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APPLICATION OF STATISTICAL DESIGN IN THE LEACHING STUDY OF LOW-GRADE MANGANESE ORE USING AQUEOUS SULFUR DIOXIDE

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ABSTRACT

Sulfur dioxide leaching studies on low-grade manganese ore were carried out at room temperature and atmospheric pressure. The experiments carried out using $-150\,\mu m$ particles aimed at determining maximum extraction of manganese, which was found to be 97.5%. It was possible to extract 96.7% manganese at twice the stoichiometric quantity of SO_2 required for dissolution of manganese. The effect of particle size, stoichiometric quantity of SO_2 added, and duration of leaching were studied using 3^3 full factorial design. The data were analyzed qualitatively as well as quantitatively. In addition to this, kinetic equations were tested to determine the rate-controlling step of the reaction.

Key Words: Manganese ore; Sulfur dioxide; Statistical design

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INTRODUCTION

Manganese and iron minerals almost always occur together in nature. Techniques such as gravity concentration, magnetic separation, and flotation are not amenable for separation from each other because of their close physical and physico-chemical properties. However, there is some difference in the chemical properties of iron oxide and manganese dioxide. The former dissolves in acidic condition whereas the dissolution of the latter is favored only by reducing conditions. Solid–liquid separation techniques can exploit effectively this difference to extract manganese selectively from manganese and iron mineral association.

The leaching of oxidic manganese ores have been reviewed by the authors (1). Manganese from the low-grade oxide ores of manganese can be extracted successfully using sulfur dioxide as the reductant (2–5). With a view to generate basic data, some studies have been carried out on dissolution of synthetic MnO_2 in acidic media (6–8).

The objectives of the present work were to find out the maximum extraction of manganese and to assess the effect of particle size, stoichiometric quantity of SO_2 added, and duration of leaching on extraction of manganese and iron using statistical design of experiment.

EXPERIMENTAL

Materials

The main manganese minerals of Singhbhum–Keonjhar–Bonai belt are psilomelane and pyrolusite with some cryptomelane, manganite, and wad. Braunite occurs in minor quantities (9). Samples of low-grade manganese ore were collected from Joda area, Keonjhar district, Orissa. A representative sample of collected material was sieved using a set of standard sieves. The size analysis data are given in Table 1. The chemical analyses of bulk sample after rejection of $-105\,\mu m$ particles and the three sized fractions chosen for the 3^3 factorial experiments are given in Table 2. The bulk ore after rejection of $-105\,\mu m$ particles was ground to $-150\,\mu m$ size. Experiments were carried out on ground ore in order to determine maximum extraction of manganese. The sulfurous acid of MERCK, India was used for leaching.

Experimental Procedure

Sulfur dioxide concentration in sulfurous acid was measured by titrating against $KMnO_4$ after addition of a few mL of H_2SO_4 to it. The SO_2 solution of 3% concentration was prepared by diluting the original solution. For each experiment

Table 1. Size Analysis of Ore After Discarding −105 μm Particles (−105 μm Particles Constitute 12.65% of the Total Feed)

Size Range (mm)	Geometric Mean Size (mm)	wt (%)	Cumulative wt% Passing at Geometric Mean Size
−19 + 16	17.43	1.19	99.41
−16 + 12.5	14.14	1.01	98.31
−12.5 + 8	10.00	22.76	86.42
−8 + 6.3	7.10	16.15	66.97
−6.3 + 5.6	5.94	6.69	55.55
−5.6 + 4.75	5.16	2.96	50.72
−4.75 + 4.0	4.36	6.19	46.15
−4.0 + 3.35	3.66	5.36	40.37
−3.35 + 2.0	2.59	11.18	32.10
−2.0 + 1.4	1.67	6.10	23.46
−1.4 + 1.0	1.18	5.35	17.74
−1.0 + 0.710	0.84	3.61	13.26
−0.710 + 0.500	0.60	2.75	10.08
−0.500 + 0.300	0.39	3.15	7.08
−0.300 + 0.208	0.25	4.12	3.49
−0.208 + 0.105	0.18	1.43	0.72

Table 2. Results of Chemical Analysis

Element	wt%			
	+105 μm–19 mm	1.7 mm	4.4 mm	7.1 mm
Mn	25.00	18.88	24.00	27.38
Fe	25.63	22.63	25.38	29.63
Al	3.31	3.38	3.38	3.31
Ba	0.72	0.60	0.83	0.97
K	0.55	0.54	0.61	0.66
Co	0.05	0.05	0.06	0.08
Na	0.43	0.50	0.44	0.50
Mg	0.02	0.04	0.03	0.02
Acid insoluble	9.54	17.52	8.92	6.00

In all the fractions W, Cr, Cu, Ni, Zn, Ag, Ca, Li, and Cd are present in less than 1 ppm.

of aqueous SO_2 leaching, a 500 mL conical flask was charged with required amount of ore and required volume of 3% SO_2 solution. The slurry was stirred continuously using a mechanical stirrer. Five-mL samples were collected at selected time intervals and analyzed for Mn and Fe with an Atomic Absorption Spectrophotometer after required dilution with acidified distilled water. Experiments were carried out on $-150\,\mu$m ore, varying the stoichiometric quantity of SO_2 to determine maximum extraction of manganese.

Variables

The effect of particle size, quantity of SO_2 added, and duration of leaching were assessed using 3^3 full factorial design. The size data are given in Table 1. Three sizes 1.7, 4.4, and 7.1 mm with equal intervals were chosen for experiments that were geometric means (rounded up to first digit after decimal) of $-2 + 1.4$, $-4.75 + 4$, and $-8 + 6.3$ mm sizes, respectively. The 1.7, 4.4, and 7.1 mm are d_{23}, d_{47}, and d_{67} passing size (d_x, $x = 23, 47, 67$: aperture size of sieve at which x% of material passes through it), respectively. The quantities of SO_2 chosen were 1.0, 1.5, and 2.0 times the stoichiometric quantity of SO_2 required for dissolution of manganese. Either of the following equations can be used for stoichiometric calculations.

$$MnO_2 + SO_2 = MnSO_4 \tag{1}$$

$$MnO_2 + SO_2{\cdot}H_2O = MnSO_4 + H_2O \tag{2}$$

The time intervals chosen were 10, 30, and 50 min. The variables and levels of 3^3 full factorial design are given in Table 3. Two tests were repeated at $P_2T_2S_2$ condition, which is the central point of the 3^3 factorial design, to estimate variance.

RESULTS AND DISCUSSION

Determination of Maximum Manganese Extraction

Manganese from its oxide ore can be extracted using SO_2 solution alone and the quantity of SO_2 available for leaching is the controlling factor for extraction of manganese rather than SO_2 concentration of the solution (5). With the increase in stoichiometric quantity of SO_2 added, extraction of manganese increased (Table 4). With twice the stoichiometric quantity of SO_2 required for dissolution of manganese, 96.7% of manganese could be extracted. Requirement of more than the stoichiometric quantity of SO_2 may be due to the formation of

Table 3. 3^3 Factorial Design for Mn and Fe Leaching

Variable	Level 1	Level 2	Level 3
Particle size (P), mm	1.7	4.4	7.1
Sulfur dioxide (S), stoichiometric quantity	1.0	1.5	2.0
Duration of leaching (T), min	10	30	50

Stirring speed: 1000 min^{-1}, temperature: ∽ 27°C.

insoluble compounds like MnS_2O_6 and dissolution of other metals. In the leach liquor 179 ppm K, 162 ppm K, 60 ppm Al, and 14 ppm Co were found at three times the stoichiometric quantity. In addition to these, Na, Ca, Mg, Cu, Zn, and Pb were present in less than 5 ppm.

Qualitative Analysis

The effect of variables have been analyzed qualitatively.

Effect of Particle Size

Decrease in extraction of manganese and iron was observed when the particle sizes were varied keeping the quantity of SO_2 added and duration of leaching

Table 4. Effect of Stoichiometric Quantity of SO_2 on Extraction of Mn and Fe

SO_2 Stoichiometric Quantity	(%) Extraction Mn	(%) Extraction Fe
1.00	69.51	1.30
1.50	86.18	1.44
1.75	92.05	1.50
2.00	96.73	1.54
2.50	97.69	1.86
3.00	97.51	1.73

Size of ore: −150 μm, Stirring speed: 1000 min^{-1}, SO_2 concentration: 3%, Duration of leaching: 30 min.

constant (Figs. 1 and 2). The smaller the particle size the better is the liberation. The decrease in metal extraction with the increase in particle size may be due to the liberation factor and decrease in the surface area per unit weight of ore.

Effect of Quantity of SO_2

The amount of manganese and iron extracted from all the particle sizes increased, with the increase in stoichiometric quantity of SO_2 added (Figs. 1 and 2). The quantity of manganese extracted at twice the stoichiometric quantity of SO_2 was double or more than double the quantity of manganese extracted at the stoichiometric quantity of SO_2. The reaction between MnO_2 and SO_2 is given below:

$$MnO_2 + SO_2 = Mn^{2+} + SO_4^{2-} \tag{3}$$

$$MnO_2 + 2SO_2 = Mn^{2+} + S_2O_6^{2-} \tag{4}$$

Effect of Duration of Leaching

With the increase in duration of leaching, the extraction of manganese and iron increased but the rate of increase in the extraction of both metals decreased

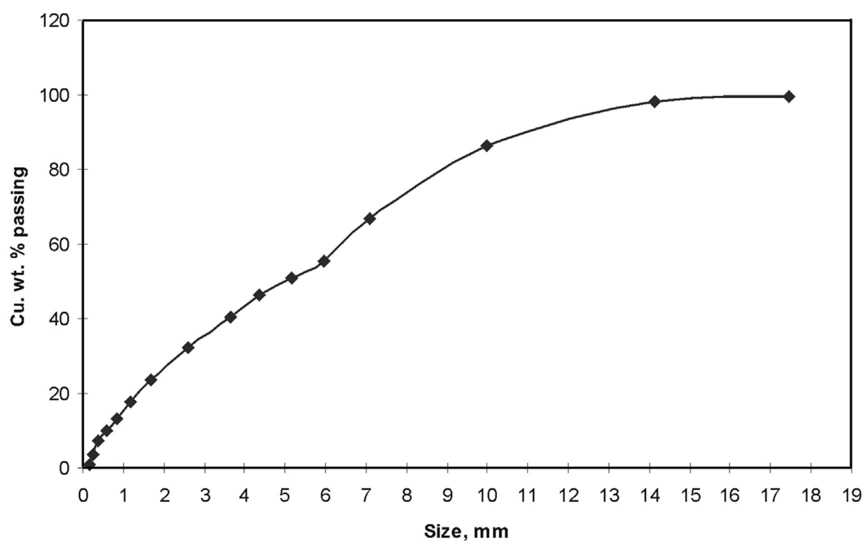

Figure 1. Experimental results of extraction of manganese for the 33 full factorial design, stirring speed 1000 min^{-1}, temperature ~27°C.

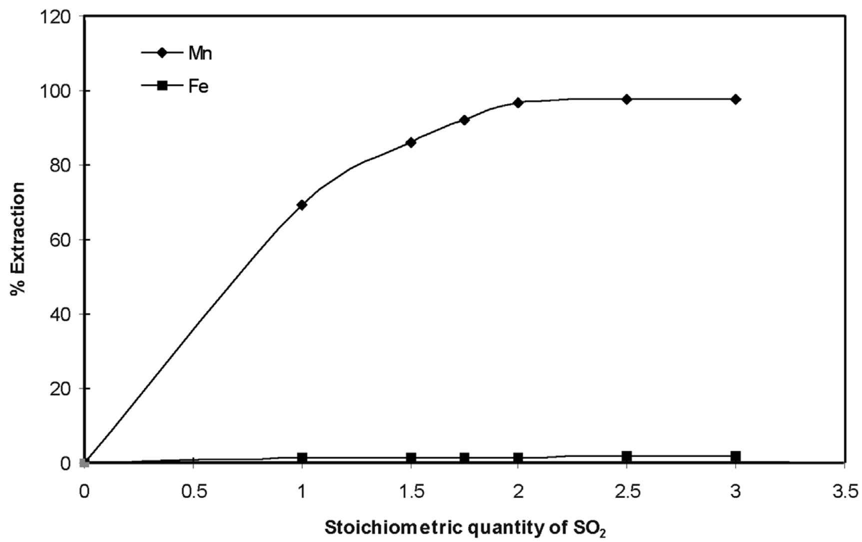

Figure 2. Experimental results of extraction of iron for the 33 full factorial design, stirring speed 1000 min^{-1}, temperature ~27°C.

with time and stabilized gradually. The lesser the quantity of SO_2 the earlier was the stabilization (Figs. 1 and 2).

Kinetic Study

The shrinking core product layer model for heterogeneous reaction was fitted to the present data to determine the rate-controlling step of the reaction.

If the reaction is controlled by chemical reaction, the following reaction rate would apply (10),

$$1 - (1 - R)^{1/3} = kt \quad (5)$$

where, R: fraction reacted, t: time (min), k: rate constant (min^{-1}).

However, if the diffusion reaction were the controlling step of the reaction then the following rate equation would apply (10),

$$1 - 2/3R - (1 - R)^{2/3} = kt \quad (6)$$

Testing Eqs. (5) and (6) it was found that manganese ore leaching followed a mathematical law such as (6) (Fig. 3). This indicates that diffusion

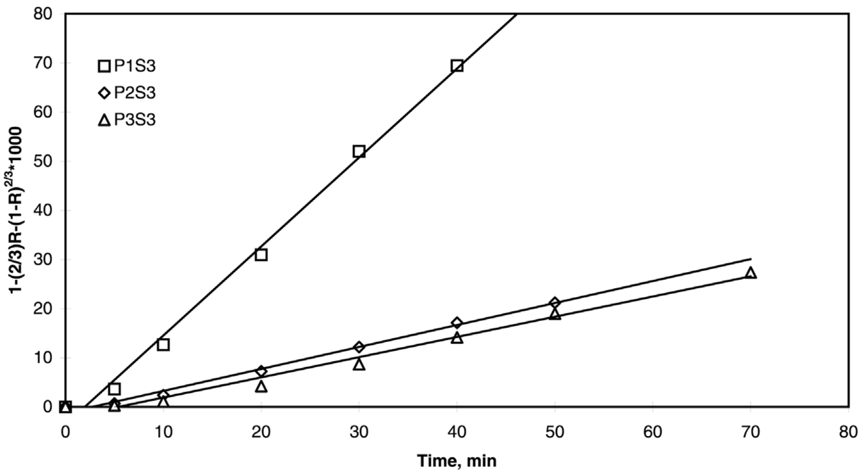

Figure 3. [1 − (2/3)R − (1 − R)2/3] vs. time plot for extraction of manganese.

reaction is the controlling step of coarse manganese ore leaching. The major phases present in the ore are oxides of manganese and iron. The manganese phase reacts rapidly with SO_2 whereas the reaction of iron phase with that of SO_2 is very slow (Figs. 1 and 2). Sometimes, after the initiation of reaction, the iron phase is likely to form a layer over the unreacted manganese phase and dissolution of this embedded manganese phase would require diffusion of SO_2 through the formed layer.

Statistical Analysis

One of the most important tools to understand a process is the factorially designed test with analysis of variance. Factorially designed test not only gives the main effects of the variables but also provides the interactional effects between them. The Fisher-test can be carried out to know the significance of effect of any variable (11). The results obtained from 3^3 full factorial design are presented in Table 5 and analyzed in the following section.

Main Effects

The mean sum square value of analysis of variance (ANOVA) shows that (Table 6), among the main effects of the variables, the size of the particles has

Table 5. Results of Aqueous SO_2 Leaching Using 3^3 Factorial Design

		(%) Metal Extraction	
S. No.	Conditions	Mn	Fe
1	$P_1S_1T_1$	24.87	0.69
2	$P_1S_1T_2$	32.44	0.79
3	$P_1S_1T_3$	33.01	0.83
4	$P_1S_2T_1$	26.75	0.74
5	$P_1S_2T_2$	46.02	0.89
6	$P_1S_2T_3$	46.07	0.92
7	$P_1S_3T_1$	31.20	0.79
8	$P_1S_3T_2$	57.78	1.16
9	$P_1S_3T_3$	66.38	1.36
10	$P_2S_1T_1$	13.93	0.45
11	$P_2S_1T_2$	16.88	0.49
12	$P_2S_1T_3$	19.01	0.54
13	$P_2S_2T_1$	14.71	0.43
14	$P_2S_2T_2$	22.56	0.51
15	$P_2S_2T_3$	25.27	0.56
16	$P_2S_3T_1$	14.11	0.46
17	$P_2S_3T_2$	30.64	0.66
18	$P_2S_3T_3$	39.39	0.67
19	$P_3S_1T_1$	4.13	0.18
20	$P_3S_1T_2$	6.87	0.26
21	$P_3S_1T_3$	6.97	0.28
22	$P_3S_2T_1$	5.38	0.19
23	$P_3S_2T_2$	10.59	0.28
24	$P_3S_2T_3$	11.75	0.29
25	$P_3S_3T_1$	9.65	0.23
26	$P_3S_3T_2$	26.19	0.40
27	$P_3S_3T_3$	37.51	0.53
Repeat tests			
28	$P_2S_2T_2$	24.13	0.54
29	$P_2S_2T_2$	20.89	0.46

maximum effect on extraction of both manganese and iron. The F-test indicates that the main effects of all the variables are significant at 99% confidence level. The order of significance in case of extraction of manganese is:

$$P > S > T$$

and that of iron is

$P > T > S$

The particle size is the most important factor in the extraction of both Mn and Fe. Leaching data also support this. With the quantity of SO_2 and time remaining the same, the extraction of Mn and Fe increases with the decrease in particle size (e.g., Table 5, S. No. 26, 17, 8 and Table 3, 6th row).

Interaction Effects

The two-factor interaction effects have been analyzed statistically.

P–S Interaction

The mean sum square value higher than the residual mean sum square and high *F*-value (Table 6) reveal that this interaction has significant effects on extraction of both manganese and iron. In the case of manganese, it is significant at 99% confidence level and that of iron at 95% confidence level.

S–T Interaction

The high mean sum square value and *F*-value (Table 6) indicate that the interaction between these two variables has significant effects on extraction of manganese and iron. In the case of manganese, this interaction is significant at 99% confidence level whereas in the case of iron it is significant at 95% confidence level.

P–T Interaction

The *F*-value (Table 6) indicates that this interaction is significant at 99% confidence level on extraction of manganese. The mean sum square value higher than residual mean square value reveals that this interaction has some effect on extraction of iron but not significant at the 95% confidence level.

On the basis of above discussion ("Main Effects" and "Interaction Effects" sections), the following conclusions may be drawn.

(1) The main effect of all the variables are significant at 99% confidence level. All the interactional effects on the extraction of manganese are significant at the 99% confidence level. In the case of extraction of iron, *P–S* and *S–T* interactions are significant at 95% confidence level.

Table 6. Results of Statistical Analysis for Extraction of Mn and Fe

Source	Manganese			Iron		
	Sum of Squares	Mean Sum of Squares	*F*-Value	Sum of Squares	Mean Sum of Squares	*F*-Value
Main effects						
P	3499.674	1749.837	713.215	1.739	0.869	389.803
S	1381.797	690.898	281.603	0.172	0.086	38.481
T	1189.063	594.432	242.325	0.189	0.095	42.461
Interactional effects						
P–S	110.162	27.540	11.225	0.058	0.015	7.500
S–T	477.244	119.311	48.630	0.057	0.014	7.000
P–T	99.908	24.977	10.180	0.024	0.006	3.000
Residual	19.628	2.453	—	0.018	0.002	—

(2) The order of significance of the main effects and interactional effects of the variables are as follows.

Extraction of manganese

$P > S > T, \quad S\text{–}T > P\text{–}S > P\text{–}T$

Extraction of iron

$P > T > S, \quad P\text{–}S > S\text{–}T > P\text{–}T$

Quantification

In order to predict extraction of manganese and iron in a particular process condition, the following type of equation was tested.

$$Y = a_0 + a_1P + a_2S + a_3T + a_4PS + a_5ST + a_6PT + a_7P^2 + a_8S^2 + a_9T^2 \tag{7}$$

where, Y is the metal extraction and a_0–a_9 are constants.

The constants were computed with the help of a package using data given in Table 5. Equation for iron and manganese are given below:

$$Y_{\mathrm{Mn}} = 56.145 - 9.046P - 33.421S + 0.243T - 0.5963PS + 0.6022ST - 0.0394PT + 0.6901P^2 + 11.7244S^2 - 0.0097T^2 \tag{8}$$

R^2 value = 0.969

$$Y_{\mathrm{Fe}} = 1.222 - 0.142P - 0.552S + 0.0028T - 0.0346PS + 0.0063ST - 0.0006PT + 0.0112P^2 + 0.2333S^2 - 0.00007T^2 \tag{9}$$

R^2 value = 0.968

The equations developed for manganese and iron were tested for goodness of fit (11) to see how it fitted the observations. The comparison of experimentally obtained variance ratio and tabulated value of Fisher's (11), for 0.05 (95% confidence level), are given in Table 7. Since $F < F_{1-\alpha}(\gamma_1 - \gamma_2)$ [γ_1 and γ_2 df],

Table 7. Comparison of Experimentally Obtained Variance Ratio and Tabulated Values of Fisher's F (11)

Eq. No.	Residual Variance	Replication Variance	Variance Ratio	Degree of Freedom γ_1	Degree of Freedom γ_2	Tabulated Value of Fisher's $F(\alpha = 0.05)$
(8) Y_{Mn}	12.3964	2.6252	4.72	17	2	19.4
(9) Y_{Fe}	0.0068	0.0016	4.25	17	2	19.4

γ_1: total number of observations minus number of coefficient in the regression equation.
γ_2: number of repeat test minus one.

the estimated regression Eqs. (8) and (9) fit the experimental data adequately. These equations can be used for the interpolation of data. The quadratic terms in Eqs. (8) and (9) indicate that the extraction of metal slows down with the increase in duration of leaching. One of the reasons for this is the diffusion reaction between MnO_2 and SO_2 ("Kinetic Study" Section).

CONCLUSIONS

1. The extraction of manganese increased with the increase in stoichiometric quantity of SO_2 added. The maximum manganese extraction from $-150\,\mu$m ore was found to be 97.5%; 96.7% of manganese and 1.54% of iron could be extracted with twice the stoichiometric quantity of SO_2 required for the dissolution of manganese.
2. The extraction of manganese and iron increases with increase in duration of leaching and decrease in particle size. The rate of increase in extraction with time decreases gradually and stabilizes after sometime.
3. All the main effects are significant at 99% confidence level. The interactional effects of manganese are significant at 99% confidence level and only $P{-}S$ and $S{-}T$ interactions for iron are significant at 95% confidence level. The order of significance is as follows:

$$P > S > T, \quad S{-}T > P{-}S > P{-}T \text{(manganese)}$$

$$P > T > S, \quad P{-}S > S{-}T > P{-}T \text{(iron)}$$

The particle size is the most important factor in the extraction of both the metals. The effect of quantity of SO_2 added is the second important factor for extraction of manganese whereas that of iron is time. So the extraction of iron can be reduced in the leach liquor by limiting the duration of leaching.

4. The regression equation with two-factor interaction coefficients and quadratic terms fits adequately to the data. These equations can be used for the interpolation of data.

5. Leaching of manganese from coarse ore is controlled by diffusion reaction.

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REFERENCES

1. Das, S. C.; Sukla, L. B.; Naik, P. K. *Report on Extraction of Manganese from Oxidic Manganese Ores—A Review*, Prepared for HM MLP-005 Project, Preparation of Mineral Based Inorganic Materials/Chemicals, Report No. T/H and EM/302/July/1999, RRL, Bhubaneswar.
2. Abbruzzese, C. Percolation Leaching of Manganese Ore by Sulfur Dioxide. Hydrometallurgy **1990**, *25*, 85–97.
3. Abbruzzese, C.; Duarte, M.Y.; Paponetti, B.; Toro, L. Biological and Chemical Processing of Low-Grade Ores. Miner. Eng. **1990**, *3* (3/4), 307–318.
4. Grimanelis, D.; Neou-Syngouna, P.; Vazarlis, H. Leaching of Rich Greek Manganese Ore by Aqueous Solution of Sulphur Dioxide. Hydrometallurgy **1992**, *31*, 139–146.
5. Naik, P.K.; Sukla, L.B.; Das, S.C. Aqueous SO_2 Leaching Studies on Nishikhal Manganese Ore Through Factorial Experiment. Hydrometallurgy **2000**, *54*, 217–228.
6. Basset, H.; Parker, W.G. The Oxidation of Sulfurous Acid. J. Chem. Soc., Part II **1951**, 1540–1560.
7. Herring, A.P.; Ravitz, S.F. Rate Dissolution of Manganese Dioxide in Sulfurous Acid. Trans. SME/AIME **1965**, *231*, 191–195.
8. Miller, J.D.; Wan, R.Y. Reaction Kinetics for Leaching of MnO_2 by Sulfur Dioxide. Hydrometallurgy **1983**, *10*, 219–242.
9. IBM. *Minerals Facts and Problems Manganese Ore*, Monograph No. 4, Publication cell, Indian Bureau of Mines: Nagpur, July 1974, 73.

10. Sohn, B.Y.; Wadsworth, M.E. *Rate Processes of Extractive Metallurgy*; Plenum Press: New York, 1979; 133–186.
11. Akhanazarova, S.; Kafarov, V. *Experiment Optimization in Chemistry and Chemical Engineering*; Mir Publishers: Moscow, 1982; 312.

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