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Chemical Processing of Low Grade Manganese Ore

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Abstract

About 95% of the world production of manganese ore is used in steel industry in the form of Ferro-manganese but the specification required for Ferro-manganese production is generally not met by low grade Manganese ore. Rest 5% of world production of Manganese ore is used for non-metallurgical purposes such as dry batteries, chemicals, paints, glass & ceramic industries. In these industries Manganese is added in the form of MnO_2/ Mn ore. The quality required by these industries is generally not met by most of the ores. Considering the importance of Manganese concentrate for metallurgical and non-metallurgical purposes the present investigation has been undertaken to upgrade Manganese ore. The main objective of the study is to improve MnO_2 content along with Mn/Fe ratio. Non-coking coal has been used as reducing agent and low intensity magnetic separator has been used for beneficiation purpose. The effect of roasting time, C/Mn ratio and roasting temperature has been studied. It has been found that Mn/Fe ratio increases with increase in roasting temperature. The next series of experiment has been carried out on leaching of roasted Manganese ore using dilute hydrochloric acid as leach ant. This treatment resulted into increased Mn/Fe ratio by dissolution of excess iron.

1. Introduction

With depletion of high grade manganese ore deposits a lot of attention is being paid to medium & low grade ores. These are future raw materials for the extraction of manganese (Mn) to be used in steel, dry-cell and chemical industries.

Indian Mn-ore deposits mainly lie in Madhya Pradesh (Balaghat, Chhindwara & Jhabua districts), Maharastra (Bhandara & Nagpur districts), Gujrat (Panchmahal district), Odisha (Sundergarh, Ganjam & Koraput districts) and Andhra Pradesh (Srikakulam & Vishkhapatnam districts).

Manganese dioxide is weakly soluble in acid or alkaline oxidizing conditions. Therefore extraction of Mn is carried out under reducing conditions. To attain the required Mn/Fe ratio & Mn recovery several reducing agents were investigated.

Das et al.[1] used ferrous sulphate for leaching of low-grade ores of Odisha. They have reported more than 90% of Mn extraction by leaching with stoichiometric amount of ferrous sulphate at 90°C for 1 hour with a solid-liquid ratio of 1:10.

Yadav et al. [2] carried out leaching experiments on samples collected from Tirodi mines of Balaghat district of Madhya Pradesh. They studied the effect of acid concentration and leaching time on the extent of metal recovery. They have reported increase in manganese recovery with increase in leaching time at a fixed concentration of acid. Increased acid strength and decreased particle size of the ore resulted into increased metal recovery.

Srivastva et al. [3] used charcoal for roasting and the magnetics were separated by low intensity magnetic separators which resulted into increased Mn/Fe ratio from 4.2 to 7 and recovery of Mn obtained was 68 to 87%.

Raisoni and Dixit [4] conducted leaching test on Mn-ore by aqueous solutions of SO2. Total manganese dissolution took place at 650 rpm with 0.2% solid of 426 micrometer at pH=1 and 310K in only 6-8 min.

Sharma [5] used charcoal as the reducing agent for reduction roasting followed by magnetic separation and also did acid leaching for production of battery grade MnO2. For different combinations of

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parameters the values of Mn/Fe were achieved from 6.8 to 7.5 with recovery of from 66.5% to 75.1%. It was observed that with decrease in particle size of Mn ore, Mn/Fe ratio increased but the ratio (6.8) suitable for ferromanganese production was obtained at a coarser size (+2 -1 mm) with good recovery (74.2%), with decrease in particle size to -0.5 mm though the Mn/Fe ratio was increased (7.9) with decrease in recovery to 60.3%.

Momade, F. W. Y., and Momade, Zs. G. [6] investigated reductive leaching of manganese ore in aqueous methanol-sulphuric acid. They have achieved 98% extraction of manganese at 160°C with a methanol dosage of 40 vol% at 0.3M sulphuric acid with in a period of 2h. However at 70°C only about 34% manganese was extracted after leaching for 1h with 50 vol% methanol and at a sulphuric acid concentration of 0.16M.

Sahoo et al. [7] studied leaching of low-grade Joda manganese ore at high temperature and atmospheric pressure using oxalic acid as reductant in sulphuric acid medium. They extracted 98.4% Mn and 8.7% Fe from -150 +105 micrometer ore with 30.6 g/L oxalic acid, 0.543 M sulphuric acid concentration at 85°C in 105 min.

Ismail et al. [8] used sawdust (C6H10O5)n and lactose (C12H22O11) as reducing agent. They achieved maximum manganese recovery 92.5% with leaching at -100 mesh particle size, 90°C, 90 min, 30% acid concentration, 1.5 acid/MnO2 stoichiometric ratio, 0.5 g/g sawdust/ ore weight ratio and 700 rpm agitation rate in sawdust case. Manganese recovery was 90.50% in case of lactose with the optimum leaching conditions: 100 mesh particle size, 90°C temperature, 120 min, 20% acid concentration, 1.8 acid/MnO2 stoichimetric ratio.

Hariprasad et al. [9] used sawdust as reductant for sulphuric acid leaching of manganese ore. They achieved~98% manganese extraction in 8h with 5% H2SO4 (v/v) & 10% pulp density at 90°C and with 5% sawdust (w/w).

Cheng et al. [10] used cornstalk as reductant and sulphuric acid was used as leachant for the roasted sample. They achieved 90.2% recovery of manganese under the optimal condition which was, manganese dioxide ore to cornstalk weight ratio of 10:3, roasting temperature 500°, time 80 min, stirring speed 400 rpm, sulphuric acid concentration 3 mol/L, leaching temperature 50°C for 40 min.

Su et al. [11] used cane molasses as a reducing agent in dilute sulphuric acid medium. They obtained 97.0% extraction of Mn, whereas 21.5% of Al and 32.4% of Fe under optimal conditions: 1.9 mol/L H2SO4 and 60.0 g/L cane molasses for 120 min at 90°C while particle smaller than 0.147 mm.

Tian et al. [12] used cornob as a reducing agent in dilute sulphuric acid medium. They achieved 92.8% leaching efficiency of manganese while iron dissolution was 24.6% under the optimal condition which was determined for 10g of MnO2 ore, cornob amount of 3g, ore size 75 micrometer, sulphuric acid concentration 1.9 mol/L, at 85°C for 60 min.

2. Methods

Dump Mn ore fines were collected from Balaghat district of Madhya Pradesh. The ore was first crushed to -1mm size. The chemical analysis of the sample is given in Table 1. Wood charcoal was prepared in laboratory by heating wood pieces in absence of air in the temperature range 650-700°C. The charcoal was ground to -75 micron size. It assayed 95.6% carbon and 4.4% ash. For acid leaching -1mm Mn ore sample was also ground to -75 micron. Deionised distilled water was used in all the experiments and reagent grade chemicals were used. The main minerals identified in the ore were Bixbyite, hausmannite, braunite, pyrolusite, quartz and hematite.

Ingredient	*Wt %*
Mn	31.35
Fe	9.32
SiO_2	14.34
Al_2O_3	5.27
P	0.20

Table: 1. Chemical analysis of manganese ore

3. Results & Discussion

Mn ore fines were mixed with charcoal fine in different proportions and heated in a reduction chamber. After roasting time was over the chamber was cooled and the charge material was taken out. Then it was subjected to low intensity induced roll magnetic separator at a constant magnetic field. After separation non-magnetic fractions were subjected to estimation of Mn & Fe content. The results obtained are shown in Table 2.

Temp (°C)	*Mn (%)*	*Fe (%)*
450	36.29	8.26
500	38.11	7.93
550	40.03	7.11
600	48.12	7.09

Table: 2. Percentage Mn & Fe after roasting for 30 minutes

The concentrate (non-magnetic content) obtained after roasting at 450°C was further subjected to acid leaching using dilute Hydrochloric acid at different temperature for different time interval for removal of excess iron present in the concentrate. The results obtained have been presented in Table 3. These results have been plotted in Fig. 1 where percentage dissolution of iron against time has been plotted for three different temperatures.

Time (min)	percentage dissolution of iron at different temperatures		
	60°C	**80°C**	**95°C**
10	12	16	22
20	23	30	41
30	31	44	52
40	39	51	59
50	45	59	66
60	48	65	71
70	50	68	76
80	51	70	78

Table: 3. Manganese ore leaching (dissolution of iron present in the roasted sample)

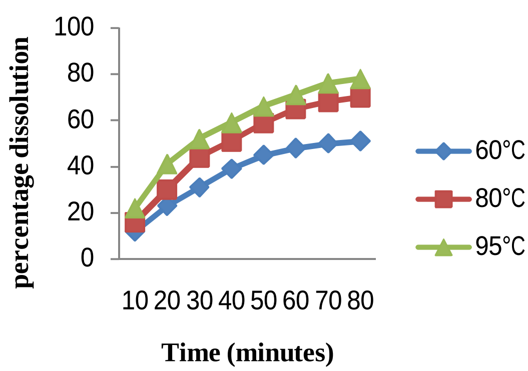

Fig: 1. Percentage dissolution of iron against time

It is observed from the results shown in Table 2 that with increase in roasting temperature the grade of concentrate increases. It is because of faster rate of conversion of hematite to magnetite. It is also observed from these results that Mn/Fe ratio obtained after reduction roasting is not up to the mark. It may be because of interlocking of iron minerals and manganese minerals. Therefore, acid leaching with dilute HCl was carried out to dissolve iron minerals from the concentrate. Leaching results shows appreciable enhancement in Mn/Fe ratio which can be seen from the results shown in Table 3 and Fig. 1. With increase in leaching temperature the dissolution rate of iron increases.

4. Conclusion

From the results obtained during present investigations the following conclusions have been drawn:

1. Reduction roasting followed by leaching with dilute HCl is capable of improving the Mn/Fe ratio of dump Mn ore fines to the desired level.
2. With increase in roasting temperature the grade of Mn concentrate increases and at the same time Mn/Fe ratio improves.
3. The excess iron present in the concentrate is decreased by leaching with dilute HCl and the dissolution rate of iron increases with increase in temperature.

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