4	94.63	2.64
Reaction time, min.	1156.11	4	289.03	8.06
Error	143.46	4	35.86 (σ_e^2)	

Table 6 – Results of the analysis of variance for the dissolution values of Fe

Quantities	Sum of squares	Degrees of freedom	Mean squares	F
Reaction temperature, °C	1133.00	4	283.25	1.60
Dissolution mass concentration	542.49	4	135.62	0.76
Acid concentration, mol dm ⁻³	1873.32	4	468.33	2.64
Stirring speed, min ⁻¹	913.59	4	228.40	1.29
Reaction time, min.	351.95	4	87.99	0.50
Error	709.79	4	177.45 (σ_e^2)	

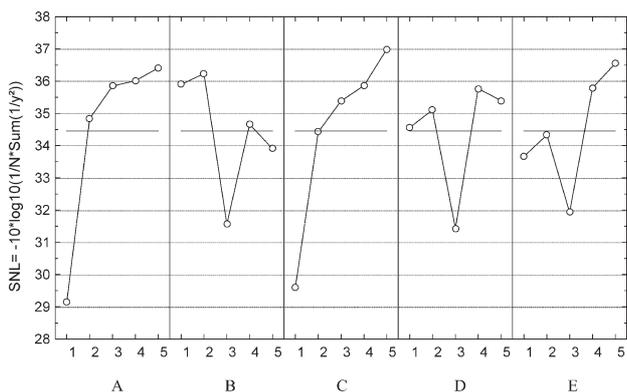


Fig. 2 – The effect of each quantity on the optimization criteria for Zn

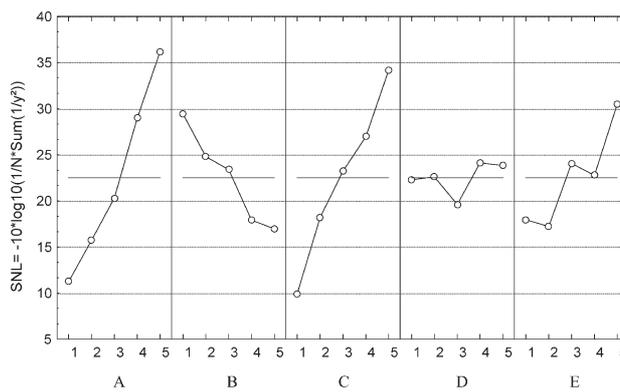


Fig. 3 – The effect of each quantity on the optimization criteria for Cu

quantity. Now let us try to determine experimental conditions for the first data point. The A for this point is level 1 which is 12 °C for this quantity. Now let us go to Table 3 and find the experiments for which A level (column A) is 1. It is seen in Table 3 that experiments for which column A is 1 are experiment no 1, 6, 14, 15 and 22. The performance characteristics value of the first data point is thus the average of those obtained from experiment no 1, 6, 14, 15 and 22. Experimental conditions for the second data point, thus are the conditions of the experiments for which column A are 2 (i.e. experiment no 2, 4, 10, 11, 12), and so on.⁹

The numerical value of the maximum point in each graph marked the best value of that particular quantity and was given in the third column of Table 7

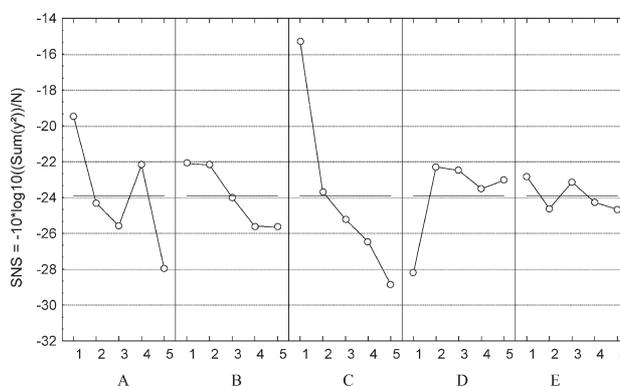


Fig. 4 – The effect of each quantity on the optimization criteria for Fe

Table 7 – Optimum working conditions and alternative working conditions for three different experimental conditions, observed and predicted dissolved quantities of ZnS

Quantities	Case 1*		Case 2		Case 3		Case 4	
	Value	level	Value	level	Value	Level	Value	Level
A Reaction temperature, °C	55	5	45	4	45	4	55	5
B Dissolution mass concentration	0.1	1	0.17	2	0.1	1	0.17	2
C Acid concentration, mol dm ⁻³	7	5	7	5	7	5	7	5
D Stirring speed, rpm	700	4	700	4	700	4	700	4
E Reaction time, min.	120	5	120	5	120	5	120	5
Observed dissolved quantity for Zn (%)	96.32		87.60		93.08		90.46	
Predicted dissolved quantity for Zn (%)	92.44		90.52		90.81		92.15	
Confidence limits of prediction for Zn (%)	85.51–99.47		83.59–97.45		83.88–97.74		85.21–99.08	
Observed dissolved quantity for Cu (%)	62.55		55.52		55.60		56.60	
Predicted dissolved quantity for Cu (%)	64.39		52.59		57.20		59.79	
Confidence limits of prediction for Cu (%)	54.56–74.22		42.75–62.43		47.36–67.04		49.95–59.63	
Observed dissolved quantity for Fe (%)	29.5		18.08		15.0		36.03	
Predicted dissolved quantity for Fe (%)	33.59		17.25		17.02		33.81	

*The quantity levels for maximum dissolution of Zn and Cu

(case 1) for each quantity. That is, quantity values given in case 1 column of Table 7, the A5 (55 °C), B2 (0.17), C5 (7 M), D4 (700 min⁻¹), E5 (120 min) are optimum conditions for Zn. The A5 (55 °C), B1 (0.1), C5 (7 M), D4 (700 rpm), E5 (120 min) are optimum conditions for Cu. Optimum conditions for minimum Fe are A1 (25 °C), B1 (0.2), C1 (3 M), D2 (500 rpm) and E1 (15 min.) from Fig. 3. The value of B1 instead of B2 can be for dissolution of zinc because they are very close to each other.

For the dissolution of Zn within the worked range, it is in Table 4 that the reaction temperature, acid concentration, dissolution mass concentration, and the dissolution time have significant effects on the dissolution process; the stirring speed has no effect. As seen in Table 5, reaction temperature is also effective on the dissolution process for Cu, and solid-to-liquid ratio and reaction time, acid concentration and stirring speed have no significant effects. No parameter has meaningful effect for the dissolution of Fe, statistically (Table 6).

Under the light of the above consideration; the dissolution rate of Zn and Cu is faster than that of Fe. For a heterogeneous reaction system, the mechanism controlling reaction rate can be determined by considering some quantities which affect the reaction rate. Accordingly, it can be deduced that for the processes whose temperature is more effective, the rate is controlled by chemical reaction while for the processes whose stirring speed is more effective, the rate is controlled by diffusion. The activation energy value of 48.15 kJ mol⁻¹ for this dissolution process²⁸ confirms this conclusion. Therefore, for the present work it can be stated that the dissolution rate of Cu and Zn is controlled by chemical reaction.²⁹ A controlling mechanism for Fe dissolution can not be predicted because, both, the temperature and stirring speed have not meaningful effect. On the other hand, under economic considerations, it is desired the dissolved amount of Fe to be minimum, temperature, stirring speed, acid concentration to be kept low, and dissolution mass concentration to be high. For this reason, it would be useful to investigate how Zn and Cu recovery would be effected with changes of the some values of the optimum conditions while keeping the others constant. Thus we selected temperature values less than the optimum temperature value and the values of the solid-to-liquid ratios higher than the optimum solid-to-liquid ratio value. Four series of experiments were carried out and the results analysed statistically were given in case 2–4 columns of Table 7.

If the experimental plan given in Table 3 is studied carefully together with Table 2, it can be seen, that the experiments corresponding to the working conditions in Table 7 have not been carried out during the planned experimental work in Table 3. Thus it should be noted that the dissolution percentages in Table 7 are predicted results obtained by using Eqs. 10–11 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 dissolution 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 $\pm 5\%$ in error. This case states that there is a good agreement between the predicted values and experimental values, and the interactive effects of the quantities are indeed negligible. It may be concluded that the additive model is adequate for describing the dependence of this dissolution process on the various quantities.²⁴

Conclusions

The major conclusions from the present work are:

1. The most important quantity affecting the solubility is dissolution temperature. The dissolution of zinc sulphide concentrate increases with increasing temperature, acid concentration, dissolution time and stirring speed, and decreasing dissolution mass concentration.
2. The optimum conditions are 55 °C for reaction temperature, 0.1 for solid to liquid ratio, 7 mol dm⁻³ for acid concentration, 50 min for reaction time, and 700 min⁻¹ for stirring speed. Under these conditions, in Table 7 it can be seen that the dissolution of 96.32 % is just for Zn while for Cu it is 62.55 % and the dissolution of Fe approximately 29.5 %.
3. The predicted and observed dissolution values are close to each other; it may be concluded that the additive model is adequate for describing the dependence of dissolution process on the various quantities.
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 very useful for processing in industrial scale.
5. The dissolution rates of Cu and Zn are controlled by chemical reaction

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