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Selective leaching of iron from low grade ferruginous manganese ores of Sandur area, Karnataka for ferromanganese production by using sucrose in sulphuric acid medium

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ABSTRACT

The vast reserves of low grade, ferruginous manganese ores from Deogiri mines, occur in to the well known Sandur greenstone belt in Bellary district, Karnataka. The ore contains 32.40% Mn, 24.49% Fe, 2.79% SiO_2 and 6.80% Al_2O_3. It was sampled and subjected to physical beneficiation and selective reductive leaching of iron with sucrose ($C_{12}H_{24}O_{11}$) in sulphuric acid medium. The aim of the present work is to raise the Mn/Fe ratio of the manganese ore which can be used as a raw material for ferro-manganese production. From XRD analysis and ore microscopic studies it was noticed that the major manganese minerals were pyrolusite, cryptomelane and lithiophorite, and the gangue minerals were hematite, goethite, limonite, manganiferous shales, quartz and aluminous clays. The ore was washed on Wilfley table to reject the possible gangue minerals. The concentrate obtained from Wilfley table was subjected to selective reductive leaching of iron using sucrose in sulphuric acid medium. The leaching experiments were carried out by varying the parameters like sucrose concentration (1-4g/100cc), time (30-120 minutes), pulp density (5-20%) and temperature (30-80°C) with constant feed size distribution of –200 mesh in all the experiments. The optimum condition of the total process of leaching obtained are 2g/100 cc of sucrose concentration, 90 minutes of time, 10% by weight pulp density 30°C of temperature with 82.23% Fe in leached liquor, 74.54% Mn in residue, 9.35% Fe in residue with a Mn/Fe ratio of 7.96.

INTRODUCTION

Manganese is essential for the production of virtually all kinds of steel and cast iron where it has no suitable substitute. The demand for manganese ore and its alloys is expected to increase. The country has vast resources of manganese ore[1], however the high grade material suitable for ferromanganese production is rather limited. It is seen that demand of manganese ore for ferromanganese production is steadily increasing and this has to match the production and demand of steel in the years to come. India is the seventh largest producer of manganese ore in the world and in terms of ferromanganese, it is the ninth largest producer accounting 3.3% of the world production[2]. The ferromanganese industry requires manganese ore with somewhat stringent specifications demanding higher Mn content and Mn/Fe ratio and lower SiO_2, Al_2O_3 and P contents. The specifications of manganese ore as per BIS (IS 4763-1982) for manufacture of ferromanganese are 38 to 48% Mn and over 7 to 15% Fe, 2.5:1 to 7:1 Mn/Fe ratio, 7.5 to 13% SiO_2, 2 to 6% Al_2O_3 and less than 0.15% P. The norm of requirement of ferromanganese in the steel production varies from 8 to 16 kg per tonne of steel (average : 12 kg per tonne of steel). Using the norm, the demand for ferromanganese in steel production by 1996-97 is estimated as 2,89,000 tonnes. Applying the average norm of requirement of 2.6 tonnes of manganese ore per tonne of ferromanganese the demand of high grade manganese ore in the ferromanganese industry is estimated as 7,52,000 tonnes.

The manganese ores are classified[3], into (a) Simple ores, (b) Ferruginous ores, (c) Garnetiferous ores and(d) Complex ores. There is huge reserve of low grade ferruginous manganese ores, not used at present for ferromanganese production, at Sandur, Bellary district, Karnataka having high iron content. In view of conservation of manganese ores and future demand for ferromanganese within the country and also for the export market, the process metallurgist can only tie-up the supply and demand, by beneficiating ferruginous manganese ores with new technological process schemes to meet the stringent specifications laid down by ferromanganese industries. Both physical and chemical methods have been used. By gravity concentration technique silica and alumina have been tried to be reduced to certain extent. An attempt has been made to reduce iron present in ferruginous manganese ores by applying chemical leaching method using sucrose as a reductive leaching agent in sulphuric acid media.

Sucrose Reductive Leaching in H_2SO_4 Media

The basis of this leaching process is the ferric iron solubilisation and its reduction to ferrous iron. Toro and Vaglio[4,5,6] (1991), Das, *et. al.*, (1986), Canterford (1986), Anand *et. al.*, (1988), Kango and Jena (1988) have studied the recovery of manganese from minerals which are not treatable by conventional process, by hydrometallurgical process.. The conventional process of iron removal are not always useful in removing iron completely (Gnimares, *et. al.*, 1987; Brain *et. al.*, 1969; Conley *et. al.*, 1970; Gurudev, *et. al.*, 1978). It is understood that the studies deal with the improvement of dissolution process of iron oxide, but most of these deal with the iron dissolution from synthetic iron oxide, not considering the presence of encapsulated iron that causes a significant change in the kinetics of dissolution.

Ferruginous manganese ore was subjected to acid reductive leaching using sucrose ($C_{12}H_{24}O_{11}$) as reducing agent in sulphuric acid media. The effect of sucrose is more important in the intermediate level of acid concentration. The dissolution process of iron can be described by the following reactions (here the iron compound is reported as iron oxide).

$$Fe_2O_3 + 6H^+ = 2Fe_{3+} + 3H_2O \quad \ldots (1)$$

$$18Fe_3 + C_{12}H_{22}O_{11} + 13H_2O = 18Fe^{2+} + 12CO_2 + 18H \quad \ldots (2)$$

In order to understand the action of the sucrose in the reductive process, it is useful to consider the kinetic behaviour of the reductive leaching and can be described by the sinking ore model with surface reaction reported by Pingmann (1956).

Action of the acid on sugar at high temperature forms highly reactive compounds for the reduction of Fe_3+ and hence for the dissolution of Fe_2O_3; glucose and fructose (from the hydrolisis of sucrose) do not react directly with Fe_2O_3. Dehydration of sucrose takes place as per the following reaction :

$$\text{Sucrose} + H^+ = \text{Glucose} + \text{Fructose}$$

The overall reaction, (equation 3) between MnO_2 and sucrose in acid leaching is as shown below using equations 1 and 2.

$$24MnO_2 + C_{12}H_{21}O_{11} + 18H = 24Mn^{+2} + 12CO_2 + 35H_2O \quad \ldots (3)$$

In this case the MnO_2 reduction to Mn^{+2} is due to chemical reduction process; it utilizes reductive substance sucrose in a sulphuric acid media and is thought to be the best.

RESULTS

The ferruginous manganese ore was obtained from Deogiri mines of M/s. SMIORE Ltd., Sandur area. The ROM analysed 32.4% Mn, 24.49% Fe, 2.79% SiO_2 and 6.80% Al_2O_3. The ore microscopic studies of the sample supplemented by XRD reveal the presence of pyrolusite, cryptomelane, lithiophorite as manganese minerals and the gaunge minerals are hematite, goethite, limonite, mangniferous shales, quartz and aluminous clays. The ore (–3 mm) was washed on Wilfley table and the concentrate obtained analysed 41.30% Mn, 19.6% Fe, 1.70% SiO_2, 4.80% Al_2O_3 which was ground to –200 mesh based on liberation studies. The sucrose leaching experiments in sulphuric acid media was carried out in a glass beaker on a magnetic stirrer cum heater by varying the parameters like. (a) sucrose concentration, (b) time of leaching, (c) pulp density and (d) temperature. The leached solution was filtered, filtrate solution and residue were analysed. The results obtained from the above experiments are shown in Tables 1,2,3 and 4.

Table 1 : Variable : Amount of sucrose in acid media (g/100cc) Constants : Time of leaching 30 minutes, temperature 30°C, pulp density 5% by weight, size –200 mesh

Amount of sucrose in acid media (gm/100cc)	% Iron in leached solution
1	58.56
2	65.52
3	67.26
4	69.03

Table 2 : Variable : Time of leaching, Constants : Temperature 30°C, pulp density : 5% by weight, size –200 mesh, concentration of sucrose 2gm/100cc

Leaching time (minutes)	% Iron in leached solution
30	58.56
60	72.32
90	86.76
120	88.21

Table 3 : Variable : Pulp density % by weight, Constants: Temperature 30°C, size –200 mesh, sucrose concentration, 2gm/100cc, leaching time 90 minutes

Pulp density (% by weight)	% Iron in leached solution
5	83.76
10	82.23
15	69.61
20	56.25

Table 4: Variable : Temperature, Constants : size –200 mesh, leaching time 90 minutes pulp density 10% by weight, amount of sucrose 2gm/100cc

Temperature (°C)	% Iron in leached solution
30	82.23
50	87.21
80	88.16

%Mn in residue : 74.54%, Fe in residue : 9.36%, Mn/Fe ratio : 7.96

CONCLUSIONS

From the results obtained of the above experiments the following conclusions were drawn.

1. Deogiri manganese ores are ferruginous in nature
2. The conditions for maximum recovery of manganese in residue with high Mn/Fe ratio on the basis of experimental results are as follows:
    - a) Amount of sucrose in acid media : 2g/100cc
    - b) Time of leaching : 90 minutes
    - c) Pulp density : 10% by weight
    - d) Temperature : 30°C
3. Low grade ferrunginous manganese ores are amenables to selective leaching of iron.
4. Manganese is lost along with the leached solution which has to be critically examined in the future study.
5. The extracted residue with higher Mn/Fe ratio may be used as a raw material for ferromanganese production.
6. The viability of the sucrose leaching process has to be examined.

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