Experimental Design Approach Regarding Kinetics of High Pressure Leaching Processes

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Abstract

Kinetics of high pressure leaching of nickel laterite ore “Rudjinci”, Serbia, was studied in this work. The following parameters: temperature, acid to ore ratio, stirring speed, and time were optimized in order to obtain the maximum efficiency. Factorial design strategy was used to determine the influence of reaction parameters on the high pressure leaching process. This approach enabled a rapid and accurate estimation of the parameters having main effects and the extent with which the parameters interact. It was found that the sulphuric acid to ore ratio and stirring speed are the most important variables in the system.

Key words: statistical software, pressure leaching, kinetics, nickel laterite

1. Introduction

In last period the different statistical software (Minitab, FactSage, HSC Chemistry 5,..) were used for the planning of experiments and evaluation of the obtained results in current metallurgical processes [1-3]. Using a statistical Minitab software, a graphical display is usually used to find a relationship between the input variables and the output performances. This approach gives the results, which can be presented on Pareto charts, main effects plots and interaction plots, and also provides the information on the reliability of the empirical methods.

1.1. The number of experiment

The number of experiments can be defined by Wheeler's formula, Equation (1).

$$n = (\frac{7 \cdot \sigma}{\Delta})^2 \qquad (1)$$

Where: n- number of experiments; σ- estimated standard deviation, Δ- required degree of confidence (as a fraction).

Thus, it is not necessary to include all experimental runs. The matrix need not be complete, and may contain duplicate points, depending on the required value Δ and accuracy to which the determinants can be defined (σ). But, the number of tests with values of determinant X_i=-1 and +1 must be equal, or the variation must be accounted. In this work the matrix data is plotted in three forms: Pareto plots, main effects plots and interaction plots.

1.2. Pareto chart

The Pareto chart allows to look at both the magnitude and the importance of an effect. This chart displays the absolute value of the effects, and draws a reference line on the chart. Any effect that extends past this reference line is potentially important. The reference line corresponds to Δ = 0.10. Lenth's method is used to draw the line [4].

The position of α on the chart is calculated from t-test, Equation (2).

$$\alpha = \frac{(X^* - \mu)}{\sigma\sqrt{n}} \qquad (2)$$

Where:

n- number of experiments, X*- average value of X_N, σ- standard deviation and μ-error. Plotting $|X_R|$ against α for each variable produces the chart. In these charts, the length of each bar is proportional to the standard effect. The standard effect is the estimated effect divided by its standard error, which is equivalent to computing a *t*-statistic for each effect. The vertical line on the plot judges the effects that are statistically significant. Bars that extend beyond the line correspond to effects that are statistically significant at the 99 % confidence level. The Pareto charts obtained for factors show which factors are significant ones.

1.3. Main effect

This type of plot illustrates the relative magnitude and sign of the effect of a variable R on a determinant X. For each factor the main effect is calculated by summing the responses multiplied by their contrast coefficients, then dividing by the number of runs /2. This is done by plotting the value of the average response X_R for the variable R, where the average response is calculated separately for R=-1 and R=1.

For parameter R, and determinant X and the test number n denoted X_R. The response from determinant X for test n is denoted X_n:

$$X_R(\pm 1) = \frac{\sum_{1}^{n} X_i \cdot R_i}{n} \quad \text{(for n where } R_n = 1 \text{ or } -1) \qquad (3)$$

Where: X_R- the response, R_i- chosen parameter, and n- test number.

Where the value of X_R is negative it means that the increasing the variable decreases the response from the determinant. In essence, X_R is the difference of the average extraction of the 8 leach test with maximal value, and to the 8 leach test with minimal value. The matrix is “orthogonal”, meaning all combination of variables in both high and low conditions do exist.

1.4. Interaction effect

The effect of one factor on the response of another, generally A by B effect is the change in the effect of A as B goes from - to + values. Calculate by summing responses multiplied by both contrast coefficients and dividing by the number of experiments /2. The interaction plot is similar to the main effect plot, except that it plots value of X_R for two values of R, $R' = (\pm 1)$ and $R'' (\pm 1)$. These data points are the average value of four tests each with a specific R' and R''. There the four data points on each chart will be as follows. The interpret the interaction plot is simply, if the lines between the points on the chart are parallel and equal in length, there is no interaction. If the lines on the chart are not parallel or unequal in length, then there is an interactive effect. The magnitude and direction of the effect can be determined from the relative location of the four data points.

Table 1: Data points presented in an interaction plot

Data Point	R'	R''
1	-1	-1
2	-1	1
3	1	-1
4	1	1

2. Experimental

2.1. Material (Ore "Rudjinci", Serbia)

"Rudjinci" deposits, near by Vrnjacka Banja are the most abundant ones in Serbia. The sample of Rudjinci ore is a clay-like, loose material. The ore has a low level of metal components and high level of SiO_2. "Rudjinci" nickel ore deposits belong to a group of exogenous nickel deposits, a subgroup of laterite-silicate deposits [5]. The sample of ore "Rudjinci" was previously homogenized with the following composition (%): 54.20 SiO_2; 14.90 Fe; 4.00 Al_2O_3; 1.09 Cr_2O_3; 1.13 Ni; 0.06 CoO; 1.40 CaO; 3.22 Mg; 0.48 MnO; 0.05 Na_2O and 0.05 K_2O

2.2. Experimental procedures and analytical methods

Under high pressure leaching conditions tests were performed in a 2 l autoclave, manufactured by the Autoclave Engineers, USA. Figure 1 shows an overview presenting the autoclave at IME, RWTH which is part of 3 reactor system from 1-50 l. Temperature was controlled within ±1^{o}C by a temperature control system, manipulating both an electrical heating mantle and a water cooling system. Agitation was provided by a titanium-made impeller that was magnetically driven. The autoclave was equipped with an acid injection device and a system to withdraw sample designed by IME. Only this allows a exact definition of the reaction starting point. A certain amount of laterite was mixed with a pre-calculated amount of deionised water and placed in an autoclave. The slurry was then heated up to a predeterminated temperature in the range of 230 to 250^{o}C under continuous agitation. Upon temperature stabilisation, a certain amount of concentrated sulphuric acid (96 wt %) corresponding to different acid-to-ore ratios, was injected into the autoclave under pressure using the injection device made at IME. Using the sampling system 20 ml of almost clear liquid was periodically withdrawn through a dip tube and then rapidly cooled (as showed at Fig.1). After the end of experiments, solutions aliquots were filtered und analysed aiming Ni, Co, Mg, Al, Fe and Si by ICP spectrophotometry [6, 7]. Eh measurement were taken using a platinum electrode and Ag|AgCl reference electrode. pH measurement was done using universal pH probe. The pH was calibrated using pH standard (pH=1 and pH=7).

Fig. 1. Sampling at the 2 l –Ti- autoclave at IME, RWTH Aachen [8].

2.3. Experimental design

The first campaign of experiments investigated four leaching variables associated with four critical factors for treatment of the "Rudjinci" ore [9].

Table 2: Leaching Variables

Variable	Parameter	Low Value	Median Value	High Value
Temperature (^{o}C)	A	230	240	250
Acid to Ore Ratio (g H_2SO_4/ g ore)	B	0.24	0.32	0.4
Stirring speed (rpm)	C	250	875	1500
Time (min)	D	30	45	60

The significance of these variable was assessed by consideration the results in a 2^4 design matrix. From the matrix data, mathematical algorithms will identify if the variation of a leach conditions alters process control, independently and in conjunction with other variables. The matrix values (A, B, C or D) can equal –1, 0 or 1.

2.4. Data analysis

The statistical data analyses in this work were performed by means of the Minitab software package (Minitab Inc., State College, PA, USA).

3. Results

3.1. Calculation of the number of experiments

The number of experiments was defined by Wheeler's formula, Equation (1):

$$n = (\frac{7 \cdot 4.7}{8})^2$$

Using the following values: $\sigma = 4.7\ \%$; $\Delta = 8\ \%$, it was calculated the number of experiments n= 17.

3.2. Matrix evaluation of ore "Rudjinci" leach parameters

The plan of leaching experiments was determined using the matrix, that is evaluated as follows. For parameter R, and determinant X and the test number n, the response is denoted X_n (as shown in Eq. 2). The response from determinant X for test n is denoted X_n.

Table 3: Test required for matrix evaluation of ore "Rudjinci" leach parameters

Number n	Values of R_N			
	Temperature (°C), A	Acid/Ore Ratio (g/g), B	Stirring Speed, (rpm), C	Time (min), D
1	1	1	-1	-1
2	-1	-1	1	1
3	-1	-1	1	0
4	1	1	1	1
5	-1	1	-1	1
6	1	1	1	-1

7	1	-1	-1	-1
8	1	-1	1	-1
9	-1	1	1	-1
10	0	0	0	0
11	-1	1	1	1
12	1	-1	1	1
13	1	-1	-1	1
14	1	1	-1	1
15	-1	1	-1	-1
16	-1	-1	-1	-1
17	-1	-1	-1	1

For these evaluation, 17 tests were performed, comprising 16 matrix points and one center point. The matrix values (A, B, C or D) can equal –1, 0 or 1, where the data points for 0 represent median values.

3.3. Nickel extraction during leaching of "Rudjinci" ore

The 17 leaching experiments were performed, as shown in Table 3 and Table 4.

Table 4: The obtained results for leaching of ore "Rudjinci" with H_2SO_4

Experiment No.	T (^oC) A 230, 240, 250	a/o (g/g) B 0.24, 0.32, 0.4	v (rpm) C 250, 875; 1500	t (min), D 30, 45, 60	Extraction of Ni, (%)
1	250	0.4	250	30	87.50
2	230	0.24	1500	60	86.70
3	230	0.24	1500	30	75.69
4	250	0.4	1500	60	99.94
5	230	0.4	250	60	92.76
6	250	0.4	1500	30	96.54
7	250	0.24	250	30	54.08
8	250	0.24	1500	30	56.78
9	230	0.40	1500	30	92.54
10	240	0.32	875	45	61.65
11	230	0.40	1500	60	94.02
12	250	0.24	1500	60	72.63
13	250	0.24	250	60	58.84
14	250	0.40	250	60	81.87
15	230	0.40	250	30	80.73
16	230	0.24	250	30	72.82
17	230	0.24	250	60	79.85

The obtained results showed that degree of nickel extraction was influenced by the chosen parameters (1. temperature; 2. sulphuric acid to ore ratio; 3. stirring speed and

4. time). The increase of an acid to ore ratio and stirring speed increase strongly the degree of nickel extraction.

3.4. Experimental design approach to the evaluation of experimental results

The obtained results in Table 3 were evaluated using Pareto plot, main effects plot and interaction plot.

3.4.1. Pareto Chart of the Effects

The vertical line on the Pareto chart judges the effects that are statistically significant on the Ni extraction. The increase of temperature, sulphuric acid to ore ratio and stirring speed have a positive influence on the nickel extraction (Fig. 2).

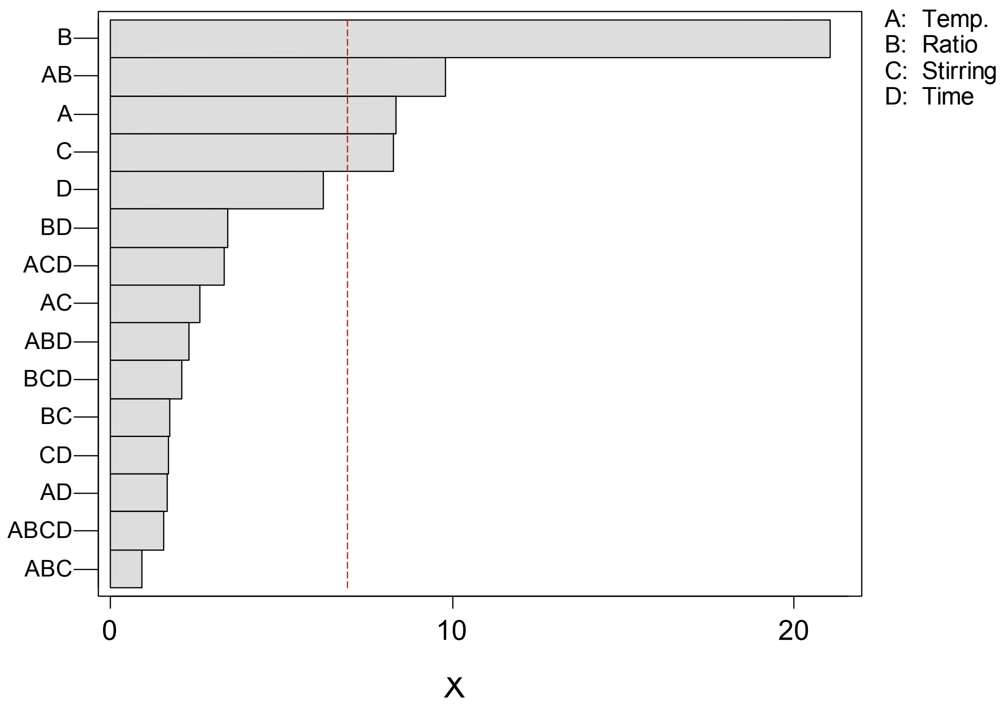

Fig. 2. Pareto plot of nickel extraction

Nickel solubility is primarily dependent on acid concentration, e.g. the acid to ore ratio (parameter B). The reaction time does not influence on the nickel extraction under the above mentioned parameter.

3.4.2. Main effect plot

The sign of effect of variable R on a determinant X was showed on Figure 4.

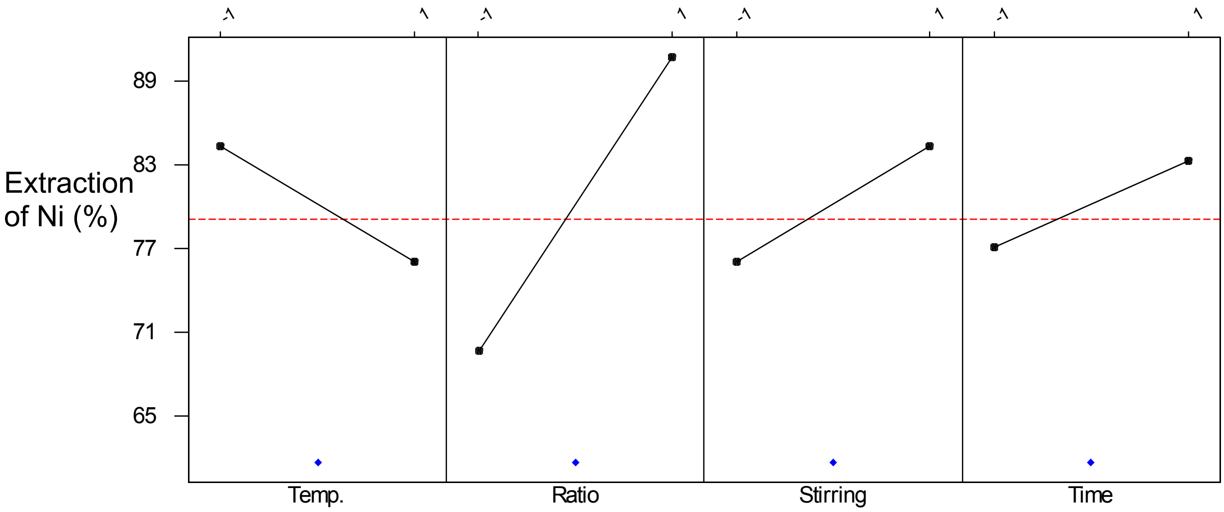

Figure 3: Main effects plot for the nickel dissolution

The values –1 and 1 show the maximum and minimum of an investigated variable (in case of temperature: T_{min}= 230°C and T_{max}=250°C). Main effects plot confirmed the positive influence the sulphuric acid to ore ratio, stirring and leaching time. Unfortunately the increase of temperature has not positive influence, what is opposite than obtained results in our experiment. The short chosen range of temperature between 230°C and 250°C could be one reason for this deviation.

3.4.3. Interaction plot

The interaction plot is similar to main effect plot. The lines on the chart are not parallel or unequal in length demonstrating that there is an interactive effect.

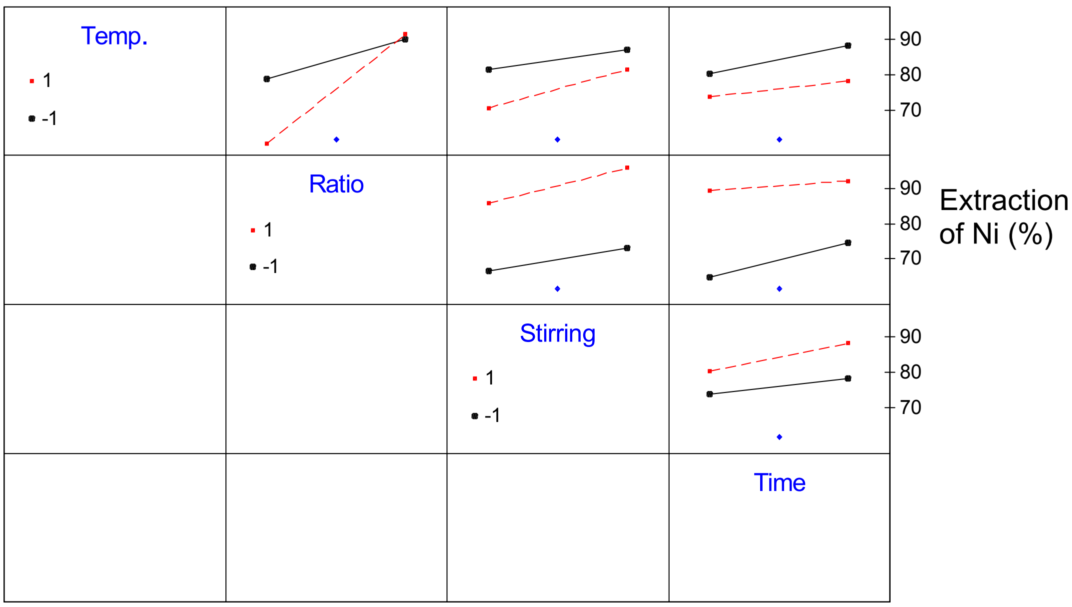

Fig. 4. Interaction ploth plot for the nickel dissolution

The maximal influence is observed by the changing of the sulphuric acid to ore ratio.

4. Conclusion

Experimental design is successful used for the planing of experiments with Minitab software and the analysis of obtained results in high pressure leaching processes. The number of experiments was calculated by Wheeler's formula. The 17 leaching experiments were performed under high pressure leaching conditions in autoclave. The calculated values with Pareto charts, main effects plots and interaction plots have provided the information on the reliability of the empirical methods. The increase of temperature, sulphuric acid to ore ratio and stirring speed have a positive influence on the nickel extraction. The maximal influence is observed by the changing of the sulphuric acid to ore ratio.

5. Acknowledgments

We would like to thank the Alexander von Humboldt Foundation for its research fellowships for Dr. Srećko Stopić allowing a 15 month stay at IME Process Metallurgy and Metal Recycling, RWTH Aachen, where this work was performed.
Authors appreciate too support obtained from Outokumpu Technology Lurgi Metallurgie GmbH, Oberursel, Germany.

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