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Determination of the optimum conditions for the leaching of Cd–Ni residues from electrolytic zinc plant using statistical design of experiments

Mohammad Sadegh Safarzadeh [a,*], Davood Moradkhani [a,b], Mehdi Ojaghi Ilkhchi [c], Negar Hamedani Golshan [d]

[a] Laboratory for Leaching and Purification Processes, R&D Center, Iranian Zinc Mines Development Company (IZMDC), Zanjan, Iran
[b] Faculty of Engineering, Zanjan University, Zanjan, Iran
[c] Faculty of Materials Engineering, Sahand University of Technology, Tabriz, Iran
[d] Department of Materials and Metallurgical Engineering, Iran University of Science and Technology, Narmak, Tehran 16846-13114, Iran

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Abstract

This research is part of a continuing effort to reduce environmental conflicts and occupational hazards of cadmium bearing zinc plant residues (ZPR's) and to break through this problem and recover valuable constituents of the wastes. In this paper, effects of influential factors on extraction efficiencies of Cd, Zn, Ni, Pb and Cu from Cd–Ni filtercake as a major ZPR were investigated. In the view of above, the systematical and analytical evaluation method of Taguchi quality engineering has been applied for the leaching of the Cd–Ni filtercake to evaluate the optimal experimental conditions and hence to achieve the highest leaching performance and the best robustness of quantitation from the least number of trials in a batch laboratory scale. An L_{25} orthogonal array (OA, five factors in five levels) was employed to evaluate the effects of temperature (T = 25, 35, 45, 55 and 65 °C), acid concentration (C = 0.31, 0.51, 0.82, 1.22 and 1.84 M), time (t = 15, 30, 45, 60 and 90 min), pulp density (S/L = 125, 142.86, 166.67, 200 and 250 g/l) and stirring speed (R = 200, 300, 400, 500 and 800 rpm) on extraction percent of the individual metals. Statistical analysis, ANOVA, was also employed to determine the relationship between experimental conditions and yield levels. The results showed that increasing temperature reduced performance characteristics. Two approaches were taken into consideration for the experiments, i.e., selective and collective leaching, and then the optimum conditions were sought for each considered approach. The experimental results for selective leaching showed that under optimal leaching conditions (T: 45 °C, C: 0.82 M, t: 60 min, (S/L): 250 g/l, R: 400 rpm), the extraction of cadmium, zinc, nickel, lead and copper were 90.29, 96.86, 8.66, 0.11 and 0.01, respectively. However, the same results for optimal collective leaching conditions (T: 25 °C, C: 1.22 M, t: 60 min, (S/L): 142.86 g/l, R: 200 rpm) showed that the extraction of Cd, Zn and Ni could be over 95%, with negligible dissolution of lead and copper.

Keywords: Zinc plant residues; Filtercake; Cadmium; Taguchi method; Leaching

1. Introduction

The amount and variety of waste materials have increased with the growing of technology and population. Of the priority pollutants, heavy metals cause adverse effects on aquatic ecosystem by entering into the food chain and accumulating in living organisms. The introduction of metal contaminants into the aquatic system has various sources a few of which are atmospheric spread, originating from smelting processes and fuel combustion, industrial leaks and effluents, land application of sewage materials and leaching of garbage. In metal extraction processes, large amounts of various solid wastes including flotation tailings, slags, slimes, filtercakes, flue dusts, etc. are generated. These wastes become activated due to the process applied such as grinding, leaching, roasting, smelting, quenching, etc. Exposure of these wastes to atmospheric oxygen and moisture results in solubilization of toxic metals which may seriously affect the water quality and biological life in surface waters. The potential release of toxic heavy metals from such by-products and waste materials to the surface and ground water are of particular concern [1].

In NILZ lead and zinc plant located in Zanjan, Iran, a leach-electrolysis process is utilized for zinc production. In this process, great amounts of filtercakes as by-product are

* Corresponding author. Tel.: +98 241 4224124; fax: +98 241 4224124.
E-mail address: sadeghsafarzadeh@gmail.com (M.S. Safarzadeh).

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generated daily. These wastes are retained for a future zinc and lead recovery and dumped in open stockpiles where they may cause heavy metal pollution problems [2]. Among the generated filtercakes, the most toxic of them is Cd–Ni filtercake; certainly for its high cadmium content.

Cadmium and its compounds are toxic and poisoning occurs through inhalation and ingestion. Industrial applications for cadmium have recently been developed and consequently the direct production of this metal has increased [2,3]. Recently, the hydrometallurgical extraction and recovery of cadmium from various resources has been reviewed by Safarzadeh et al. [3]. Electrolytic zinc plants produce a major amount of Cd-bearing wastes which may be stockpiled as a potential waste for recovery in the future in some countries or may be used readily to recover its metal values in the others. However, contamination of the environment has been accruing throughout this period. Because of its potential for uncontrolled widespread introduction into the environment, cadmium has been designated "the dissipated element". Industrial and municipal wastes are the main sources of cadmium pollution [3]. Hence, it would be worthwhile to diminish this potential risk from an environmental point of view.

To the authors' knowledge, no experimental research on the determination of the optimum conditions for the leaching Cd–Ni or Cd–Cu filtercake exists in the relevant literature. However, many researchers have reported the selective leaching of Cd–Cu filtercake by sulfuric acid in order to dissolve Cd and Zn (which are easily dissolved in sulfuric acid) and separate Cu as copper filtercake (which sometimes is called copper mud), since copper is not dissolved in the leaching stage [4–6]. They have described their approach in general without discussing the hydrometallurgical details of the process. However, the chemical composition of the cadmium filtercake may vary due to the variation of zinc calcine used for the hydrometallurgical extraction of zinc. For instance, the average composition of the cadmium waste in Žorka Šabac Yugoslav electrolytic zinc and cadmium plant is as follows [3]:

Zn = 40–60%, Cu = 10–16%, Cd = 2–10%, Co = 0.1%, H_2O = 30–35%.

Also the analysis of such a filtercake in NILZ plant is as follows:

Zn = 40–47%, Cd = 3–11%, Cu = 1–3%, Pb = 0.3–1.2%, Ni = 1.5–4%, humidity = 35% [3].

However, the high nickel content in Iranian zinc concentrates leads to accumulation of almost all nickel content in the cadmium purification filtercake, since they are removed simultaneously in the process. Clear of the economic value of high nickel in the waste, the problem of economic separation of nickel from zinc and cadmium still stands. Problematical is also the partial dissolution and cementation of nickel in the so called "selective leaching and cementation" stages, respectively. Thus, here we face with the problem of "nickel" which may not be subject of discussion in other zinc plants, on behalf of their low nickel content in the wastes.

Nevertheless, the metals present in the residue will dissolve according to the following reactions [7]:

$$\mathrm{Zn + H_2SO_4 = ZnSO_4 + H_2} \quad E^\circ_{\mathrm{Zn^{2+}/Zn}} = -0.763\,\mathrm{V} \quad \Delta H^\circ_{298} = -39.352\,\mathrm{kcal} \quad \Delta G^\circ_{298} = -43.64\,\mathrm{kcal} \tag{1}$$

$$\mathrm{ZnO + H_2SO_4 = ZnSO_4 + H_2O} \quad \Delta H^\circ_{298} = -23.896\,\mathrm{kcal} \quad \Delta G^\circ_{298} = -23.747\,\mathrm{kcal} \tag{2}$$

$$\mathrm{Cd + H_2SO_4 = CdSO_4 + H_2} \quad E^\circ_{\mathrm{Cd^{2+}/Cd}} = -0.403\,\mathrm{V} \quad \Delta H^\circ_{298} = -28.552\,\mathrm{kcal} \quad \Delta G^\circ_{298} = -31.76\,\mathrm{kcal} \tag{3}$$

$$\mathrm{CdO + H_2SO_4 = CdSO_4 + H_2O} \quad \Delta H^\circ_{298} = -34.967\,\mathrm{kcal} \quad \Delta G^\circ_{298} = -33.631\,\mathrm{kcal} \tag{4}$$

$$\mathrm{Ni + H_2SO_4 = NiSO_4 + H_2} \quad E^\circ_{\mathrm{Ni^{2+}/Ni}} = -0.25\,\mathrm{V} \quad \Delta H^\circ_{298} = -14.082\,\mathrm{kcal} \quad \Delta G^\circ_{298} = -17.308\,\mathrm{kcal} \tag{5}$$

$$\mathrm{NiO + H_2SO_4 = NiSO_4 + H_2O} \quad \Delta H^\circ_{298} = -25.107\,\mathrm{kcal} \quad \Delta G^\circ_{298} = -23.41\,\mathrm{kcal} \tag{6}$$

Copper is not dissolved, since it is the most precious metal present in the residue.

$$\mathrm{Cu + H_2SO_4 = CuSO_4 + H_2}$$
$$E^\circ_{\mathrm{Cu^{2+}/Cu}} = +0.337\,\mathrm{V} \quad \Delta G^\circ_{298} = 6.9\,\mathrm{kcal} \tag{7}$$

Also, lead forms $PbSO_4$ which is insoluble in the leaching conditions and is easily separated.

$$\mathrm{Pb + H_2SO_4 = PbSO_4 + H_2}$$
$$E^\circ_{\mathrm{Pb^{2+}/Pb}} = -0.126\,\mathrm{V} \quad \Delta G^\circ_{298} = -30.182\,\mathrm{kcal} \tag{8}$$

As could be deduced, from a practical standpoint, copper and lead will easily be separated at the leaching stage. Notice that ΔG°_{298} generally represents the tendency of a reaction to proceed. So we expect the leaching efficiencies to be in the following order:

$$R_{\mathrm{Zn}} > R_{\mathrm{Cd}} > R_{\mathrm{Ni}}$$

In which R stands for leaching efficiency.

Moreover, our observations confirmed this prediction. Another acid consuming reaction is also as follows:

$$\mathrm{CaO + H_2SO_4 = CaSO_4 + H_2O}$$
$$\Delta H^\circ_{298} = -65.618\,\mathrm{kcal} \quad \Delta G^\circ_{298} = -64.309\,\mathrm{kcal} \tag{9}$$

As can be seen, this is the most exothermic reaction among the others. Also, the presence of copper enhances the dissolution of other metals through anodic dissolution of Zn, Cd and Ni.

The aim of this research is to evaluate the leaching behavior of the filtercake and thus to find out the conditions in which the best leaching efficiencies could be achieved. For this reason, the Taguchi method has been used to optimize the process using an L_{25} (5^5) orthogonal array.

2. Experimental

2.1. Materials and methods

After drying the sample at 100 °C for 24 h, the pieces of filtercake were crushed using a ball-mill, and then was directly used for the experiments as ball-milled without any particle size fractionation, since the preliminary tests showed that the effect of particle size on leaching efficiency of cadmium and other associating metals was not significant. As a result, this parameter was not taken into consideration and the illustrated particle size distribution was used in all experiments (Fig. 1).

The leaching experiments were performed in a 2l pyrex beaker set up in a thermostatically controlled water bath, equipped with a digitally controlled thermometer (within ±0.5 °C). Mechanical stirrer (Heidolf RZR 2020) had a controller unit and its twin-bladed impeller and shaft were coated by Teflon. For minimizing aqueous loss when the system is heated, a reflux condenser mounted on top of the cell. After adding 1l of acid with a known concentration to the reaction vessel and setting the temperature at the desired value, a known weight of sample was added to the reactor while stirring the content of the reactor at a certain speed. After each run, the leach slurry was vaccum filtered immediately using S&S 589/2 white ribbon filter paper circles and the leach solution was diluted with double distilled water. The diluted clear leach solution sample was analyzed for Cd, Zn, Ni, Pb and Cu using an AA-300 Perkin-Elmer model atomic absorption spectrometer.

Experimental parameters and their levels were determined in the light of preliminary tests and as mentioned earlier it was observed that particle size distribution could be neglected. However, the acid consumption was calculated using Eqs. (1)–(9).

2.2. Experimental plan

To seek the optimum conditions for the leaching of filtercake, the effect of some parameters on the process was investigated.

Based on our previous experience in related works and those experimental conditions reported by other researchers for the leaching of similar residues and preliminary tests performed (a) temperature, (b) sulfuric acid concentration, (c) time, (d) pulp density and (e) stirring speed were chosen as the five factors to be investigated and five levels are the exclusory set for each of our five factors. Low, medium and high levels of the factors are given in Table 1. According to the Taguchi parameter design methodology, one experimental design should be selected for the controllable factors.

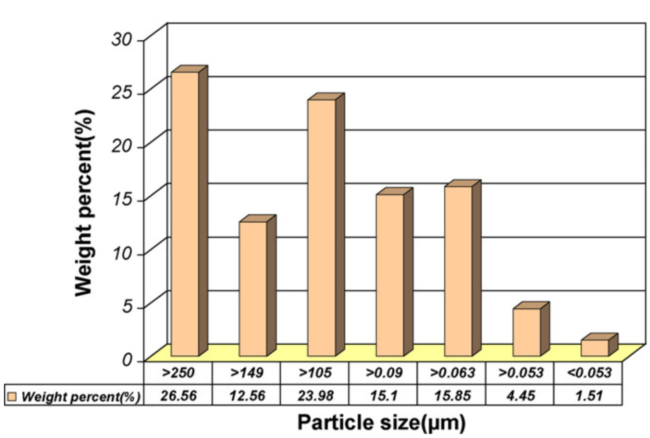

Fig. 1. Particle size distribution of the sample used in the experiments.

Table 1
Experimental parameters and their levels

Parameters	Levels				
	1	2	3	4	5
Temperature (°C)	25	35	45	55	65
Sulfuric acid concentration (M)	0.31	0.51	0.82	1.22	1.84
Time (min)	15	30	45	60	90
Pulp density (g/l)	125	142.86	166.67	200	250
Stirring speed (rpm)	200	300	400	500	800

The orthogonal array experimental design method was chosen to determine experimental plan. Orthogonal array (OA), $L_{25}(5^5)$, which denotes five parameters each with five levels, was chosen since it is the most suitable for the conditions being investigated and each experiment was repeated twice under the same conditions at different times to monitor the effects of noise sources such as the temperature and the humidity of the laboratory medium in the leaching practice. The performance statistics were chosen as the optimization criterion.

The order of experiments was obtained by inserting parameters into columns of orthogonal array, $L_{25}(5^5)$, chosen as the experimental plan given in Table 2, 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.

The interactive effect of parameters was not taken into consideration while some preliminary tests showed that they could be neglected. The validity of this assumption was checked by confirmation experiments conducted at the optimum conditions.

Table 2 is an L_{25} orthogonal array, a table of integers whose column elements (1–5) represent the low, medium and high levels of the column factors. Each row of orthogonal array represents a run, which is a specific set of factor levels to be tested [8].

One of the advantages of Taguchi method over the conventional experimental design methods, in addition to keeping the experimental cost at minimum level, is that it minimizes the variability around the target when bringing the performance to the target value. Another advantage is that optimum working conditions determined from the laboratory work can also be reproduced in the real production environment [9].

Taguchi method recommends the use of the loss function to measure the performance characteristics deviating from the desired value [9]. The value of the loss function is further transformed into a signal-to-noise (SN) ratio. Usually, there are three categories of performance characteristics in the analysis of the SN ratio: that is, the lower, the better; the higher, the better and the nominal, the better. The SN ratio for each level of the process parameters is computed based on the SN analysis.

Table 2
$L_{25}(5^5)$ experimental plan table

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

Regardless of the category of the performance characteristics, the larger SN ratio corresponds to the better performance characteristic. Therefore, the optimal level of the process parameters is the level with the highest SN ratio.

The two performance characteristics were evaluated using the following equations:

- The lower, the better:

$$SN_S = -10\log\left(\frac{1}{n}\sum_{i=1}^{n}Y_i^2\right) \tag{10}$$

- The higher, the better:

$$SN_L = -10\log\left(\frac{1}{n}\sum_{i=1}^{n}\frac{1}{Y_i^2}\right) \tag{11}$$

where SN_S and SN_L are the performance characteristics, n the number of repetition performed for an experimental combination and Y_i the performance value of ith experiment [9]. We would use SN_L if the system is optimized when the response is as large as possible, and we use SN_S if the system is optimized when the response is as small as possible. Eq. (11) was used for calculating performance statistics of cadmium because we wish to have maximum leaching of cadmium. Eq. (10) was used for calculating performance statistics of nickel because we wish to have minimum leaching of nickel (approach 1).

In Taguchi method, the experiment corresponding to optimum working conditions might not have 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 following equation [9]:

$$Y_{\text{opt}} = \frac{T}{n} + \left(\overline{A_i} - \frac{T}{n}\right) + \left(\overline{B_j} - \frac{T}{n}\right) + \cdots \tag{12}$$

where n is the total number of trials, T the sum of all responses and $\overline{A_i}, \overline{B_j}, \ldots$ the average of responses at levels i, j, etc.

The confidence interval at chosen error level may be calculated by [9]:

$$\text{C.I.} = \pm\sqrt{\frac{F(1, n_2)V_e}{N_e}} \tag{13}$$

where F is the value of F table at desired confidence level at degrees of freedom of 1 and degrees of freedom of error, n_2; V_e the variance of error and N_e the effective number of replications. If experimental results are in percentage (%), before evaluating Eqs. (10)–(12) first omega transformation of percentage values should be applied using the following equation [9]:

$$\Omega(\text{dB}) = -10\log\left(\frac{1}{P} - 1\right) \tag{14}$$

where (dB) is the decibel value of percentage value subject to omega transformation and P percentage of the product obtained experimentally. Once the statistical analysis is done, the percentage values can be recovered by inverting the omega transformation [9].

Using of the SN ratio of the results, instead of the average values, introduces some minor changes in the analysis as follows:

- Degrees of freedom of the entire experiments are reduced:

  DOF with SN ratio = number of trial conditions − 1 (i.e., number of repetitions is reduced to 1).

- SN ratio must be converted back into meaningful terms [9].

When the SN ratio is used, the results of the analysis such as estimated performance from the main effects or confidence intervals are expressed in terms of SN. To express the analysis in terms of experimental results, the ratio must be converted back into the original units of measurements [8].

3. Results and discussion

The chemical analysis of the filtercake is given in Table 3. As can be seen from Table 3, the filtercake is mostly composed of zinc, cadmium and nickel.

Mineralogical analysis determined by X-ray diffractometry using a JEOL JDX 8030 model X-ray diffractometer with Cu

Table 3
Chemical analysis of the Cd–Ni filtercake

Element	Zn	Cd	Ni	Cu	Pb	Fe	Mn	Ca	S
Content (wt.%)	44.32	15.17	3.94	1.44	1.08	0.09	0.08	2.27	8.01

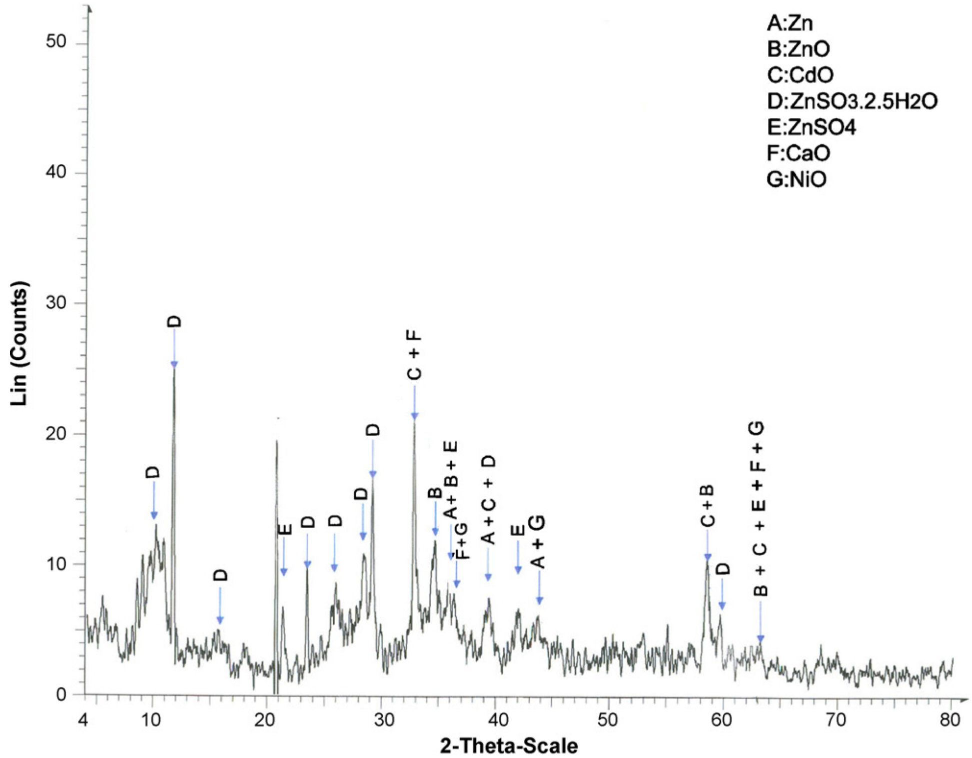

Fig. 2. X-ray diffraction analysis of the Cd–Ni purification filtercake used in the study.

Kα radiation at 30 kV, 20 mA at a scanning rate of 0.4° min^{-1}, indicated that Zn, $ZnSO_4$, $ZnSO_3{\cdot}2.5H_2O$, CdO, NiO, CaO and ZnO were the foremost mineralogical phases in the filtercake, respectively. An X-ray diffractogram illustrating the contents of the sample is given in Fig. 2.

Moreover, using the elemental and mineralogical analysis, the quantitive compositional analysis of the filtercake was sought (Table 4), which demonstrates the high content of zinc and zinc compounds in the sample (∼69%).

The five level $L_{25}(5^5)$ orthogonal table used for the optimization process for cadmium, zinc, and nickel and the corresponding leaching efficiencies with two replications (responses 1 and 2) obtained under the candidate conditions are displayed in Table 5. The collected data were then analyzed by an EXCELL program to evaluate the effect of each parameter on the optimization criteria. Two different approaches were selected to evaluate the leaching behavior of the filtercake, i.e., selective and collective leaching routes. In the view of above, SN_S calculation was performed to minimize the dissolution of Ni, as selective leaching approach. However, SN_L calculation was performed to maximize Cd, Zn and Ni as collective leaching approach (lead and copper were not dissolved at any conditions). The last columns of this table contain SN_L or SN_S values for each run. Notice that to better realize the experimental conditions related to each response, the corresponding conditions are brought in each raw of this table.

The optimization criteria were as follows:

1. Maximum amount of dissolved cadmium and zinc and minimum dissolved amount of the other constituents (selective leaching).
2. Maximum amount of dissolved cadmium, zinc and nickel (collective leaching).

The data obtained from the experiments may now be analyzed. Taguchi recommends analyzing the mean response for each run and also suggests analyzing variation using an appropriately chosen signal-to-noise ratio (SN). In the first optimization criterion, system is optimized when the response is as large as possible for cadmium and zinc, so we deal with the SN_L and factor levels that maximize the SN_L ratio are optimal. Vice versa, the system is optimized when the response is as small as possible for nickel, copper and lead, so we deal with the SN_S and factor levels that maximize the SN_S ratio are optimal.

The Taguchi method uses graphs of the marginal means of each factor, as shown in Figs. 3 and 4, but these graphs are only used to show the trend of each factor more understandable and it is incorrect to use these graphs to predict other values which were

Table 4
The compositional analysis of the main constituents of the filtercake

Composition	CdO	$ZnSO_4$	$ZnSO_3{\cdot}2.5H_2O$	Zn	ZnO	NiO	CaO	L.O.I.
Content (wt.%)	15.04	22.45	21.19	25.27	0.88	4.37	3.17	5.00

Table 5
SN values for cadmium, zinc and nickel

Run	Controllable factors					Response (Cd)			Response (Zn)			Response (Ni)			
	T (°C)	C (M)	t (min)	S/L (g/l)	R (rpm)	1	2	SN_L	1	2	SN_L	1	2	SN_L	SN_S
1	25	0.31	15	125	200	0.04	1.22	27.43	23.27	34.52	10.79	0.79	1.41	25.84	−25.92
2	35	1.84	15	142.86	400	12.00	14.81	18.14	76.81	73.15	13.48	3.13	3.22	23.43	−23.43
3	45	0.51	60	125	400	85.37	92.35	18.93	99.99	99.98	31.69	5.21	5.30	21.98	−21.98
4	35	0.31	30	166.67	500	99.98	99.99	31.69	99.99	99.98	31.69	19.28	24.53	14.70	−14.95
5	65	0.31	60	142.86	800	0.44	3.21	24.97	42.93	49.46	−17.57	1.61	1.95	24.82	−24.83
6	25	0.82	45	166.67	400	99.99	99.99	32.04	75.82	72.8	13.22	35.29	46.51	−1.55	−5.62
7	45	1.84	30	200	200	1.49	2.04	24.84	19.06	19.63	15.85	1.02	1.10	25.89	−25.89
8	65	1.84	45	125	500	0.07	2.47	26.08	91.52	90.49	20.04	2.57	3.09	23.73	−23.74
9	65	1.22	30	250	400	60.51	61.33	5.68	41.94	42.46	2.70	27.26	31.23	11.55	−11.75
10	35	0.82	60	250	200	18.40	21.94	15.47	27.08	26.02	12.90	2.51	3.20	23.71	−23.73
11	35	1.22	90	125	300	99.98	99.99	31.69	99.98	99.99	31.69	12.54	16.03	17.77	−17.88
12	35	0.51	45	200	800	22.71	22.85	14.49	62.51	66.93	8.10	2.33	2.75	24.00	−24.01
13	65	0.82	15	200	300	1.11	0.72	26.18	39.31	40.26	5.08	0.81	1.03	26.16	−26.18
14	25	1.22	60	200	500	0.32	0.46	27.64	20.88	21.23	15.18	0.71	0.96	26.35	−26.36
15	25	1.84	90	250	800	90.74	98.39	21.77	65.33	70.29	9.92	47.74	53.70	−6.48	5.46
16	55	0.82	30	125	800	2.46	7.18	22.22	37.5	44.87	1.39	0.51	1.63	25.97	−26.24
17	55	0.51	15	250	500	82.40	89.95	17.79	61.92	65.24	7.47	63.94	69.30	9.18	−9.71
18	45	0.31	45	250	300	69.89	75.45	12.33	57.34	51.88	−6.98	43.29	41.56	2.28	−2.51
19	45	1.22	15	166.67	800	85.59	62.46	9.56	77.2	73.97	13.75	5.80	3.49	22.35	−22.48
20	55	0.31	90	200	400	0.61	0.27	27.49	38.45	37.8	6.45	1.17	1.11	25.75	−25.75
21	65	0.51	90	166.67	200	0.20	0.47	27.93	59.8	55.23	1.14	0.03	0.06	30.53	−30.57
22	25	0.51	30	142.86	300	24.48	13.51	15.44	61.02	33.11	7.31	3.14	1.63	24.17	−24.30
23	55	1.22	45	142.86	200	99.99	99.99	32.04	99.98	90.75	22.64	99.99	99.99	32.04	−32.04
24	45	0.82	90	142.86	500	8.51	8.29	20.32	99.99	99.98	31.69	2.71	2.82	23.78	−23.79
25	55	1.84	60	166.67	300	0.03	0.03	30.94	76.89	72.16	13.23	0.04	0.02	30.98	−31.01

not experimented. The usual approach is to examine the graphs and pick the winner. The performance statistics of the first data point is thus the average of those obtained from experiments with experiment nos. 1, 6, 14, 15 and 22. Experimental conditions for the second data point therefore are the conditions for the experiments for which column T is 2 (i.e., experiments with experiment nos. 2, 4, 10, 11 and 12), and so on. In Fig. 3, the effects of controllable factors on SN_L for cadmium, zinc and nickel are displayed.

It was verified that temperature is conversely proportional to SN_L. According to Fig. 3 for cadmium, increasing of temperature decreases the SN_L and hence the dissolution of cadmium is better carried out at low temperature. This is due to exothermic nature of the dissolution reactions. However, the relevant reactions and their associated enthalpies confirmed this conclusion ($\Delta H < 0$) (Eqs. (1)–(9)).

However, for nickel the situation is absolutely different. In Fig. 4, the effects of controllable factors on SN_S for Ni are displayed, whereby the usual approach here, is also to single out the maximum points in the SN_S curves. Also notice that the variation of experimental conditions had not any conspicuous effect on the dissolution of copper and lead and they were separated as solid wastes. So we just deal with Cd, Zn and Ni in the prediction of optimum conditions. So in terms of maximizing the SN_L for cadmium, T_1 (25 °C), C_1 (0.31 M), t_4 (60 min), $(S/L)_3$ (166.67 g/l) and R_1 (200 rpm) [notice that C and t are pooled for cadmium] were selected. Also in terms of maximizing SN_L for zinc, T_2 (35 °C), C_4 (1.22 M), t_2 (30 min), $(S/L)_1$ (125 g/l) and R_4 (500 rpm) [notice that t is pooled for zinc] were selected. Next, in terms of maximizing the SN_S for nickel, T_3 (45 °C), C_1 (0.31 M), t_5 (90 min), $(S/L)_5$ (250 g/l) and R_3 (400 rpm) [notice that C is pooled for nickel] were selected. As can be understood, the leaching behavior of zinc closely resembles that of cadmium. Furthermore, it is well known that the presence of zinc is not problematic in electrowinning of cadmium; even at concentrations several times more than cadmium (notice that cadmium is nobler than zinc and so is reduced prior to zinc). Thus, this primary approach was taken into consideration to separate cadmium and zinc and keeping nickel in the residues.

Taguchi oriented practitioners often use analysis of variance (ANOVA) to determine the factors that influence the average response and signal-to-noise ratio. So the statistical analysis of variance (ANOVA) was performed to see whether the process parameters are statistically significant. The F-value for each parameter indicates which parameter has a significant effect on the leaching efficiency and is simply a ratio of the squared deviations to the mean of the squared error. Usually, the larger F-value, the greater the effect of the leaching efficiency due to the change of the process parameter. Optimal combination of the process parameters can be predicted using ANOVA analysis and performance characteristics. Sum of squares (S), mean square (variance), F (variance ratio), S' (pure sum of squares) and P (percentage contribution on response) based on SN data are presented in Tables 6–9 for cadmium, zinc and nickel, respectively. According to these results, pulp density has the greatest effect on performance characteristics for cadmium. The F-value for all factors is smaller than the extracted F-value from the table for 95% confidence level ($F = 3.2592$). This means that the vari-

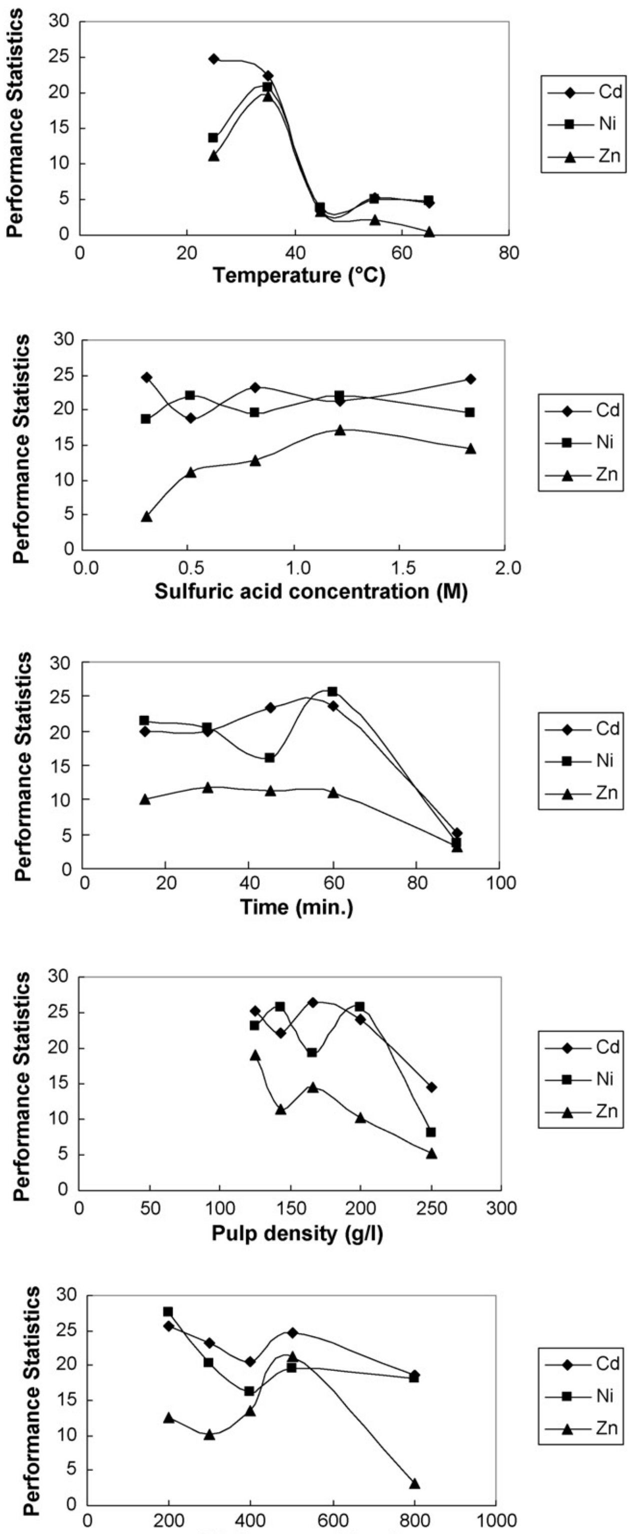

Fig. 3. Effect of controllable factors on performance statistics (SN_L) for cadmium, zinc and nickel.

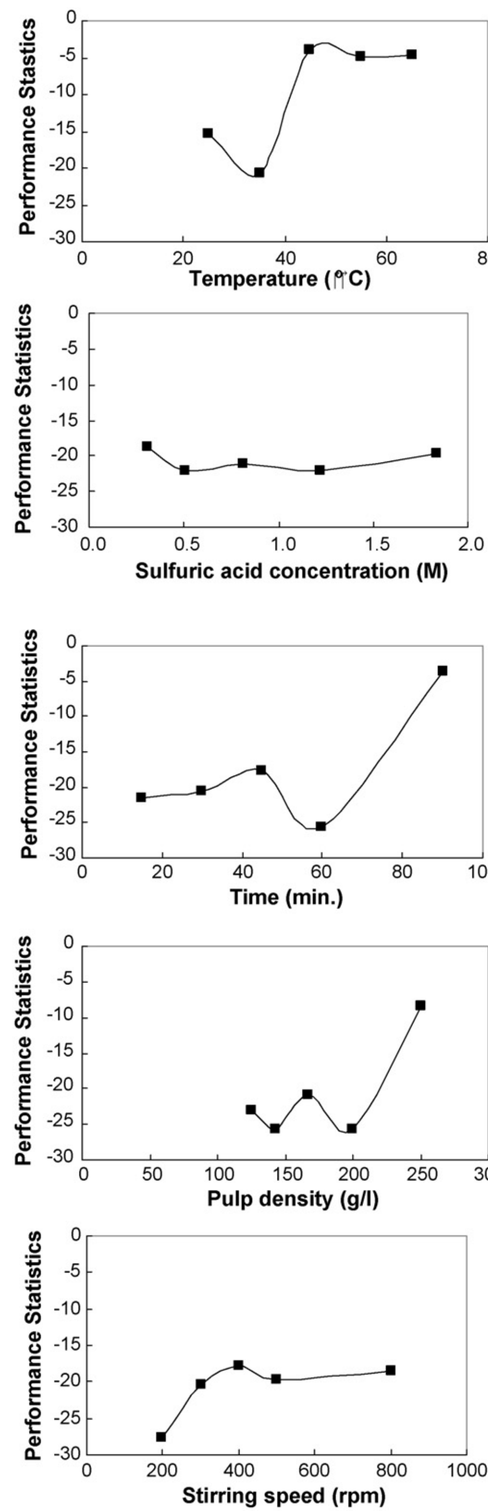

Fig. 4. Effect of controllable factors on performance statistics (SN_S) for nickel.

ance of all factors is insignificant compared with the variance of error and none of them have meaningful effect on the responses. Also, temperature, stirring speed and pulp density have greater influence on the response for zinc, respectively. However, the preference of the factors is different for nickel. Yet, the effect of pulp density on the response is higher and the effects of stirring speed and temperature are lower, compared to those values for zinc. However, the most influential factor for nickel is also pulp density. Furthermore, the F-value for S/L factor is greater than the extracted F-value from the table for 95% confidence level ($F = 3.8378$) for nickel, which means that the variance of this

Table 6
Statistical results based on SN_L data for cadmium

Factor	S	f	V (S/f)	F	S'	P
T	233.87	4	58.47	1.41	68.50	5.11
C			Pooled			
T			Pooled			
S/L	440.86	4	110.22	2.67	275.49	20.53
R	170.80	4	42.70	1.03	5.43	0.40
Error	496.10	12	41.34	1.00		73.96
Total	1341.63	24				100

$F = 3.2592$ (at 95% confidence level).

Table 7
Statistical results based on SN_L data for zinc

Factor	S	f	V (S/f)	F	S'	P
T	912.47	4	228.12	2.50	547.88	15.85
C	426.77	4	106.69	1.17	62.18	1.80
T			Pooled			
S/L	536.78	4	134.20	1.47	172.19	4.98
R	850.62	4	212.65	2.33	486.03	14.06
Error	729.18	8	91.15	1.00		63.30
Total	3455.82	24	143.9924			100

$F = 3.8378$ (at 95% confidence level).

Table 8
Statistical results based on SN_L data for nickel

Factor	S	f	V (S/f)	F	S′	P
T	373.53	4	93.38	2.27	208.86	8.67
C			Pooled			
t	253.48	4	63.37	1.54	88.80	3.68
S/L	1077.84	4	269.46	6.55	913.16	37.89
R	375.66	4	93.92	2.28	210.99	8.76
Error	329.35	8	41.17	1.00		41.00
Total	2409.87	24	100.4111			100

$F = 3.8378$ (at 95% confidence level).

factor is significant compared with the variance of error and has a meaningful effect on the responses.

For better comparing, percentage contribution of all factors are plotted for cadmium, zinc and nickel as Pareto charts in Figs. 5 and 6.

Finally, using these findings and modeling significant effects by the Taguchi method, results for all combination of levels could be predicted. Then these predictions should be confirmed by some experiments. The confidence intervals for ±5% risk are

Table 9
Statistical results based on SN_S data for nickel

Factor	S	f	V (S/f)	F	S′	P
T	279.49	4	69.87	2.21	153.22	7.40
C			Pooled			
t	195.26	4	48.82	1.55	68.98	3.33
S/L	1026.66	4	256.66	8.13	900.38	43.50
R	316.11	4	79.03	2.50	189.83	9.17
Error	252.55	8	31.57	1.00		36.60
Total	2070.08	24	86.2532			100

$F = 3.8378$ (at 95% confidence level).

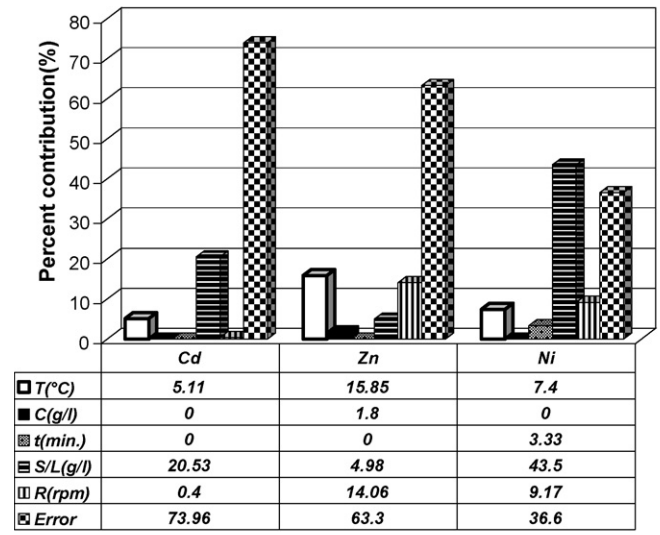

Fig. 5. Contribution of each factor on the performance statistics (approach 1).

given in Table 10 for cadmium, zinc and nickel, respectively. So with spending less time and cost, acceptable results can be derived.

Under economical considerations, it is desired that the temperature and acid consumption be kept low. The results showed that maximum cadmium and zinc and minimum Ni content occurred in conditions $T_3C_3t_4(\mathrm{S/L})_5R_3$. These results were accepted by confidence limits that were calculated in each case (see Table 10). It can be seen that experiments corresponding to optimum conditions for maximizing cadmium (T_1: 25 °C, C_1: 0.31 M, t_4: 60 min, $(\mathrm{S/L})_3$: 166.67 g/l, R_1: 200 rpm) and zinc (T_2: 35 °C, C_4: 1.22 M, t_2: 30 min, $(\mathrm{S/L})_1$: 125 g/l, R_4: 500 rpm) and also minimizing nickel (T_3: 45 °C, C_1: 0.31 M, t_5: 90 min, $(\mathrm{S/L})_5$: 250 g/l, R_3: 400 rpm) have not been carried out during the experimental work. Furthermore, the experiment corresponding to ultimate optimum condition, which is obtained by combining

Table 10
Optimum working conditions, observed and predicted dissolved quantity (%) for cadmium, zinc, nickel, lead and copper in the experiments (approach 1)

Parameters	Optimum working conditions	
	Value	Level
T, temperature (°C)	45	3
C, sulfuric acid concentration (M)	0.82	3
t, time (min)	60	4
S/L, pulp density (g/l)	250	5
R, stirring speed (rpm)	400	3
Observed leaching efficiency for cadmium (%)	90.29	
Predicted leaching efficiency for cadmium (%)	88.82	
Predicted confidence interval for cadmium (%)	78.71–98.92	
Observed leaching efficiency for zinc (%)	96.86	
Predicted leaching efficiency for zinc (%)	93.23	
Predicted confidence interval for zinc (%)	75.08–100.00	
Observed leaching efficiency for nickel (%)	8.66	
Predicted leaching efficiency for nickel (%)	10.94	
Predicted confidence interval for nickel (%)	0.26–21.63	
Observed leaching efficiency for lead (%)	0.11	
Observed leaching efficiency for copper (%)	0.01	

Table 11
Optimum working conditions, observed and predicted dissolved quantity (%) for cadmium, zinc, nickel, lead and copper in the experiments (approach 2)

Parameters	Optimum working conditions (case I)		Optimum working conditions (case II)	
	Value	Level	Value	Level
T, temperature (°C)	25	1	35	2
C, sulfuric acid concentration (g/l)	1.22	4	1.22	4
t, time (min)	60	4	60	4
S/L, pulp density (g/l)	142.86	2	142.86	2
R, stirring speed (rpm)	200	1	200	1
Observed leaching efficiency for cadmium (%)	99.84		97.14	
Predicted leaching efficiency for cadmium (%)	99.41		98.95	
Predicted confidence interval for cadmium (%)	89.31–100.00		88.84–100.00	
Observed leaching efficiency for zinc (%)	100.00		99.57	
Predicted leaching efficiency for zinc (%)	97.61		99.63	
Predicted confidence interval for zinc (%)	79.46–100.00		81.48–100.00	
Observed leaching efficiency for nickel (%)	95.27		97.54	
Predicted leaching efficiency for nickel (%)	99.32		99.86	
Predicted confidence interval for nickel (%)	87.12–100.00		87.66–100.00	
Observed leaching efficiency for lead (%)	0.20		0.20	
Observed leaching efficiency for copper (%)	0.01		0.01	

the three series of optimum conditions in a logical manner, has not been performed during the experiments.

As can be seen from Table 10, ∼8.66% (∼300 ppm) of nickel was also dissolved at optimum working conditions. However, the concentration of the cadmium and zinc in the filtrate were 19.98 and 62.12 g/l, respectively. Since the concentration of nickel in the resulted solution is higher than maximum allowed nickel content in the electrowinning of cadmium, the resulted solution could not be directly used for electrowinning process and a purification stage is needed.

At the second approach, we targeted the collective leaching route. So the SN_L analysis has been performed to maximize nickel in the filtrate. So in terms of maximizing the SN_L, T_2 (35 °C), C_4 (1.22 M), t_4 (60 min), $(S/L)_2$ (142.86 g/l) and R_1 (200 rpm) [notice that C is pooled for nickel] were selected.

The ultimate optimum condition in this approach is also achieved by mixing the three optimum conditions in a sense manner. In the view of above, T_1 (25 °C), C_4 (1.22 M), t_4 (60 min), $(S/L)_2$ (142.86 g/l) and R_1 (200 rpm) were selected as ultimate optimum conditions (see Table 11).

According to the results, case I was selected as optimum collective leaching condition for approach 2.

As can be seen from Table 11, ∼99.84% (24.30 g/l) of cadmium, ∼100% (69.34 g/l) of zinc and also ∼95.27% of nickel (7.11 g/l) dissolved at optimum working conditions. Now from this point on, the problem of economical separating of the metals begins. Recently, Safarzadeh et al. have evaluated the separation of cadmium from nickel through cementation by zinc powder. Based on their work, it was difficult to achieve selectivity by this method and ∼7% of nickel was also cemented at optimum conditions [7]. However, it seems inevitable to use SX method to efficient separation of these metals.

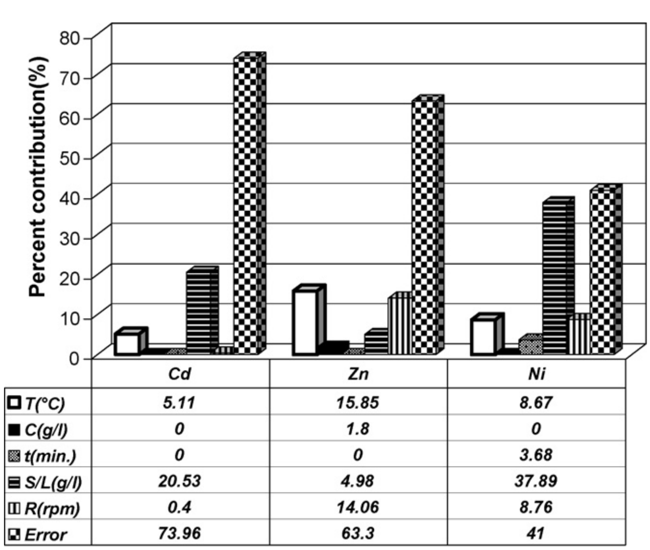

Fig. 6. Contribution of each factor on the performance statistics (approach 2).

4. Conclusions

Taking into consideration the number of parameters used in the experiments (temperature (T), acid concentration (C), time (t), pulp density (S/L) and stirring speed (R)) and their level, one of the standard experimentation plans was chosen using an L_{25} orthogonal array. Two approaches were considered for optimization process, i.e., selective and collective leaching routes. As a result, T_3 (45 °C), C_3 (0.82 M), t_4 (60 min), $(S/L)_5$ (250 g/l) and R_3 (400 rpm) are recommended for optimal selective leaching conditions and T_1 (25 °C), C_4 (1.22 M), t_4 (60 min), $(S/L)_2$ (142.86 g/l) and R_1 (200 rpm) are attained for collective leaching conditions. The most effective parameter for maximum dissolution of cadmium and zinc and minimum dissolution of nickel is found to be pulp density. Also, increasing the temperature resulted in reduction of leaching efficiencies, due to exothermic dissolution reactions.

According to our observations, the variation of the experimental conditions had no decisive effect on the dissolution of lead and copper, which suggests the simple separation of these ions.

Thus, it should be noted that the leaching percentages given in Tables 10 and 11 are predicted by using Eqs. (12)–(14). Also, 95% significance level confidence intervals of prediction are given in Tables 10 and 11. From the fact that the leaching percentages obtained from confirmation experiments are within the calculated confidence intervals (see Tables 10 and 11), it can be concluded that experimental results are within ±5% in error. This proves that interactive effects of parameters are indeed negligible.

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