Extraction of manganese from low-grade Nishikhal ore using pyritiferous lignite in acidic medium

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Abstract

Leaching studies of low-grade manganese ore containing 31.77% Mn and 23.71% Fe from Nishikhal, India, were carried out using pyritiferous lignite as a reductant in sulfuric acid medium. The variables studied were quantity of lignite, sulfuric acid concentration and temperature. Regression equations for the extraction of manganese and potassium were determined from 2^3 full factorial design data. The experimental conditions for the extraction of manganese were optimized using the steepest-ascent method. It was found that 99.03% of the manganese could be extracted in three hours with an ore to lignite ratio of 1:1.8, a sulfuric acid concentration of 1.9 M and a temperature of 99°C.

Key words: Leaching, Manganese ore, Lignite, Statistical design

Introduction

Manganese is used in the steel industry in the form of ferromanganese for deoxidation, desulfurization and alloying. It acts as a deoxidizer because of its lower value of standard free energy change for oxide formation; hence, it reduces the iron present in the melt. Its higher affinity to sulfur prevents the formation of iron sulfide in the melt.

The manganese reserves of India are on the order of 176.5 Mt (194.5 million st) (Indian Bureau of Mines, 1995). In 1992-93, the production of manganese ore was 1.90 Mt (2.09 million st), out of which 47% was of low grade (Indian Bureau of Mines, 1995). Manganese can be extracted effectively from these low-grade ores using suitable hydrometallurgical techniques.

The total lignite resources of India are estimated to be 27,500 Mt (30,300 million st) (Ministry of Information and Broadcasting, Government of India, 1998). In Rajasthan, 1,434 Mt (1,581 million st) of the lignite reserves have been assessed, with the Giral area alone contributing 101.90 Mt (112.3 million st) (Sharma, 1999). The lignite contains pyrite. As both carbon and pyrite are reducing agents, these can be used as reductants for Mn extraction.

Manganese dioxides are stable in acid or alkaline oxidizing conditions. Therefore, the extraction of manganese must be carried out in reducing condition. Leaching studies using charcoal (Das et al., 1989; Sanjay et al., 1996), coal and lignite (Hancock and Fray, 1986) and pyrite (Parida et al., 1990; Vracar and Cerovic, 2000) have been reported. Leaching of manganese in sulfuric acid medium using lignite as a reductant produces a manganese sulfate leach liquor that can be used for the production of Mn metal, electrolytic manganese dioxide or manganese sulfate monohydrate. $MnSO_4{\cdot}H_2O$ is used as the base for other value-added high-purity manganese chemicals.

The carbon present in the coal or lignite is likely to react with manganese dioxide. The electrochemical reaction between carbon and water is (Shereir, 1976)

$$C + 2H_2O = CO_2 + 4H^+ + 4\,e^- \qquad E^\circ_{SHE},\ -0.21\ V \quad (1)$$

A possible reaction at ambient temperature is

$$MnO_2 + 4H^+ + 2e^- = Mn^{2+} + 2H_2O \quad E^\circ_{SHE},\ 1.23\ V \quad (2)$$

Combining Eqs. (1) and (2) gives

$$2MnO_2 + 4H^+ + C = CO_2 + 2Mn^{2+} + 2H_2O \quad (3)$$
$$\Delta E,\ 1.02\ V;\quad \Delta G^\circ,\ -394\ kJ$$

In the present work, leaching studies were carried out on low-grade Nishikhal ore, which is not suitable for industrial purposes because of its high iron and phosphorus contents, using high-sulfur lignite from Rajasthan. The high sulfur content of this lignite prevents its use for any purpose.

Experimental

Materials. Samples of manganese ore were collected from the Nishikhal deposit, Rayagada district, Orissa, India. The major manganese minerals occurring in this deposit are cryptomelane, psilomelane and pyrolusite, with minor amounts of jacobsite, hausmannite and wad. The other ore minerals present are goethite, hematite, pyrite and traces of chalcopyrite. The gangue minerals are quartz, orthoclase, garnet and kaolinite with minor amounts of apatite, fibrolite (sillimanite), zircon, muscovite and biotite (Acharya et al., 1990). The ore was ground to -150 µm for the experiments. Chemical analysis of the ore is given in Table 1.

The lignite sample was collected from the Giral lignite area, Barmer district, Rajasthan. The lignite was ground to -72 µm for the testing. The proximate analysis and the sulfur and iron contents of the lignite are given in Table 2.

Experimental procedure. In the test procedure, 100 mL of sulfuric acid solution of the required strength was placed in a conical flask. The solution was stirred with a magnetic stirrer. The heating system was then switched on, and the solution was allowed to attain a predetermined temperature. Then, 5 g of manganese ore was thoroughly mixed with the required quantity of lignite, and the mixture was poured into the flask. A

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Table 1 — Chemical analysis of ore.

Element	Percentage
Mn	31.77
Fe	23.71
K	1.18
Al	2.38
Zn	0.04
Ni	0.04
Cu	0.02
Co	0.02
Na	0.03
Ca	0.01
Mg	0.01
P	0.81
Acid insoluble	0.89
L.O.I. (1,000°C)	11.78

Table 2 — Proximate analysis data and S and Fe content of lignite.

Parameter	Contents, %w/w
Moisture	19.5
Volatile matter	52.2
Ash (dry)	11.1
Fixed carbon	17.3
Sulfur	7.2
Iron	2.56

Table 3 — 2^3 factorial design for Mn leaching.

- Size of ore: -150 µm
- Weight of ore: 5 g
- Duration of leach: 3 hrs.

Variables	Low level	Base level	High level
Lignite, g	0.5	0.75	1.0
H_2SO_4 conc., M	0.2	0.3	0.4
Temp., °C	30	40	50

Table 4 — 2^3 full factorial design for Mn and K extraction.

Conditions:
"–" = low level; "+" = high level; "0" = base level
x_1 = quantity of lignite; x_2 = sulfuric acid concentration; x_3 = temperature

Observation	Coded factors x_1	x_2	x_3	Extraction Mn	K
1	–	–	–	1.37	1.00
2	+	–	–	1.89	1.29
3	–	+	–	1.62	1.12
4	+	+	–	2.00	1.36
5	–	–	+	2.66	1.53
6	+	–	+	5.02	2.73
7	–	+	+	4.05	1.86
8	+	+	+	5.65	2.83
9	0	0	0	2.40	1.48
10	0	0	0	2.38	1.42
11	0	0	0	2.52	1.44

Table 5 — Experimental matrix for 2^3 full experimental design for Mn and K.

Conditions:
"–" = low level; "+" = high level
x_1 = quantity of lignite; x_2 = sulfuric acid concentration; x_3 = temperature

N	x_0	x_1	x_2	x_3	x_1x_2	x_1x_3	x_2x_3	$x_1x_2x_3$	Response Mn	K
1	+	–	–	–	+	+	+	–	1.37	1.00
2	+	+	–	–	–	–	+	+	1.89	1.29
3	+	–	+	–	–	+	–	+	1.62	1.12
4	+	+	+	–	+	–	–	–	2.00	1.36
5	+	–	–	+	+	–	–	+	2.66	1.53
6	+	+	–	+	–	+	–	–	5.02	2.73
7	+	–	+	+	–	–	+	–	4.05	1.86
8	+	+	+	+	+	+	+	+	5.65	2.83

condenser was fitted in the mouth of the flask to minimize reduction of volume of slurry. The slurry was then agitated with the help of a magnetic paddle. The duration of the leach was three hours for all experiments.

Samples of leach liquor and wash solution were diluted with acidified distilled water and then analyzed for Mn and K using an atomic adsorption spectrophotometer (AAS).

Variables. The effects of the quantity of lignite added, sulfuric acid concentration and temperature were studied using 2^3 full factorial design. The levels of variables are given in Table 3.

Results and discussion

The data of factorial experiment were used to develop regression equations. The significance of the terms was tested using Students t-test (Akhnazarova and Kafarov, 1982).

The variables and levels of 2^3 full factorial design are given in Table 3. The high level was designed as "+" and lower level as "–". The matrix for three variables varied at two levels (+, -), and the corresponding extraction percentage Y_{Mn} and Y_K are shown in Table 4. According to the principles for designing experiments, three experiments were carried out at base level (quantity of lignite, 0.75 g; sulfuric acid concentration, 0.3 M; temperature, 40°C) to estimate error and standard deviation. The experimental matrix for 2^3 full factorial design for manganese is given in Table 5.

The regression model equation with interaction terms can be written as

$$Y = b_0 + b_1x_1 + b_2x_2 + b_3x_3 + b_4x_1x_2 + b_5x_1x_3 + b_6x_2x_3 + b_7x_1x_2x_3 \quad (4)$$

where

Y is the percentage of metal extracted; and

x_1, x_2 and x_3 are the dimensionless coded factors for quantity of lignite, sulfuric acid concentration and temperature, respectively.

The main and interaction coefficients are evaluated and tested for significance by the Student t-test. All the coefficients of Eqs. (5) and (6) are significant at 95% confidence level.

The regression equation for Mn and K are as follows

$$Y_{Mn} = 3.0325 + 0.6075x_1 + 0.2975x_2 + 1.3125x_3 - 0.1125x_1x_2 + 0.3825x_1x_3 + 0.2075x_2x_3 - 0.0775x_1x_2x_3 \quad (5)$$

$$Y_K = 1.715 + 0.3375x_1 + 0.0775x_2 + 0.5225x_3 - 0.035x_1x_2 - 0.205x_1x_3 + 0.03x_2x_3 - 0.0225x_1x_2x_3 \quad (6)$$

The adequacies of Eqs. (5) and (6) were tested by Fisher's test (Akhnazarova and Kafarov, 1982) to determine how well it fitted with the observations. In all cases, the experimentally obtained variance ratio are lower than the tabulated value of Fisher's F (Akhnazarova and Kafarov, 1982) for $\alpha = 0.05$ (95% confidence level), which indicate that the

Table 6 — Evaluation of optimized parameters.

Parameter	Quantity of lignite, x_1	Sulfuric acid conc., x_2	Temp., x_3
Principal level, Zj°	0.75	0.3	40
Increment, ΔZ_j	0.25	0.1	10
Coefficient, b_j	0.6075	0.2975	1.3125
$b_j \times \Delta Z_j$	0.1519	0.0298	13.125
Normal steps	0.1157	0.0227	10

Table 7 — Optimization study (1st set).

- Size of ore: -150 μm
- Weight of ore: 5 g
- Temperature: 99°C

Observation	Quantity of lignite, g	Sulfuric acid, M	Temp., °C	Extraction, % Mn	K
12	0.8657	0.3227	50	N.C.	
13	0.9814	0.3454	60	N.C.	
14	1.0971	0.3681	70	12.30	7.55
15	1.2128	0.3908	80	16.06	10.47
16	1.3285	0.4135	90	23.81	15.40
17	1.4442	0.4362	99	25.13	14.71

N.C. = Experiment not conducted.

Table 8 — Optimization study (2nd set).

- Size of ore: -150 μm
- Weight of ore: 5 g
- Temperature: 99°C

Observation	Quantity of lignite, g	Sulfuric acid, M	Extraction, % Mn	K
18	2.0227	0.5497	N.C.	
19	2.6012	0.6632	N.C.	
20	3.1797	0.7767	N.C.	
21	3.7582	0.8902	N.C.	
22	4.3367	1.0037	48.25	37.87
23	4.9152	1.1172	55.75	42.23
24	5.4937	1.2307	69.65	48.59
25	6.0722	1.3442	81.64	53.66
26	6.6507	1.4577	82.56	57.48
27	7.2292	1.5712	87.61	59.97
28	7.8077	1.6847	93.78	68.85
29	8.3862	1.7982	97.86	76.08
30	8.9647	1.9117	99.03	80.11

N.C. = Experiment not conducted.

estimated regression Eqs. (5) and (6) fit the experimental data adequately.

All the terms of Eqs. (5) and (6) are significant at the 95% confidence level. The main effects have a positive effect on the extraction of both Mn and K. Temperature has the strongest effect on extraction of both Mn and K, followed by quantity of lignite and sulfuric acid concentration.

Optimization study. The objective was to maximize extraction of manganese. Therefore, another set of experiments was conducted by the steepest-ascent method to arrive at optimized parameters for manganese extraction. The optimized parameters were evaluated from the regression equation for manganese (Eq. (5)) and the next set of experiments were carried out. The details are given in Table 6. In the optimization experiments, the quantity of lignite, sulfuric acid concentration and temperature were increased as they have positive effect on the extraction of manganese. The positive effect of pyritiferous lignite could be due to reducing nature of carbon and pyrite. The reaction of carbon and pyrite with MnO_2 may be given as

$$2MnO_2 + 2H_2SO_4 + C = 2MnSO_4 + 2H_2O + CO_2 \quad (7)$$

$$3MnO_2 + 2FeS_2 + 6H_2SO_4 = Fe(SO_4)_3 + 3MnSO_4 + 6H_2O + 4S^\circ \quad (8)$$

The first set of experiments (Table 7) shows that 25.13% of the Mn and 14.71% of the K could be extracted with 1.4442 g of lignite, 0.4362 M sulfuric acid and 99°C. In the 2nd set of experiments (Table 8), the normal step for lignite and sulfuric acid concentration was increased five times and the temperature was kept constant. It was found that , 99.03% of the manganese and 80.11% of the potassium could be extracted with an ore to lignite ratio of 1:1.79 and a sulfuric acid concentration of 1.9117M.

Conclusions

The following are some of the conclusions drawn from the study:

- Manganese can be extracted effectively from Nishikhal manganese ore using pyritiferous lignite as reductant at high temperature in sulfuric acid medium.
- The regression equations for calculating the extraction of Mn and K are given in Eq. (5) and (6) above, where x_1, x_2 and x_3 are coded factors for quantity of lignite, sulfuric acid concentration and temperature, respectively. All the main and interaction effects are significant at 95% confidence level. The equations are valid within the range of variables studied.
- Temperature has the strongest effect on the extraction of both Mn and K, followed by quantity of lignite and sulfuric acid concentration.
- From -150-μm material, 99% of the Mn could be extracted with an ore to lignite ratio of 1:1.79 and a sulfuric acid concentration of 1.91M at 99°C.

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