

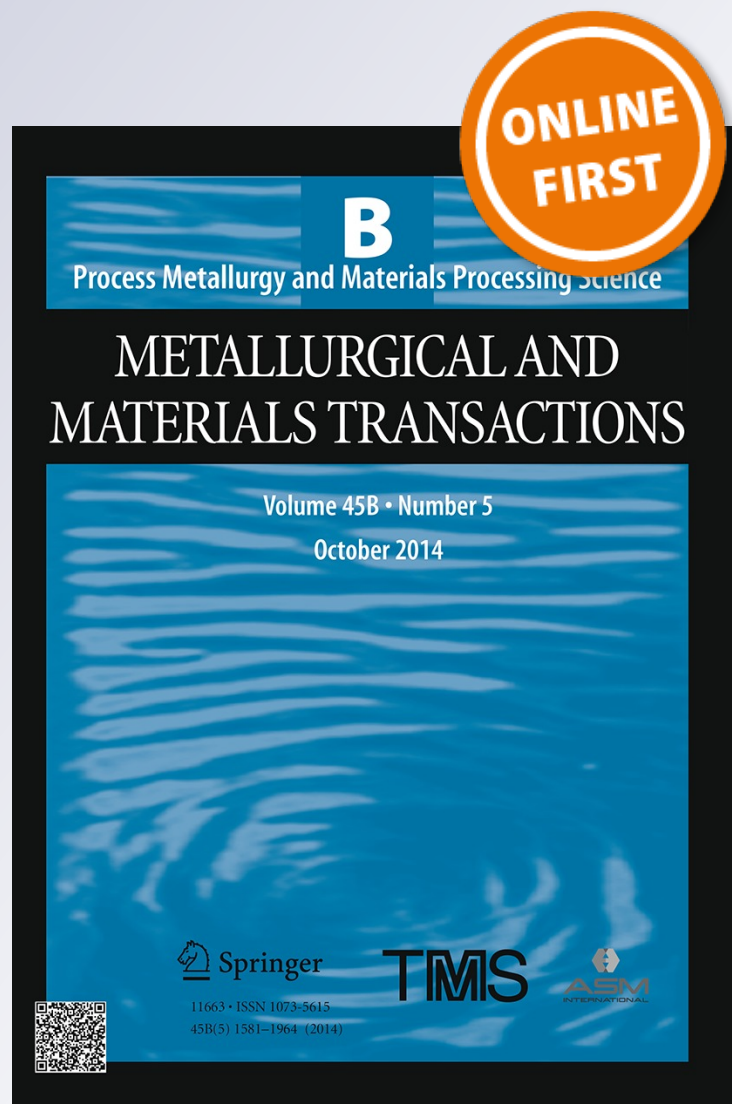
Selective Acidic Leaching of Spent Zinc-Carbon Batteries Followed by Zinc Electrowinning

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Selective Acidic Leaching of Spent Zinc-Carbon Batteries Followed by Zinc Electrowinning

HOSSEIN SHALCHIAN, ALI RAFSANJANI-ABBASI, JALIL VAHDATI-KHAKI,
and ABOLFAZL BABAKHANI

In this work, a selective acidic leaching procedure was employed for recycling zinc from spent zinc-carbon batteries. Leaching experiments were carried out in order to maximize zinc recovery and minimize manganese recovery in diluted sulfuric acid media. Response surface methodology and analysis of variance were employed for experimental design, data analysis, and leaching optimization. The experimental design has 28 experiments that include 24 main runs and four replicate in center point. The optimal conditions obtained from the selective acidic leaching experiments, were sulfuric acid concentration of 1 pct v/v, leaching temperature of 343 K (70 °C), pulp density of 8 pct w/v, and stirring speed of 300 rpm. The results show that the zinc and manganese recoveries after staged selective leaching are about 92 and 15 pct, respectively. Finally, metallic zinc with purity of 99.9 pct and electrolytic manganese dioxide were obtained by electrowinning.

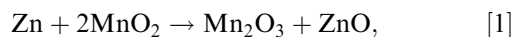
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I. INTRODUCTION

IN developing countries like Iran, almost all of the used household batteries are discarded in municipal solid waste (MSW) without any special recycling program.^[1] MnO₂-Zn cell batteries represent a major amount among the spent batteries waste.^[2] The MnO₂-Zn battery importation in Iran has rapidly increased since 2000, and its market share reached about 30 pct in 2004. Demand for MnO₂-Zn battery consumption is expected to increase in following years due to their high performance, long shelf life, and suitable price. On the other hand, the limitation of natural sources and the tremendous demand for using of household batteries has stimulated efforts to recycle valuable components from spent batteries.^[1,3]

At present, many researchers have studied how to recycle the zinc-carbon and alkaline batteries. The overall discharge reaction of MnO₂-Zn batteries could be expressed as:



This is the most probable reaction, but sometimes the products may change depending on the battery discharging conditions,^[4] thus, recycling processes were performed on final Mn-Zn oxide mixtures.

In most hydrometallurgical recycling processes, reductive acidic leaching with various reducing agents

has been employed to bring both zinc and manganese to leach liquor. Hydrogen peroxide^[5,6] and organic reductants such as glucose, lactose, oxalic acid, ascorbic acid, and citric acid^[7-9] have been used as chemical reductants in previous studies. Selective separation of zinc and manganese from leach liquors also has been conducted by liquid-liquid extraction^[2,10] and chemical precipitation methods.^[5,9] Although these combined methods appear to be technically effective to recycle spent alkaline and zinc-carbon batteries, cost issues should also be evaluated especially due to the use of various chemical reagents and their considerable prices that can increase the final cost, such as some solvent extractants. They are very expensive and consequently might result in too high treatment costs when scaled up in industry practice.^[9,11]

Selective separation of zinc and manganese from leach liquors is necessary before zinc electrowinning. The behavior of Manganese during zinc electrodeposition was studied by many researchers. MacKinnon and Brannen^[12] mentioned that too much Mn²⁺ (>4 g/L) create an anode sludge disposal problem and increase the frequency of anode cleaning. Mn²⁺ ions oxidize to Mn⁴⁺ resulting in MnO₂ formation in electrowinning cell. Presence of high concentrations of MnO₂ up to 10 g/L in electrolyte resulted in progressive decrease in current efficiency. Furthermore, high concentrations of MnO₂ cause the quality of zinc deposits to deteriorate.^[13]

The present study focuses on zinc recovery from spent zinc-carbon batteries. Direct separation of zinc from manganese could be possible by employing selective acidic leaching on black paste of spent batteries. Zinc oxide could be fully dissolved by sulfuric acid solutions whereas the dissolution of Mn₂O₃ and Mn₃O₄ oxides is partial.^[5] Metallic zinc and electrolytic manganese

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dioxide could be obtained from resulting leach liquor by electrowinning. In comparison with reductive acidic leaching, the recovery of zinc could be more reasonable because the leaching and separation procedures conduct simultaneously without any reducing agent. The most important parameters affecting zinc and manganese

Table I. Material Content of Dismantled Batteries

Components	Weight Percentages
Steel	38
Plastic	3
Paper	2
Carbon rod	7
Black paste	48
Loss during dismantling	2

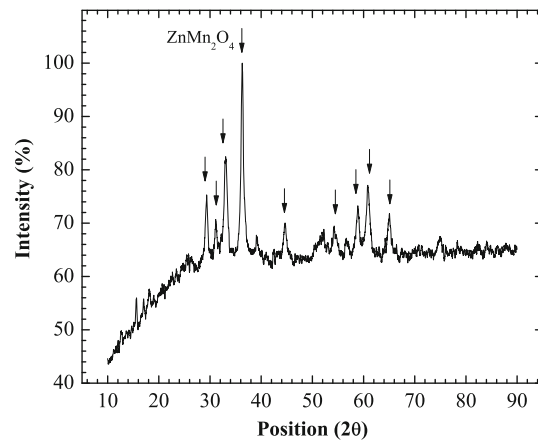


Fig. 1—XRD pattern of dried powder from zinc-carbon batteries.

Table II. Independent Variables and Their Levels Used in the Experimental Design

Variables	X variable	Variable levels				
		$-\alpha$	-1	0	+1	$+\alpha$
Temperature K (°C)	A	298 (25)	313 (40)	328 (55)	343 (70)	358 (85)
Sulfuric acid concentration(pct v/v)	B	0.25	0.5	0.75	1	1.25
Pulp density (pct w/v)	C	2	4	6	8	10
Stirring speed (rpm)	D	100	200	300	400	500

Table III. Experimental Design and Metal Recoveries

Run	Temperature [K (°C)]	Sulfuric Acid Concentration (pct v/v)	Pulp Density (pct w/v)	Stirring Speed (rpm)	Zn Recovery (pct)	Mn Recovery (pct)
1	298 (25)	0.75	6	300	36.58	7.84
2	343 (70)	1	8	400	54.4	8.69
3	343 (70)	0.5	8	200	26.07	3.56
4	328 (55)	0.75	6	300	40.86	9.18
5	343 (70)	1	4	400	68.82	21.37
6	328 (55)	0.75	6	300	38.55	9.51
7	343 (70)	1	8	200	52.23	7.74
8	313 (40)	0.5	8	400	23.59	2.73
9	328 (55)	0.25	6	300	20.82	2.3
10	313 (40)	0.5	4	200	35.3	7.3
11	358 (85)	0.75	6	300	48.82	7.56
12	328 (55)	0.75	6	300	39.02	9.45
13	313 (40)	1	4	200	53.11	17.98
14	328 (55)	0.75	6	300	34.25	6.95
15	328 (55)	1.25	6	300	51.66	17
16	328 (55)	0.75	2	300	81.03	28.7
17	328 (55)	0.75	10	300	25.11	3.88
18	328 (55)	0.75	6	100	34.17	7.45
19	343 (70)	0.5	4	400	36.94	7.45
20	313 (40)	1	8	400	41.55	7.3
21	313 (40)	1	4	400	59.8	22.22
22	313 (40)	1	8	200	38.01	8.84
23	343 (70)	0.5	8	400	33.42	3.39
24	343 (70)	1	4	200	65.21	23.4
25	313 (40)	0.5	4	400	33.75	7.05
26	328 (55)	0.75	6	500	36.28	7.32
27	343 (70)	0.5	4	200	36.78	8.25
28	313 (40)	0.5	8	200	23.72	3.52

recoveries including sulfuric acid concentration, leaching temperature, pulp density, and stirring speed were studied. In selective acidic leaching experiments, the response surface methodology (RSM) was applied for optimization of desirable responses which are maximum value of zinc recovery and minimum value of manganese recovery. The RSM is a combination of mathematical and statistical techniques that are useful for designing experiments, modeling, evaluating the effects of variables, and optimization of problems in which a response of interest is influenced by several variables.^[14]

II. MATERIALS AND METHODS

A. Pretreatment of Zinc-Carbon Batteries

Discharged zinc-carbon batteries (size AA) from the same manufacturer were used in this research. Spent batteries were manually dismantled, and both plastic and steel shells were removed using saw and screwdriver.

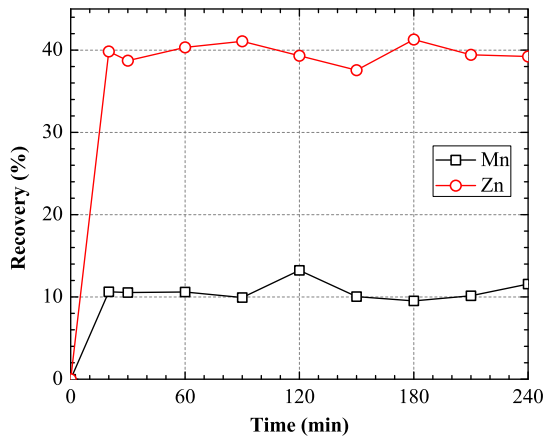


Fig. 2—Manganese and zinc recoveries as a function of time (temperature, sulfuric acid concentration, pulp density, and stirring speed were kept constant at 328 K (55 °C), 0.75 pct v/v, 6 pct w/v, and 300 rpm, respectively).

All battery components were separated and weighted. The weight percentages of battery components are listed in Table I. The black paste was dried for 24 hours at 378 K (105 °C). To obtain a homogenous fine powder, dried paste was milled for 10 minutes using planetary ball mill at room temperature and rotation speed of 260 rpm. The ball to powder weight ratio was 2:1. This homogenous powder was screened in a sieve with 75 μm openings (−200 mesh) and subjected for subsequent leaching tests.

B. Characterization of Battery Powder

Phase detection and chemical analysis of the original powder were done using X-ray diffraction (XRD) analyzer (Philips PW1800) and X-ray fluorescence (XRF) spectroscopy (Philips PW1480). The XRD pattern including the major phase present in the sample is shown in Figure 1. The XRF semi-quantitative results showed that the original homogenous powder contained 29.24 pct Mn, 17.54 pct Zn, 6.24 pct Cl, 0.17 pct Mg, 0.16 pct S, 0.05 pct P, 0.03 pct Ca, 0.03 pct K₂O, and 0.02 pct Cu. An atomic absorption spectrophotometer (AAS, PG 990) was used to determine the accurate contents of manganese and zinc in washed powder after neutral leaching.

C. Experimental Design

The RSM used in the present study was a central composite design (CCD), involving four factors at three levels. These four independent variables were sulfuric acid concentration, temperature, pulp density, and stirring speed. Table II gives the range of used variables in this study. The experimental design which included 24 experiments is shown in Table III. In addition, to detect the quadratic effects of factors, four center point runs were considered in the design. In order to minimize the effect of systematic errors, the experiments were carried out in random. Finally, a verification experiment was done according to the optimal condition.

Table IV. Analysis of Variance for the Responses of Zinc and Manganese Recoveries

Source	df	Zn			Mn		
		Mean Square	p value	Significance	Mean square	p value	Significance
Model	14	376.09	<0.0001	significant	87.94	<0.0001	significant
A (temperature)	1	333.91	0.0098	significant	1.68	0.4830	—
B (acid concentration)	1	2505.94	<0.0001	significant	447.98	<0.0001	significant
C (pulp density)	1	1812.39	<0.0001	significant	588.95	<0.0001	significant
D (stirring speed)	1	28.3	0.3948	—	0.018	0.9422	—
AB	1	61.39	0.2175	—	0.49	0.7019	—
AC	1	11.32	0.5872	—	1.52	0.5044	—
AD	1	1.4	0.8476	—	0.86	0.6140	—
BC	1	38.38	0.3241	—	78.99	0.0003	significant
BD	1	6.48	0.6806	—	0.82	0.6216	—
CD	1	1.01	0.8705	—	0.46	0.7119	—
A ²	1	39.07	0.32	—	2.2	0.4238	—
B ²	1	2.76	0.7877	—	0.82	0.6223	—
C ²	1	359.14	0.0079	significant	81.69	0.0002	significant
D ²	1	8.44	0.6389	—	3.49	0.3169	—

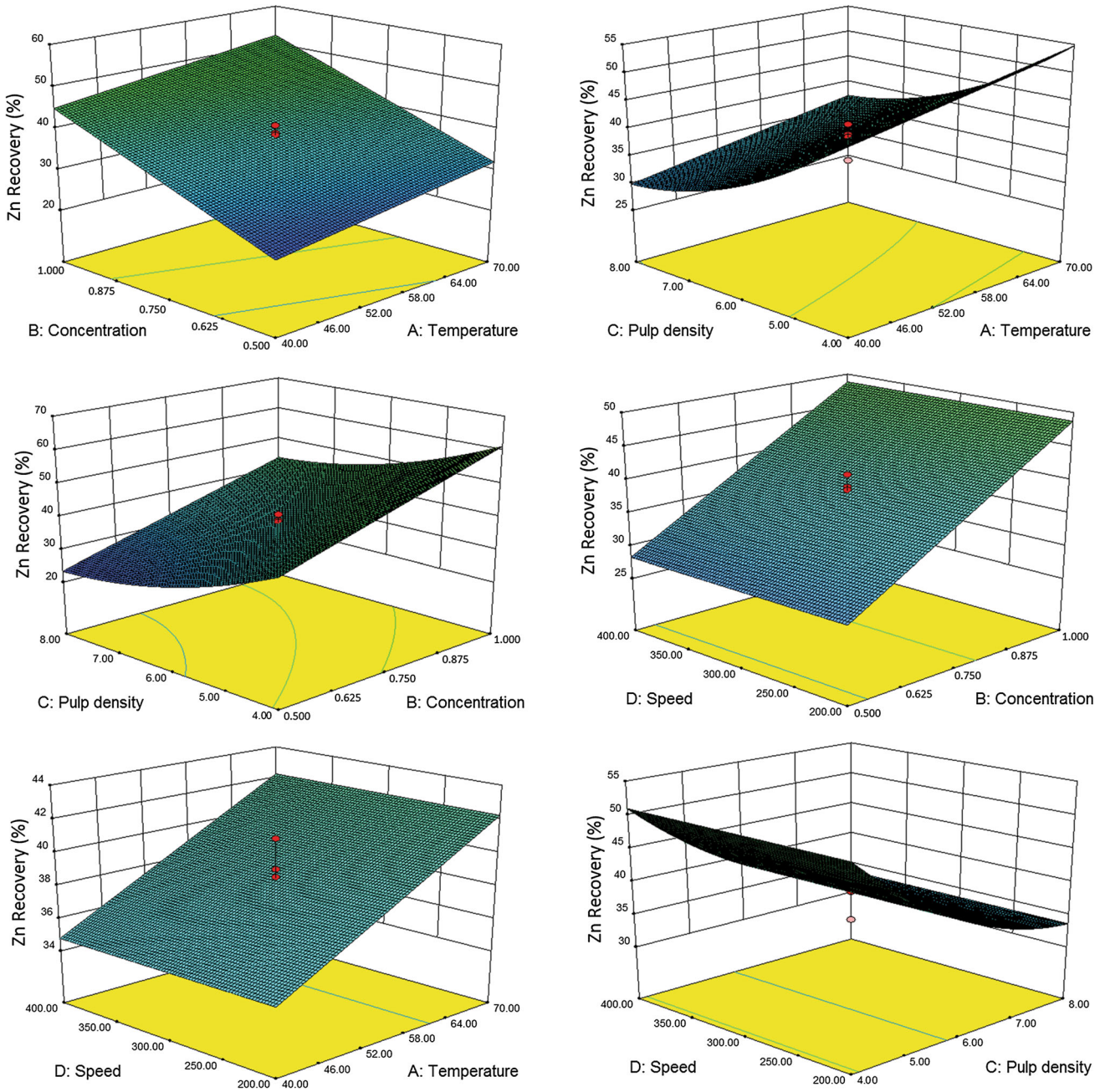


Fig. 3—Graphical representations for response surfaces of zinc recovery.

The independent variables used in this study were coded according to Eq. [2]:

$$X = \frac{x_i - x_0}{\Delta x}, \quad i = 1, 2, \dots, k \quad [2]$$

where X is the dimensionless value of a variable, x_i the actual value of a variable, x_0 the value of X at the center point, and Δx is the step change.^[15]

In general, the response for the quadratic polynomials is described in Eq. [3]:

$$Y = \beta_0 + \sum_{i=1}^k \beta_i X_i + \sum_{i=1}^k \beta_{ii} X_i^2 + \sum_{i=1}^{k-1} \sum_{j=2}^k \beta_{ij} X_i X_j + \varepsilon, \quad [3]$$

where Y is the predicted response, X_i and X_j are the input variables, β_0 is the intercept term, β_i is the linear effects, β_{ii} is the squared effect, and β_{ij} is the interaction term.^[14]

D. Leaching

Leaching experiments were performed in two sequential steps. At first, neutral leaching was carried out according to the procedure described in previous publication to remove zinc chloride electrolyte.^[7] This step is carried out three times just by using distilled water at room temperature for 1 hour and resulted in 14 pct weight loss. Neutral leaching was efficient in recovery of

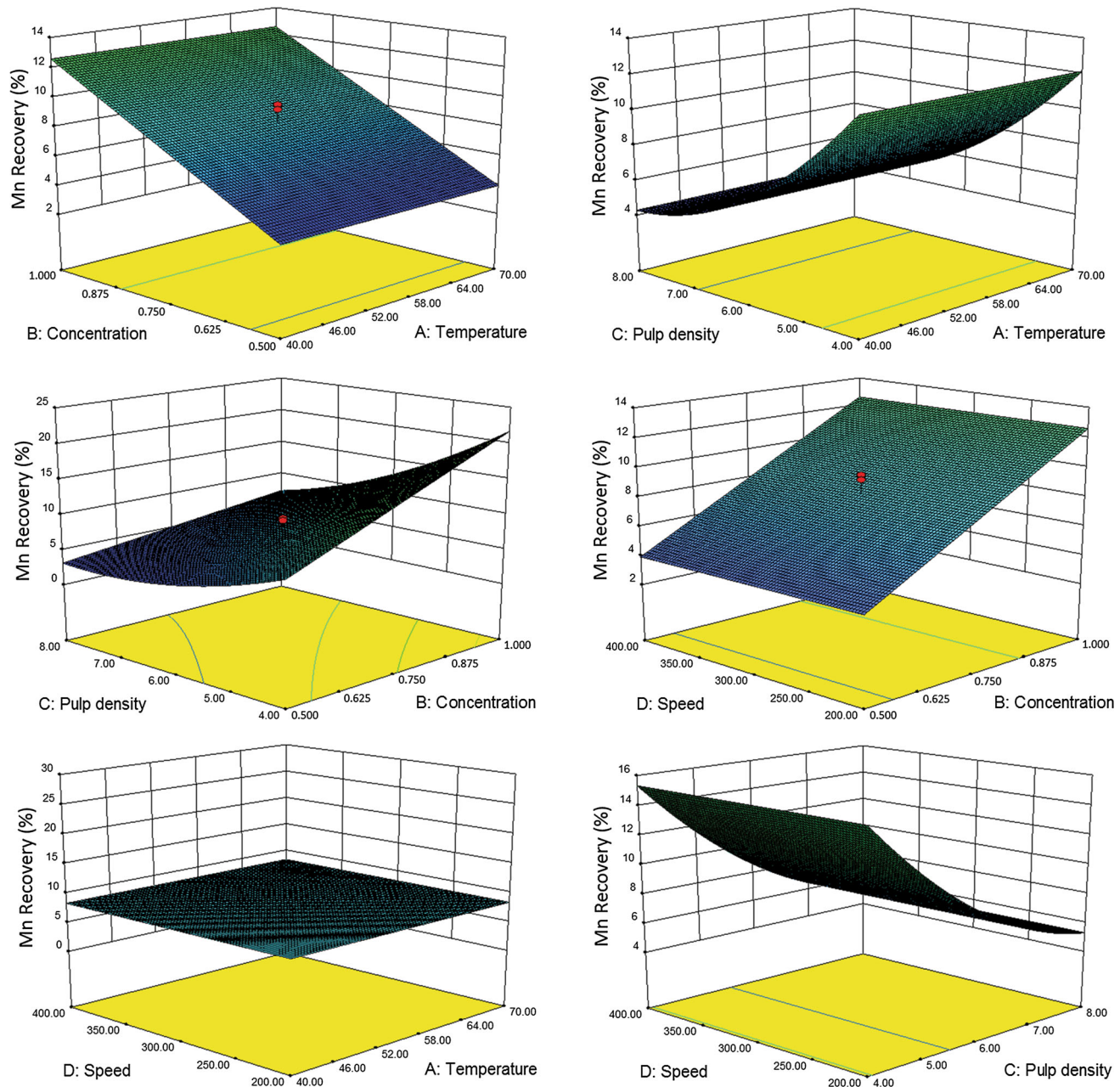


Fig. 4—Graphical representations for response surfaces of manganese recovery.

33 pct of total zinc. Then, selective acidic leaching in diluted sulfuric acid was done in a 250 mL glass reactor (solution volume 100 mL) immersed in a controlled temperature bath equipped with a glass mechanical stirrer. A plastic cap was used at the reactor opening to reduce the loss of water by evaporation.

The raw acid used to produce the leaching solution was 98 pct (18 M) analytical grade (Merck).

In this stage the following reactions may occur during the dissolution process^[4]:



Zinc oxide can be fully dissolved by sulfuric acid solutions according to Eq. [4], but the dissolution of Mn oxides is partial because resulting MnO₂ (Eqs. [5] and [6]) is insoluble.^[5]

After each leaching test, the leaching liquor was filtered and the solid residue remained on the paper. The filtrate was analyzed for manganese and zinc by atomic absorption spectrometry.

To determine an appropriate leaching time, some experiments were done using four independent variables at their zero levels. Results are shown in Figure 2. This figure indicates that zinc and manganese recoveries did not

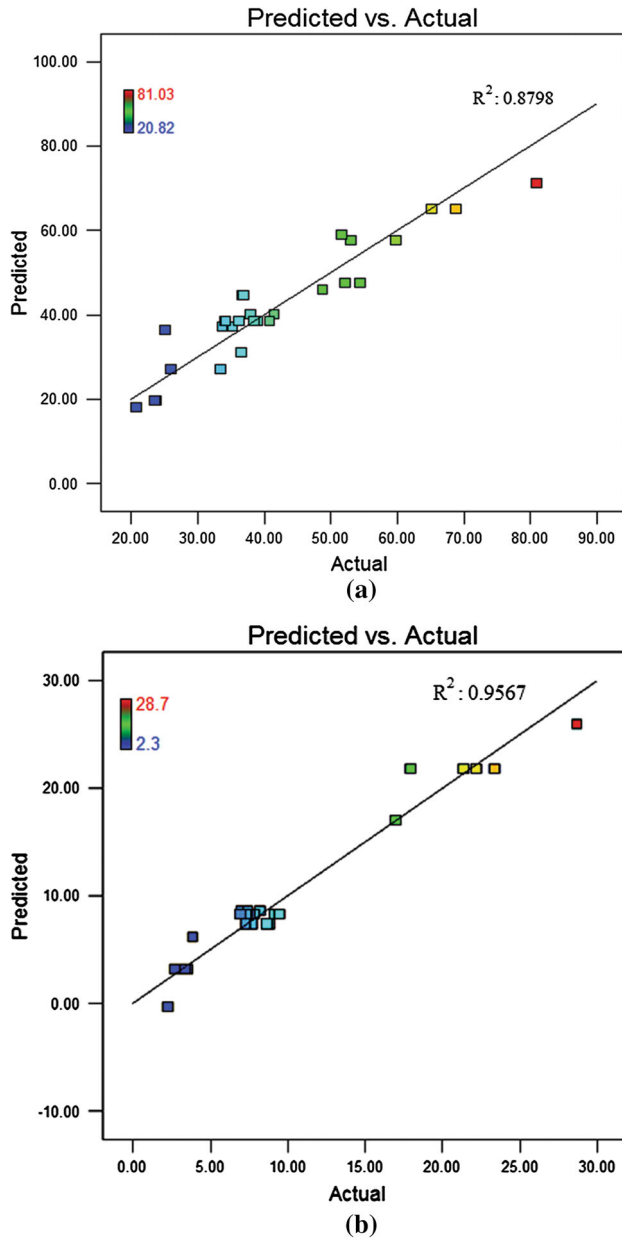
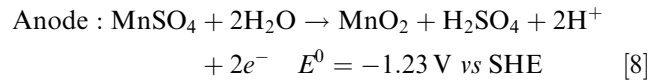
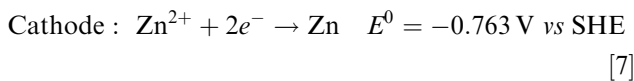


Fig. 5—The graphical plots of actual vs predicted values for: (a) zinc recovery and (b) manganese recovery.

significantly increase after 20 minutes. Consequently, 20 minutes is considered as a reasonable time for leaching experiments.

E. Electrowinning

In this step, the recovery of metallic zinc and electrolytic manganese dioxide from leach liquor by electrowinning was evaluated. Simultaneous electrowinning of these two materials is described elsewhere.^[16] In this case, zinc and manganese dioxide are deposited on the cathode and anode by the following reactions, respectively^[17]:



The cathode and anode in the electrowinning cell were made by an aluminum 1050 sheet with the geometric area of 4 cm², and a lead/silver alloy with the geometric area of 2.8 cm², respectively. A 20 mm distance was kept constant between the electrodes. Current was supplied by a D.C. power supply. A magnetic stirrer provided solution homogenization during electrowinning tests. The mass of deposited zinc was calculated by weight difference of dried cathode before and after the experiment. The obtained pulp after each test was filtered, and solid residues were dried. All experiments were carried out in a 500 mL beaker (250 mL fresh liquor) for 1 hour. The cell voltage was measured by a digital voltammeter. Finally, a sample of deposited Zn was fully dissolved in acidic solution, and zinc content and other probable impure elements in solution like Mn and Pb were measured by atomic absorption spectrophotometer.

III. RESULTS AND DISCUSSION

A. Data Analysis

The data obtained from the selective acidic leaching experiments were analyzed using Design-Expert Version 8.0.0 trial software. Analysis of variance (ANOVA) was employed to determine the statistical significance of main variable effects as well as the interaction effects. The significance level employed in the analysis evaluated by p-values is less than 0.05 (Table IV). In addition, the graphical representations for response surfaces of leaching tests are drawn in Figures 3 and 4. The desired responses were zinc and manganese recoveries.

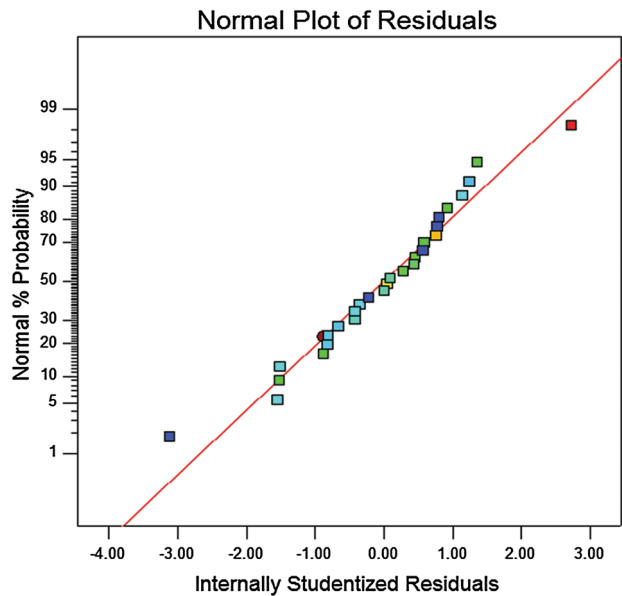
Based on ANOVA calculations two polynomial equations for zinc and manganese recoveries were proposed as follows:

$$\begin{aligned} \text{Zn recovery(pct)} = & 38.51 + 3.73(A) + 10.22(B) - 8.69(C) \\ & + 3.81(C)^2 \quad [9] \end{aligned}$$

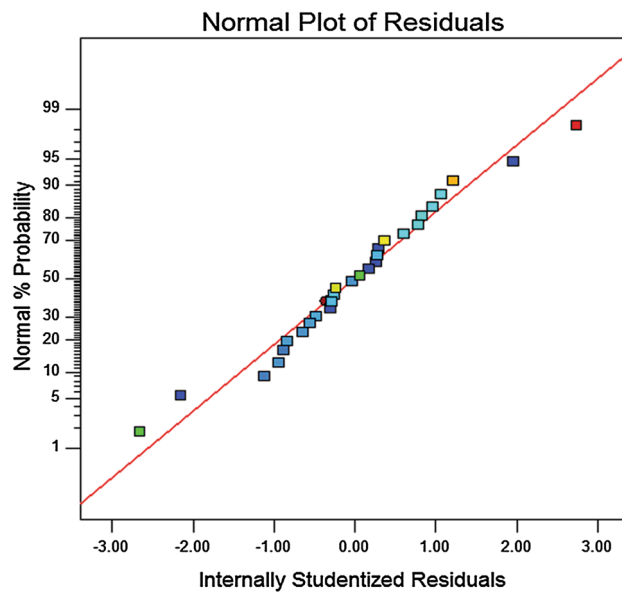
$$\begin{aligned} \text{Mn recovery(pct)} = & 8.27 + 4.32(B) - 4.95(C) - 2.22(BC) \\ & + 1.93(C)^2 \quad [10] \end{aligned}$$

In these equations, *A* is temperature, *B* is sulfuric acid concentration, and *C* is pulp density (S/L).

The *R*² for zinc and manganese recoveries are 0.880 and 0.957, respectively. These values indicate a reasonable agreement between actual and predicted values in the range of the studied experimental variables. The graphical plots of these comparisons are shown in Figure 5. In addition, the normal probability plot of the studentized residuals is another tool for judging the adequacy of the fitted model, as the data points follow a straight line.^[18] Figure 6 illustrates these plots for zinc and manganese recoveries. As it can be seen, both plots satisfy the normal distribution of data points.



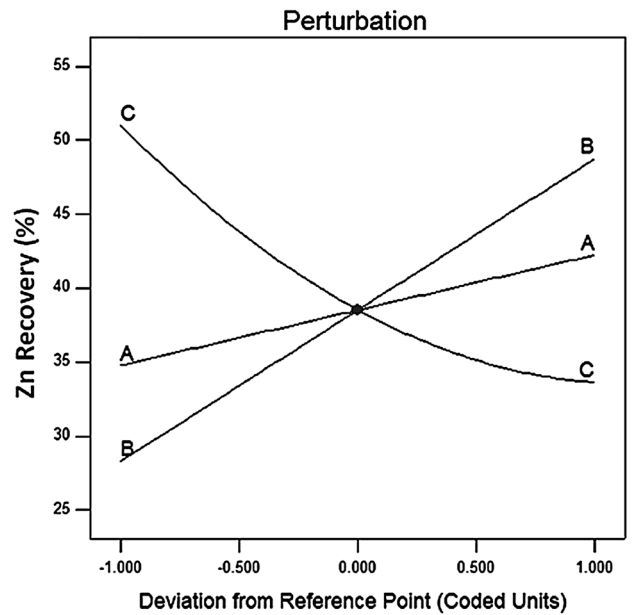
(a)



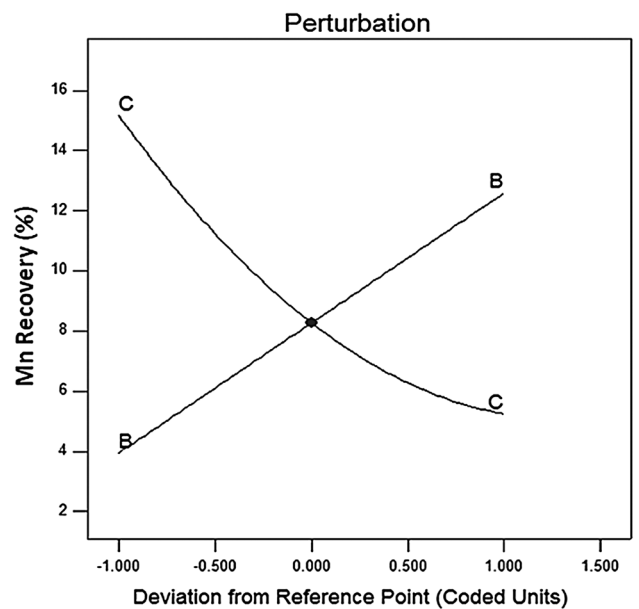
(b)

Fig. 6—The normal probability plots of the studentized residuals for: (a) zinc recovery and (b) manganese recovery.

Perturbation plots (Figure 7) show a comparison between coded model variables and their effects on desired responses. The recovery percentages were plotted by changing only one factor over its range, while the other factors were held at their zero levels. These plots show that sulfuric acid concentration had a positive effect on zinc and manganese recoveries, while pulp density had an expected negative effect. Zinc recovery was increased by increasing the temperature, while manganese recovery showed insensitivity to this factor. Perturbation plots showed that there was no effect of stirring speed on metal recoveries.



(a)



(b)

Fig. 7—Perturbation plots showing the effect of independent coded variables on: (a) zinc recovery and (b) manganese recovery (A: temperature, B: acid concentration, C: pulp density).

B. Optimization and Validation

To optimize the selective acidic leaching of zinc, manganese recovery was minimized and zinc recovery was maximized using the optimization tool of design-expert 8.0.0 trial. The optimum condition is shown in Table V. Model-predicted and validation experimental results with 95 pct confidence interval values at the optimum condition are given in Table VI. Since validation experimental results are within this interval, these experiments can be taken as the confirmation of the

Table V. The Optimum Conditions for Selective Acidic Leaching of Zinc

Temperature K (°C)	Sulfuric Acid Concentration (pct v/v)	Pulp Density (pct w/v)	Stirring Speed (rpm)
343 (70)	1	8	300

Table VI. Model-Predicted and Validation Experimental Results at the Optimum Conditions

Response	Prediction	Low Value (95 pct Confidence Interval)	High Value (95 pct Confidence Interval)	Validation
Zn recovery (pct)	47.58	43.03	52.13	50.23
Mn recovery (pct)	7.35	5.98	8.71	7.21

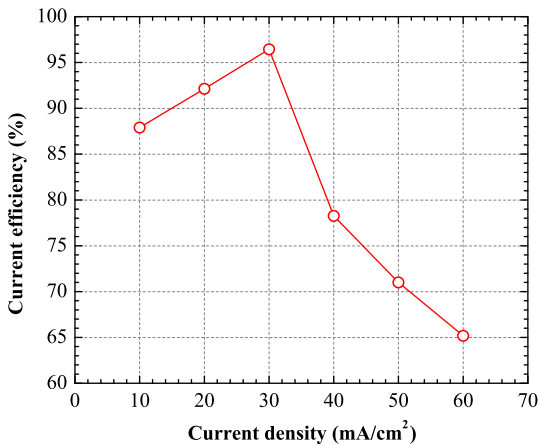


Fig. 8—The effect of current density on current efficiency for zinc electrodeposition in sulfuric acid solution.

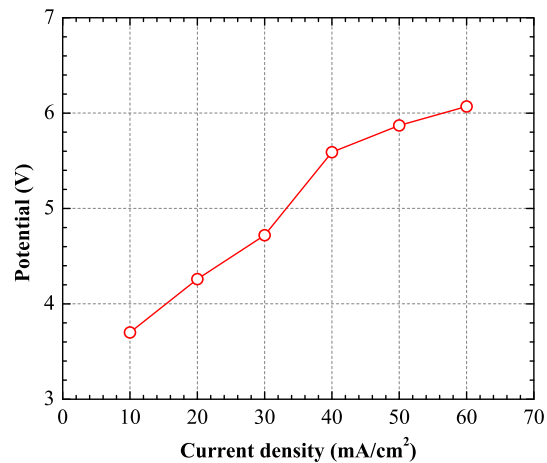


Fig. 10—The cell potential as a function of current density for zinc electrodeposition in sulfuric acid solution.

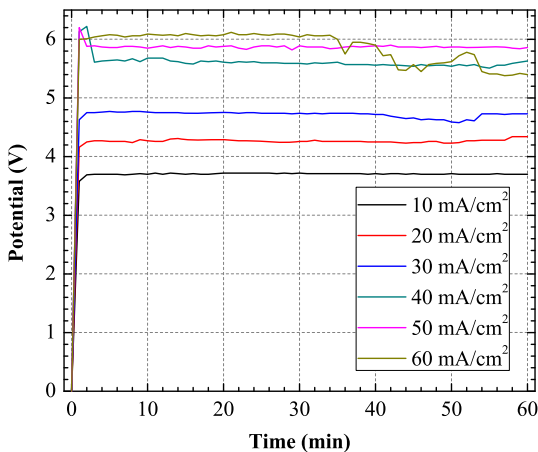


Fig. 9—Cell potentials for zinc electrodeposition in sulfuric acid solution.

desirability of the proposed model for predictive purposes.^[14]

Finally, to increase the zinc recovery to an acceptable amount, a staged selective acidic leaching was performed. In each stage, the acid concentration decreased by half due to decrease of about 50 pct of zinc content in previous leaching stage. After three stages of leaching operation, about 92 pct of zinc and 15 pct of manganese were withdrawn to the leach liquor from primary

washed powder. In fact, the aim of selective leaching of zinc was achieved by this simple method.

C. Electrowinning

The electrowinning experiments of zinc were carried out at room temperature using the sulfate solution containing 8.4 g/L zinc and 2.2 g/L manganese provided from one-stage selective acidic leaching test. In these experiments, the effect of current density on current efficiency ($\eta = Q_{\text{deposited metal}}/Q_{\text{applied}}$) for zinc electrodeposition was evaluated. The results are shown in Figure 8. In addition, the cell potential was measured in each test (Figure 9). The cell potential as a function of current density is plotted in Figure 10. As it can be seen, cell potential increases with increasing current density.

Figure 8 depicts that the maximum current efficiency is equal to 96.0 pct at current density of about 30 mA/cm². The current efficiency decreases with increase in potential at higher densities up to 60 mA/cm².

Photographs of zinc deposited layers under various current densities are shown in Figure 11. It seems that zinc deposition tends to dendritic growth by increasing current density. Dendritic growth and hydrogen evolution at the cathode surface cause to change in current efficiency. During deposition process, some of zinc branches detached from substrate (especially in higher current densities) and settled down at bottom of the cell

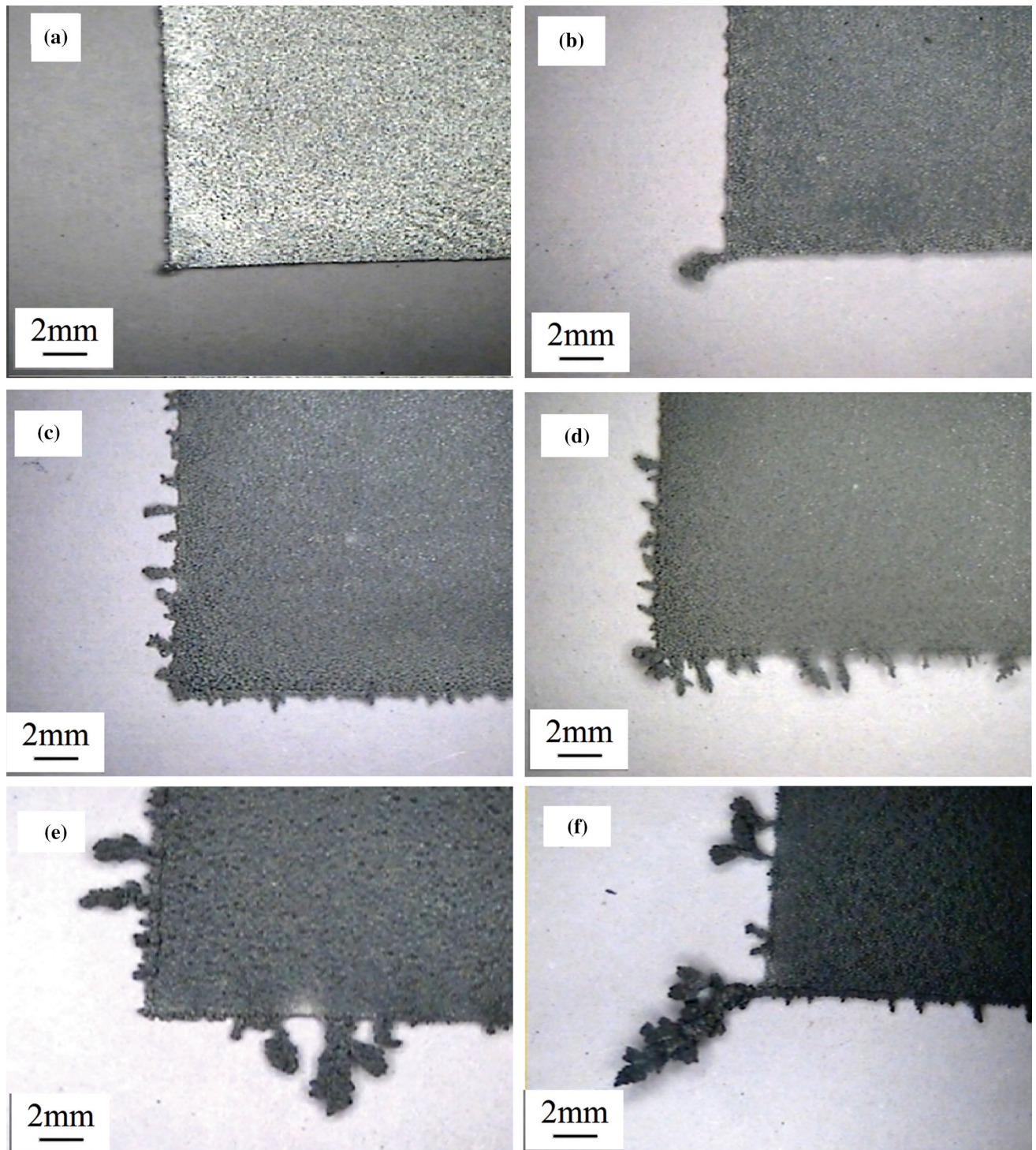


Fig. 11—Photographs of zinc deposited layers under various current densities in sulfuric acid solution: (a) 10 mA/cm², (b) 20 mA/cm², (c) 30 mA/cm², (d) 40 mA/cm², (e) 50 mA/cm², (f) 60 mA/cm².

decreases current efficiency. Zinc purity was 99.9 pct, and manganese and lead were the main contaminants.

Some manganese is advantageous for electrolysis. About 1.5 to 3 g/L Mn²⁺ is required in the electrolyte to minimize lead anode corrosion.^[12] It seems that adequate manganese content of sulfate solution (2.2 g/L

Mn²⁺) resulted from optimized selective leaching has been helpful in 99.9 pct zinc purity.

Finally, filtered and dried pulp (residues of electro-winning cell) was analyzed by XRD technique. Figure 12 shows XRD spectrum of dried pulp in maximum current efficiency (96 pct) which results in minimum zinc

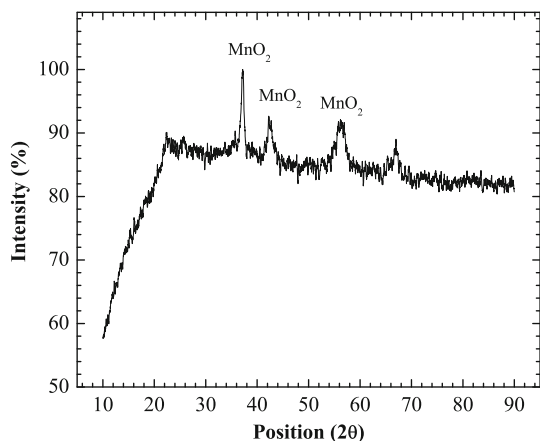


Fig. 12—XRD pattern of filtered and dried residues of electrowinning cell.

loss in cell bottom precipitations. It can be seen from the figure that the by-product of electrowinning cell is MnO_2 . This electrolytic MnO_2 forms on the anode, due to oxidation of Mn^{2+} ions.

IV. CONCLUSIONS

Based on ANOVA calculations in RSM, sulfuric acid concentration had a positive effect on zinc and manganese recoveries, while pulp density had an expected negative effect. Zinc recovery was increased by increasing the temperature, while manganese recovery showed insensitivity to this factor. Stirring speed had no effect on metal recoveries.

A maximum zinc recovery of 50.23 pct and minimum manganese recovery of 7.21 pct were obtained in one-stage selective acidic leaching under following optimum condition: 1 pct (v/v pct) sulfuric acid at 343 K (70 °C) with pulp density of 8 pct (w/v pct) agitated at 300 rpm. In addition, after three stages of leaching operation, about 92 pct of zinc and 15 pct of manganese were withdrawn to the leach liquor from primary washed powder.

In electrowinning experiments, the maximum current efficiency of 96.0 pct at current density of about 30 mA/

cm^2 was obtained. The current efficiency decreases with increase in potential at higher densities up to 60 mA/ cm^2 and zinc purity was 99.9 pct.

REFERENCES

1. A. Daryabeigi Zand and M.A. Abduli: *Waste Manag.*, 2008, vol. 28, pp. 2085–90.
2. Y.A. El-Nadi, J.A. Daoud, and H.F. Aly: *J. Hazard. Mater.*, 2007, vol. 143, pp. 328–34.
3. L. Pietrelli, B. Bellomo, D. Fontana, and M. Montereali: *Waste Manag.*, 2005, vol. 25 (2), pp. 221–26.
4. C.C.B.M. De Souza, D.C. De Oliveira, and J.A.S. Tenorio: *J. Power Sources*, 2001, vol. 103, pp. 120–26.
5. L.R.S. Veloso, L.E.O.C. Rodrigues, D.A. Ferreira, F.S. Magalhães, and M.B. Mansur: *J. Power Sources*, 2005, vol. 152, pp. 295–302.
6. T.-H. Kim, G.G. Senanayake, J.-G. Kang, J.-S. Sohn, K.-I. Rhee, S.-W. Lee, and S.-M. Shin: *Hydrometallurgy*, 2009, vol. 96, pp. 154–58.
7. G. Furlani, E. Moscardini, F. Pagnanelli, F. Ferella, F. Vegliò, and L. Toro: *Hydrometallurgy*, 2009, vol. 99, pp. 115–18.
8. I. De Michelis, F. Ferella, E. Karakaya, F. Beolchini, and F. Vegli: *J. Power Sources*, 2007, vol. 172, pp. 975–83.
9. E. Sayilgan, T. Kukrer, N.O. Yigit, G. Civelekoglu, and M. Kitis: *J. Hazard. Mater.*, 2010, vol. 173, pp. 137–43.
10. A.L. Salgado, A.M.O. Veloso, D.D. Pereira, G.S. Gontijo, A. Salum, and M.B. Mansur: *J. Power Sources*, 2003, vol. 115 (2), pp. 367–73.
11. E. Sayilgan, T. Kukrer, G. Civelekoglu, F. Ferella, A. Akcil, F. Vegliò, and M. Kitis: *Hydrometallurgy*, 2009, vol. 97, pp. 158–66.
12. D.J. MacKinnon and J.M. Brannen: *Hydrometallurgy*, 1991, vol. 27, pp. 99–111.
13. R.S. Vakhidov and G.Z. Kiryakov: *Izv. Vissh. Ucheb. Zaved. Khim. Technol.*, 1959, vol. 2, pp. 238–43.
14. D.C. Montgomery: *Design and Analysis of Experiments, Chapter 11*, 5th ed., John Wiley & Sons, New York, 2001, pp. 427–29.
15. Z.M. Zheng, Q.I. Hu, J. Hao, F. Xu, N.N. Guo, Y. Sun, and D.H. Liu: *Bioresour. Technol.*, 2008, vol. 99, pp. 1052–56.
16. C.C.B.M. De Souza and J.A.S. Tenório: *J. Power Sources*, 2004, vol. 136, pp. 191–96.
17. M.T. Binsfield: *Proceedings of the Second International Symposium on Extraction and Processing for the Treatment and Minimization of Wastes*, Minerals, Metals & Materials Society, 1996, pp. 719–29.
18. R.H. Myers, D.C. Montgomery, and C.M. Anderson-Cook: *Response Surface Methodology: Process and Product Optimization Using Designed Experiments, Chapter 2*, 3rd ed., John Wiley & Sons, New York, 2009, pp. 81–93.