METALLURGY OF NONFERROUS METALS

Application of Response Surface Methodology and Central Composite Rotatable Design for Modeling and Optimization of Sulfuric and Nitric Leaching of Spent Catalyst1

Ahmadreza Raei Niaki^a, Armin Abazarpoor^{a, *}, Mohammad Halali^a, **Mahdi Maarefvand***^b* **, and Ghasem Ebrahimi***^a*

*a Sharif University of Technology, Department of Materials Science and engineering, Tehran, Iran b Islamic Azad University of Karaj branch, Material engineering, Karaj, Iran *e-mail: Abazarpoor@mehr.sharif.edu*

Abstract—The optimization of leaching parameters for the Ni recovery of the used catalyst was developed using response surface methodology. The relationship between the Ni recoveries, and four main leaching parameters, temperature, acid concentration, leaching time and particle size were presented as empirical model equations. The predicted values of nickel recoveries were found to be in a reasonable agreement with the experimental values, with R^2 as correlation factor being 0.9669 and 0.9869 for sulfuric and nitric acids, respectively. The model equations were then optimized using the quadratic programming method to maxi mize nickel recovery. The optimum conditions were found to be 103.4°C temperature, 246.5 min leaching time, 4.9 mol/L acid concentration and 30.6 μ m particle size to achieve the maximum Ni recovery (73.51%) for sulfuric leaching. Similarly, the conditions for maximum nickel recovery were found to be 104.1°C tem perature, 199.5 min leaching time, 4.45 mol/L acid concentration and 96.6 µm particle size to achieve the maximum Ni recovery (99.76%) for nitric leaching.

Keywords: sulfuric acid, nitric acid, leaching, response surface method, catalyst **DOI:** 10.3103/S1067821215020145

1. INTRODUCTION

A catalyst consisting mainly of Aluminum and Nickel oxide is often used to break methane gas in iron production industries [1]. The spent catalysts are a potential source of the contained critical metals [2]. After the usage of catalyst for a certain period of time, its activity reduces, at this stage, it is considered as a spent. Spent catalysts are harmful to the environment due to the presence of soluble/leachable organic and inorganic compounds and so their disposal in landfills is restricted [3–5].

Hydrometallurgical processing is a suitable method for metals recovery from industrial wastes. Acid leach ing of spent catalyst is a preferred route as the first step to extract the valuable metals. Numerous studies reported on the extraction of nickel from spent cata lyst using mineral acids.

Al-Mansi and abdel Monem [6] reported the opti mum condition of sulphuric acid leaching of Egyptian spent catalyst with more than 99% under the men tioned conditions: leaching time of 5 h, 50% H₂SO₄ concentration, 100°C reaction temperature, S/L ratio

of 1 : 12 and particle size less than 500 μm. Abdel-Aal and Rashad [7] investigated leaching of spent catalyst (NiO/Al_2O_3) and reported that 94% Ni recovery could be achieved at 50% sulphuric acid concentration, 150 min leaching time, reaction temperature of 70°C. Using 1 M HCl and 70°C, Chaudhury et al. reported the maximum 68% recovery [8]. Nitric acid leaching of nickel spent catalyst has not been studied exten sively. Most of these studies reported on the optimum conditions for maximum recovery of Ni using conven tional methods and no studies on interaction of differ ent parameters and impact of them have been reported.

The optimization process is one of the most impor tant activities in recent competitive industry. The high costs of research projects and development have resulted in using the design of experiments (DOE) to minimize the number of tests as well as determination of influenced parameter values on the leaching pro cess. Thus the application of different DOE has been developed in the last two decades [9–11]. The general practice to determine the important leaching process parameters is by varying one parameter and keeping the others constant. The major disadvantage of this technique is that it includes no interactive effects

 $¹$ The article is published in the original.</sup>

Table 1. Relationship between coded and actual values of a variable

among the variables and eventually does not depict the complete effects of various parameters on the process [12–14].

This study involved modelling and optimization of some parameters affecting leaching process for Ni extraction from spent catalyst used in iron-making industry using sulphuric and nitric acids. Response surface methodology (RSM) and central composite rotatable design (CCRD) were used to model and optimize the influence of some parameters affecting acidic leaching process. The parameters selected in this investigation were the acid concentration, particle size, leaching time and temperature.

2. RESPONSE SURFACE METHODOLOGY (RSM)

RSM is a collection of statistical and mathemati cal methods that are useful for the modelling and analyzing engineering problems. In this technique, the main objective is to optimize the response surface that is influenced by various process parameters. RSM also quantifies the relationship between the controllable input parameters and the obtained response surfaces [15].

The design procedure for the RSM is as follows [16]:

(i) Designing of a series of experiments for adequate and reliable measurement of the response of interest.

(ii) Developing a mathematical model of the second order response surface with the best fittings.

(iii) Finding the optimal set of experimental parameters that produce a maximum or minimum value of response.

(iv) Representing the direct and interactive effects of process parameters through two and three-dimen sional (3D) plots.

If all variables are assumed to be measurable, the response surface can be expressed as Eq. (1):

$$
y = f(x_1, x_2, x_3...), \tag{1}
$$

where y is the answer of the system, and x_i the variables of action called factors.

The goal is to optimize the response variable (*y*). It is assumed that the independent variables are contin uous and controllable by experiments with negligible errors. It is required to find a suitable approximation for the true functional relationship between indepen dent variables and the response surface [16].

3. CENTRAL COMPOSITE ROTATABLE DESIGN (CCRD)

The experimental design techniques commonly used for process analysis and modeling are the full fac torial, partial factorial and central composite rotatable designs. A full factorial design requires at least three levels per variable to estimate the coefficients of the quadratic terms in the response model. Thus for the four independent variables 81 experiments plus repli cations would have to be conducted [17]. A partial fac torial design requires fewer experiments than the full factorial. However, the former is particularly useful if certain variables are already known to show no inter action [18, 19].

An effective alternative to the factorial design is the central composite rotatable design (CCRD), origi nally developed by Box and Wilson [17] and improved upon by Box and Hunter [20]. The CCRD gives almost as much information as a three-level factorial, requires much fewer tests than the full factorial and has been shown to be sufficient to describe the major ity of steady-state process responses [17–20].

The number of tests required for the CCRD includes the standard 2*^k* factorial with its origin at the center, 2^k points fixed axially at a distance, say β, from the center to generate the quadratic terms, and repli cate tests at the center; where *k* is the number of variables. The axial points are chosen such that they allow rotatability [20], which ensures that the variance of the model prediction is constant at all, points equidistant from the design center. Replicates of the test at the center are very important as they provide an indepen dent estimate of the experimental error. For four vari ables, the recommended number of tests at the center is six [20]. Hence the total number of tests required for the four independent variables is $2^4 + (2 \times 4) + 6 = 30$ [19, 20].

Once the desired ranges of values of the variables are defined, they are coded to lie at ± 1 for the factorial points, 0 for the center points and \pm β for the axial points. The codes are calculated as functions of the range of interest of each factor as shown in Table 1.

4. EXPERIMENTAL

4.1. Materials

The used catalyst (based $NiO/Al₂O₃$) for direct reduction (MIDREX) in Khuzestan steel company used in the leaching tests. Before use, the catalyst was milled and then roasted in tunnel furnace at 700°C for

Table 2. Chemical composition of used catalyst

Oxides	Al_2O_2	N _i O	SiO ₂	CoO	MgO	FeO	Ta_2O_5
Wt $%$	77.12	18.25	0.52	1.82	0.64	0.91	0.73

Table 3. Factors and their levels for central composite design (CCD)

120 min under air blowing condition to remove the precipitated carbon and sulfur on catalyst surface. The chemical composition of catalyst is summarized in Table 2. All other reagents used for leaching experi ments and chemical analysis were of analytical grade and used without any purification.

4.2. Apparatus and Experimental Procedure

The leaching experiments were carried out in a 1000 mL three necked glass fitted with a reflux con denser. A magnetic heater stirrer (Multi stirrer DM-8 Scinics, Japan) was used as the base of the setup. The reactor was fitted on the magnetic stirrer. The reactor had three entrances. Every entrance was considered for special purpose that consisted of temperature mea surement, feed entrance and condenser. The con denser was needed because some solution was evapo rated and the content of pulp might be changed by evaporation during the experiment. Therefore, the condenser was used to keep the content of pulp con stant by means of distillation of water vapor. In the leaching experiments, the solution was prepared using distilled water and sulfuric acid (H_2SO_4) or nitric acid $(HNO₃)$ from Merck Chemicals Co. After the desired temperature of the reactor was reached, the predeter mined amount of catalyst was added to 500 mL leach ing solution based on the 20 g L^{-1} pulp density and the agitation rate of 800 r/min in all of the leaching exper iments, by which all the solid particles were fully sus pended in the solution. Samples were taken out after reaction period at pre-determined intervals and were filtered using a paper filter. The filtered solution was analyzed for Ni, using an atomic absorption spectrom eter (AAS). To calculate the percentage of Ni leached, the Eq. (2) was used:

$$
R_{Ni} = C_{Ni} \times (D_{Ni} \times m)^{-1} \times 100,
$$
 (2)

where, R_{Ni} (%), C_{Ni} (g/L), D_{Ni} (g/L) and *m* (wt %) indicate Ni recovery, Ni in the solution, pulp density and Ni content of the solid respectively.

5. RESULTS AND DISCUSSIONS

According to the design matrix, 30 set of tests with appropriate combination of the temperature (A), time (B), acid concentration (C) and Particle size (D) were designed for each of acids. The factors and the coded/actual values are given in Table 3. Also the cen tral composite design with the coded/actual values and the results of experiments are given in Table 4.

If all variables are assumed to be measurable, then the response surface can be expressed as Eq. (3):

$$
y = f(A, B, C, ..., x_i),
$$
 (3)

where y is the output and x_i the variables of action called factors. For the central composite design, a total of 30 experimental runs are required [21]. The results were inserted to "Design Expert (DX)" software and a model was chosen and fitted to the results.

5.1. Model Construction for Nickel Recovery of Catalyst

The results of analysis of variance (ANOVA) con sisting of *p*-value, sum of square, mean square, *F*-value and degree freedom (df) for sulfuric and nitric leach ing are shown in Tables 5 and 6.

The results showed that the prediction models of the Ni recoveries are significant for both sulfuric and nitric acid, because *p*-values of the models are under 0.05. The influences of temperature, time and acid concentration on the Ni recovery by sulfuric acid are significant, while the interactions don't have main effect. The influences of temperature, time, acid con centration, interaction between acid concentra tion/time and also quadratic effect of temperature and particle size are significant on the Ni recovery using nitric acid.

The quantity effect of each parameters and their interaction for sulfuric and nitric acid is different as Table 7.

AHMADREZA RAEI NIAKI et al.

Std.	Run			Coded level of variables			Actual level of variables	Observed nickel recovery, %			
order	order	\mathbf{A}	$\, {\bf B}$	$\mathbf C$	${\bf D}$	$A,$ ^o C	B, \min	C, mol/L	D, μm	sulfuric	nitric
$\mathbf{1}$	$\,8\,$	-1	-1	-1	-1	60	160	$\overline{2}$	50	22.42	12.24
$\sqrt{2}$	15	$+1$	-1	-1	-1	90	160	$\overline{2}$	50	35.50	43.41
$\overline{3}$	20	-1	$+1$	-1	-1	60	240	$\overline{2}$	50	37.02	30.52
$\overline{\mathbf{4}}$	18	$+1$	$+1$	-1	-1	90	240	\overline{c}	50	45.11	58.53
5	9	$-1\,$	-1	$+1$	$-1\,$	60	160	$\overline{4}$	50	27.42	46.73
6	$\overline{2}$	$+1$	-1	$+1$	-1	90	160	4	50	47.83	75.64
$\overline{7}$	10	-1	$+1$	$+1$	-1	60	240	4	50	42.24	41.29
8	30	$+1$	$+1$	$+1$	-1	90	240	4	50	56.96	77.34
9	11	-1	-1	-1	$+1$	60	160	\overline{c}	90	20.67	10.12
10	28	$+1$	-1	-1	$+1$	90	160	\overline{c}	90	37.84	44.36
11	26	-1	$+1$	-1	$+1$	60	240	\overline{c}	90	32.16	23.15
12	14	$+1$	$+1$	$-1\,$	$+1$	90	240	$\overline{2}$	90	40.17	53.82
13	27	-1	-1	$+1$	$+1$	60	160	4	90	22.17	46.72
14	17	$+1$	-1	$+1$	$+1$	90	160	4	90	44.15	70.40
15	23	-1	$+1$	$+1$	$+1$	60	240	4	90	35.38	32.24
16	29	$+1$	$+1$	$+1$	$+1$	90	240	4	90	51.31	74.12
17	19	-2	$\boldsymbol{0}$	$\boldsymbol{0}$	$\boldsymbol{0}$	45	200	3	70	23.62	23.50
18	12	$+2$	$\boldsymbol{0}$	$\boldsymbol{0}$	$\boldsymbol{0}$	105	200	3	70	60.43	75.88
19	$\overline{7}$	$\boldsymbol{0}$	-2	$\boldsymbol{0}$	$\boldsymbol{0}$	75	120	3	70	34.42	32.69
$20\,$	13	$\boldsymbol{0}$	$+2$	$\boldsymbol{0}$	$\boldsymbol{0}$	75	280	3	70	44.39	64.26
21	24	$\boldsymbol{0}$	$\boldsymbol{0}$	-2	$\boldsymbol{0}$	75	200	$\mathbf{1}$	70	34.36	25.63
22	\mathfrak{Z}	$\boldsymbol{0}$	$\boldsymbol{0}$	$+2$	$\boldsymbol{0}$	75	200	5	70	50.62	58.04
23	$\mathbf{1}$	$\boldsymbol{0}$	$\boldsymbol{0}$	$\boldsymbol{0}$	-2	75	200	3	30	45.17	53.70
24	25	$\boldsymbol{0}$	$\boldsymbol{0}$	$\boldsymbol{0}$	$+2$	75	200	3	110	42.50	46.08
25	5	$\boldsymbol{0}$	$\boldsymbol{0}$	$\boldsymbol{0}$	$\boldsymbol{0}$	75	200	3	70	39.12	38.33
26	$\overline{\mathbf{4}}$	$\boldsymbol{0}$	$\boldsymbol{0}$	$\boldsymbol{0}$	$\boldsymbol{0}$	75	200	3	70	42.53	36.43
27	21	$\boldsymbol{0}$	$\boldsymbol{0}$	$\boldsymbol{0}$	$\boldsymbol{0}$	75	200	3	70	41.22	36.47
28	22	$\boldsymbol{0}$	$\boldsymbol{0}$	$\boldsymbol{0}$	$\boldsymbol{0}$	75	200	3	70	39.28	32.34
29	16	$\boldsymbol{0}$	$\boldsymbol{0}$	$\boldsymbol{0}$	$\boldsymbol{0}$	75	200	3	70	40.37	35.72
30	6	$\boldsymbol{0}$	$\boldsymbol{0}$	$\boldsymbol{0}$	$\boldsymbol{0}$	75	200	3	70	41.27	33.05

Table 4. Design matrix and the responses for central composite design (CCD)

The experimental results in Table 4 were fitted to a full quadratic second order model equation by apply ing multiple regression analysis for Ni recovery using the software mentioned above. The models equation representing the Ni recovery using sulfuric acid (R_1) and nitric acid $(R₂)$ were expressed as functions of temperature (A) , time (B) , acid concentration (C) and particle size (D) for coded unit as Eqs. (4) and (5) :

$$
R_1 = +40.67 + 8.17A + 4.46B + 3.99C - 0.69D
$$

- 1.26AB + 1.65AC + 0.46AD + 0.34BC - 0.82BD
- 0.34CD-0.12A² - 1.40B² - 0.14C² + 0.077D², (4)

$$
R_2 = +35.68 + 14.30A + 4.77B + 10.87C - 2.10D
$$

+ 0.41AB + 0.14AC + 0.025AD – 4.02BC
- 0.89BD + 0.24CD + 3.47A² + 1.91B² (5)
+ 1.56C² + 3.55D².

The predicted values of nickel recovery obtained from Eqs. (4) and (5) were given in Table 8.

The Figs. 1 and 2 represented the coefficient of multiple determinations, \mathbb{R}^2 , for sulphuric and nitric acid respectively. The high value of \mathbb{R}^2 (0.9669 for sulphuric, 0.9869 for nitric) indicates that the quadratic

Source	Sum of square	Df	Mean square	\boldsymbol{F} Value	p -value (Prob > F)	Note
Model	2614.43	14	186.47	6.66	0.0004	Significant
\mathbf{A}	1600.67	1	1600.67	57.08	0.0001	Significant
\bf{B}	477.04	1	477.04	17.01	0.0009	Significant
$\mathbf C$	382.40	$\mathbf{1}$	382.40	13.64	0.0022	Significant
D	11.48	$\mathbf{1}$	11.48	0.41	0.5319	
$\mathbf{A}\mathbf{B}$	25.50	$\mathbf{1}$	25.50	0.91	0.3554	
$\mathbf{A}\mathbf{C}$	43.56	$\mathbf 1$	43.56	1.55	0.2318	
AD	3.42	$\mathbf{1}$	3.42	0.12	0.7317	
BC	1.82	$\mathbf{1}$	1.82	0.065	0.8022	
BD	10.89	$\mathbf{1}$	10.89	0.39	0.5425	
CD	1.82	$\mathbf{1}$	1.82	0.065	0.8022	
A^2	0.41	1	0.41	0.015	0.9049	
B ²	53.60	$\mathbf{1}$	53.60	1.91	0.1871	
$\overline{C^2}$	0.50	$\mathbf{1}$	0.50	0.018	0.8952	
D^2	0.16	$\mathbf{1}$	0.16	0.006	0.9402	
Residual	533.9	15	35.6			
Lack of fit	519.8	10	51.98	1.15	0.316	Not significant
Pur error	14.1	5	2.82			
Cor total	3148.33	29				

Table 5. Analysis of variance table for the response surface model to predict Ni recovery with sulfuric acid

equation is capable of representing the system under the given experimental domain.

5.2. Three Dimensional (3D) Response Surface Plots

The three-dimensional (3D) response surface plots demonstrate the effect of different variables of leach ing on Ni recovery of catalyst and depicted in Figs. 3a–3f and 4a–4f. The Figs. 3a–3f shows the 3D

Fig. 1. Plot of predicted versus observed values for sulfuric acid.

RUSSIAN JOURNAL OF NON-FERROUS METALS Vol. 56 No. 2 2015

level of other two variables. Figure 3a shows the effect of temperature and time on Ni recovery using sulphuric acid at centre level of acid concentration and particle size. Noting that tem-

response surface plots relationship between two vari ables of sulphuric leaching and Ni recovery at centre

perature and time have a positive major effect on Ni recovery; the more Ni recovery is obtained at the max imum levels of temperature and time. Figure 3b shows

Fig. 2. Plot of predicted versus observed values for Nitric acid.

Source	Sum of square	Df	Mean square	\boldsymbol{F} Value	p -value (Prob > F)	Note
Model	9299.10	14	664.22	12.81	0.0001	Significant
\mathbf{A}	4907.76	$\mathbf{1}$	4907.76	94.65	0.0001	Significant
\bf{B}	545.31	$\mathbf{1}$	545.31	10.52	0.0055	Significant
\bf{B}	2834.03	1	2834.03	54.66	0.0001	Significant
D	105.84	$\mathbf{1}$	105.84	2.04	0.1736	
AB	2.72	1	2.72	0.05	0.8219	
AC	0.30	$\mathbf{1}$	0.30	0.006	0.9401	
AD	0.01	1	0.01	0.001	0.9891	
BC	259.21	1	259.21	5.00	0.041	Significant
BD	12.60	$\mathbf{1}$	12.60	0.24	0.6291	
CD	0.90	$\mathbf{1}$	0.90	0.017	0.8968	
$\overline{A^2}$	330.42	$\mathbf{1}$	330.42	6.37	0.0234	Significant
$\overline{B^2}$	99.89	1	99.89	1.93	0.1854	
$\overline{C^2}$	66.61	$\mathbf{1}$	66.61	1.28	0.2748	
D^2	344.86	$\mathbf{1}$	344.86	6.65	0.021	Significant
Residual	315.0	15	21.0			
Lack of fit	311.4	10	31.1	1.8	0.376	Not significant
Pure error	3.6	5	0.7			
Cor total	9614.1	29				

Table 6. Analysis of variance table for the response surface model to predict Ni recovery with nitric acid

Table 7. Quantity effect of effective parameters and their interaction on sulfuric and nitric leaching

Effects	Α	D			AВ	AC	AD	BC	BD	CD	Λ^2	\mathbf{R}^2	\sim	\mathbf{D}
Sulphuric leaching, %	34.15 18.6		16.7	2.88	5.27	6.9	ا921،	1.42	3.43	.42 ¹	0.5	5.85	0.6	0.3
Nitric leaching, %	29.6	9.88	22.J	4.35	0.8	0.2	0.05	8.3	1.9	0.5	\cdot	3.9		

the effect of acid concentration and temperature on Ni recovery using sulphuric acid at centre level of time and particle size. As can be seen in Fig. 3b Ni recovery depends more on the temperature rather than acid concentration. Figure 3c shows the effect of tempera ture and particle size on Ni recovery at centre level of time and acid concentration. As can be seen in this fig ure, particle size has no significant effect on Ni recov ery. Figure 3d shows the effect of acid concentration and time on Ni recovery at centre level of temperature and particle size. A minimum Ni recovery is obtained with minimum levels of time and acid concentration. Figure 3e shows the effect of particle size and time on Ni recovery at centre level of temperature and acid concentration. It is worth noting that maximum Ni recovery obtained at the minimum level of particle size and maximum level of time. Figure 3f shows the effect of particle size and acid concentration on Ni recovery

at centre level of other parameters. Noting that acid concentration has a significant effect on Ni recovery using sulphuric whilst particle size has a trivial effect.

Figure 4a shows the effect of temperature and time on Ni recovery using nitric acid at centre level of acid concentration and particle size. The positive effect of temperature and time is shown in Fig. 4a; the maxi mum recovery is obtained in high level of temperature and time. Figure 4b shows the effect of acid concen tration and temperature on Ni recovery using nitric acid at centre level of time and particle size. Ni recov ery depends more on the temperature rather than other parameters. Figure 4c shows the effect of temper ature and particle size on Ni recovery at centre level of time and acid concentration. It can be seen that particle size has the less effect on Ni recovery. Figure 4d shows the effect of acid concentration and time on Ni recov ery at centre level of temperature and particle size. As

Fig. 3. Response surface plots showing the effect of two variables on Ni recovery of catalyst using sulphuric acid. Other two variables are held at centre level. (a) Temperature and Time; (b) temperature and acid concentration; (c) temperature and particle size; (d) time and acid concentration; (e) time and particle size; (f) acid concentration and particle size.

it can be seen, time has a negative effect on Ni recovery at high level of acid concentration. Figure 4e shows the effect of particle size and time on Ni recovery at centre level of temperature and acid concentration. The effect of time and acid concentration is similar to Fig. 3e. Figure 4f shows the effect of particle size and acid concentration on Ni recovery at centre level of other parameters. Noting that, as acid concentration is increased, Ni recovery is increased steadily, and not ing also that centre level of particle size is not good for getting a higher Ni recovery.

5.3. Optimization of Nickel Recovery

Finding an optimum condition of leaching process with the highest Ni recovery was the main object of this investigation. The response surface methodology can be used to find desirable location in the design space. Variables can be minimized or maximized in this loca tion. In this research, the response surface methodol ogy was used by DX7 software to find the best condi tion of sulfuric and nitric leaching process.

The optimum process parameters in sulfuric leach ing were found to be 103°C for temperature, 246.5 min

Fig. 4. Response surface plots showing the effect of two variables on Ni recovery of catalyst using Nitric acid. Other two variables are held at centre level. (a) Temperature and Time; (b) temperature and acid concentration; (c) temperature and particle size; (d) time and acid concentration; (e) time and particle size; (f) acid concentration and particle size.

for leaching time, 4.9 mol/L for acid concentration and 30.6 μm for particle size with a prediction of 73.51% maximum Ni recovery, whereas the maximum Ni recovery was 60.43 in the experiments conducted. A 13.08% upgrading in Ni recovery could be obtained using leaching conditions identified by the quadratic programming.

In the same way, the optimum process parameters in nitric leaching were also found to be 104.1°C for temperature, 199.6 min for leaching time, 4.45 mol/L for acid concentration and 96.6 μm for particle size with a prediction of 99.76% maximum Ni recovery, whereas the maximum Ni recovery was 77.33% in the experiments conducted. A 22.43% improvement in Ni recovery could be obtained by optimizing the leaching parameters using quadratic programming.

6. CONCLUSIONS

In this study, the effect of temperature, acid con centration, leaching time, and particle size on sulfuric and nitric leaching of catalyst was investigated using RSM and CCD. A second-order model, representing the nickel recovery expressed as a function of these four variables, was developed by computer simulation programming applying least squares method using

APPLICATION OF RESPONSE SURFACE METHODOLOGY 163

			B, min	C, mol/L	D, μm	Nickel recovery, %				
Std. order	Run order	$A,$ ^o C					sulfuric		nitric	
						observed	predicted	observed	predicted	
$\mathbf{1}$	$\,8\,$	60	160	$\overline{2}$	50	22.42	23.19	12.24	14.23	
$\sqrt{2}$	15	90	160	$\sqrt{2}$	50	35.50	37.85	43.41	41.68	
$\overline{\mathbf{3}}$	$20\,$	60	240	$\overline{2}$	50	37.02	35.59	30.52	32.78	
$\overline{\mathbf{4}}$	18	90	240	$\overline{2}$	50	45.11	45.19	58.53	61.87	
5	9	60	160	$\overline{\mathbf{4}}$	50	27.42	27.87	46.73	43.89	
$\sqrt{6}$	$\overline{2}$	90	160	$\overline{4}$	50	47.83	49.11	75.64	72.76	
$\overline{7}$	10	60	240	$\overline{\mathbf{4}}$	50	42.24	41.63	41.29	43.71	
$\,8\,$	30	90	240	$\overline{\mathbf{4}}$	50	56.96	57.83	77.34	75.41	
9	11	60	160	\overline{c}	90	20.67	22.21	10.12	11.26	
$10\,$	28	90	160	$\overline{2}$	90	37.84	39.69	44.36	42.84	
11	26	60	240	$\overline{2}$	90	32.16	31.65	23.15	25.12	
$12\,$	14	90	240	$\overline{2}$	90	40.17	42.77	53.82	54.46	
13	27	60	160	$\overline{4}$	90	22.17	24.53	46.72	44.78	
14	17	90	160	$\overline{\mathbf{4}}$	90	44.15	47.61	70.40	69.38	
15	23	60	240	$\overline{\mathbf{4}}$	90	35.38	37.01	32.24	34.46	
16	29	90	240	$\overline{4}$	90	51.31	53.19	74.12	72.32	
$17\,$	19	45	200	\mathfrak{Z}	70	23.62	24.32	23.50	21.29	
18	12	105	200	$\overline{3}$	70	60.43	57.32	75.88	77.33	
19	$\overline{7}$	75	120	3	70	34.42	33.41	32.69	33.63	
$20\,$	13	75	280	3	70	44.39	46.42	64.26	61.39	
21	24	75	200	$\mathbf{1}$	70	34.36	33.26	25.63	22.4	
22	\mathfrak{Z}	75	200	5	70	50.62	48.67	58.04	61.45	
23	$\mathbf{1}$	75	200	3	30	45.17	43.64	53.70	53.86	
24	25	75	200	3	110	42.50	40.02	46.08	45.54	
25	5	75	200	$\overline{3}$	70	39.12	40.67	38.33	35.68	
26	$\overline{4}$	75	200	$\overline{3}$	70	42.53	40.67	36.43	35.68	
27	21	75	200	3	70	41.22	40.67	36.47	35.68	
28	22	75	200	$\overline{3}$	$70\,$	39.28	40.67	32.34	35.68	
29	16	75	200	\mathfrak{Z}	$70\,$	40.37	40.67	35.72	35.68	
30	6	75	200	\mathfrak{Z}	70	41.27	40.67	33.05	35.68	

Table 8. Experimental (observed) and predicted values for nickel recovery of catalyst

DX7 software. A statistical analysis (ANOVA) was car ried out to study the effects of the individual variables as well as their combined interactive effects on nickel recovery.

The predicted values of nickel recovery using model equations were in good agreement with the experimental values (\mathbb{R}^2 value of 0.9669 and 0.9869 for sulfuric and nitric leaching respectively). In order to gain a better understanding of the effect of the vari ables on nickel leaching process, the predicted models are presented as the 3D response surface plots. Finally, the optimum conditions for both sulfuric and nitric

leaching were obtained in the range of studied param eters. This study represented that the development of mathematical models for leaching process based on statistics can be useful for predicting and understand ing the effects of experimental factors. What must be noted here is that RSM does not explicate the mecha nism of the studied leaching process, but only as cer tain the effects of variables on response and interac tions between the variables. It can also be stated that it would be a scientific and economic approach to obtain the maximum amount of information in a short period of time and with the lowest number of experiments.

REFERENCES

- 1. Idris, J., Musa, M., Yin, C.Y., and Hamid, K.HK., *J. Ind. Eng. Chem.*, 2010, vol. 16, no. 1, pp. 251–255.
- 2. Sheik, A.R., Ghosh, M.K., Sanjay, K., Subbaiah, T., and Mishra, B.K., *J. Taiwan Inst. Chem. Eng.*, 2013, vol. 44, no. 3, pp. 34–39.
- 3. Lee, J.Y., Rao, S.V., Kumar, B.N., Kang, D.J., and Reddy, B.R., *J. Hazardous Mater.*, 2010, vol. 176, no. 6, pp. 1122–1129.
- 4. Rapaport, D., *Hydrocarbon Process*, 2000, vol. 79, no. 2, pp. 49–56.
- 5. United Stated Environmental Protection Agency (USEPA), Hazardous waste management system, Fed eral Register, 2003, vol. 68, p. 59935.
- 6. Al-Mansi, N.M. and Abdel Monem, N.M., *Waste Management*, 2002, vol. 22, no. 1, pp. 85–90.
- 7. Abdel-Aal, E.A. and Rashad, M.M., *Hydrometallurgy*, 2004, vol. 74, no. 3, pp. 189–197.
- 8. Chaudhury, A.J., Donaldson, J.D., Boddington, S.C., and Grimes, S.M., *Hydrometallurgy*, 1983, vol. 34, no. 2, pp. 137–146.
- 9. Montgomery, D.C., *Design and Analysis of Experiments*, New York: John Wiley & Sons, 2001.
- 10. Abazarpoor, A., Halali, M., Maarefvand, M., Khati bnczhad, H., *Russ. J. Non-Ferrous Met.*, 2013, vol. 54, No. 5, pp. 388–397.
- 11. Hinkelman, K. and Kempthorne, O., *Design and Anal ysis of Experiments*, Hoboken, NJ: John Wiley & Sons, 2005.
- 12. Kincl, M., Turk, S., and Vrecer, F., *Int. J. Pharmaceutics*, 2009, vol. 291, no. 3, pp. 39–46.
- 13. Simate, G., Ndlovu, S., and Gericke, M., *Hydrometal lurgy*, 2008, vol. 98, no. 8, pp. 241–254.
- 14. Asian, N. and Unal, I., *Fuel*, 2008, vol. 88, no. 7, pp. 490–502.
- 15. Obeng, D.P., Morrell, S., Napier-munn, T.J., *Int. J. Mineral Processing*, 2005, vol. 76, no. 4, pp. 181–188.
- 16. Özgen, S., Yildiz, A., Çaliskan, A., and Sabah, E., *Appl. Clay Sci.,* 2009, vol. 46, no. 4, pp. 305–404.
- 17. Tripathi, S.M., Ramamurthy, Y., and Raghukumar, C., *Powder Technol.*, 2010, vol. 201, no. 3, pp. 181–194.
- 18. Mehrabani, J.V., Noaparast, M., Mousavi, S.M., Deh ghan, R., and Ghorbani, A., *Separation Purification Technol.*, 2010, vol. 27, no. 6, pp. 242–249.
- 19. Asian, N., *Powder Technol.*, 2008, vol. 185, no. 4, pp. 80–87.
- 20. Anderson, M.J. and Whitcomb, P.L., *DOE Simplified: Practical Tools for Effective Experimentation*, Productivity Inc., 2000.
- 21. Boulifi, N.E., Aracil, J., and Martinez, M., *Bio-Res. Technol.*, 2010, vol. 101, pp. 8520–8531.