

Mn recovery from medium grade ore using a waste cellulosic reductant

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Medium grade siliceous manganese ore containing 38.22% Mn was leached in sulphuric acid medium using shredded newspaper as reducing agent. Objective of the present study was to investigate the effectiveness of ligno-cellulosic base wastes such as used newspaper as a reducing agent. The experimental parameters chosen for this study were: H₂SO₄ concentration (2-5% v/v), temperature (60-90°C), reductant to ore ratio (0.4-1) and ore particle size (57 – 274 µm). Optimum conditions for >90% extraction were: 90°C, 5% H₂SO₄ (v/v), reductant to ore ratio 0.5, 8 h, 10% pulp density and ore particle size -100 µm. Newspaper was found to be equally effective as a reducing agent for low grade ore (15.83% Mn) also wherein the amount of reductant and acid needed were proportional to Mn content of the ore. The leach solution was enriched to 87 g/L by recycling process. The enriched solution was purified by pH adjustment to 4.7 using 20% lime slurry. MnSO₄.H₂O was crystallized from purified solution. A schematic flow-sheet has been included.

Keywords: Manganese ore, Leaching, Cellulosic reductant, Waste newspaper

Manganese is the fourth most used metal after iron, aluminum and copper. Over 90% of the world's production of manganese is utilized in the desulphurization and strengthening of steel. Manganese is also used in the manufacture of dry batteries, as a colorant and as an ingredient in plant fertilizers and animal feed. In view of the continuing depletion of high grade ores exploitation of low and medium grade ore bodies has become more important.

Manganese occurs in nature mostly as pyrolusite (MnO₂) which is stable in acid or alkaline oxidizing conditions hence the extraction of manganese from such source has to be carried out under reducing conditions. Several reducing agents have been used previously under different acidic media e.g. coal^{1,2}, pyrite³, ferrous sulphate⁴, aqueous sulphur dioxide⁵⁻⁹ and hydrogen peroxide¹⁰. The work carried out on leaching of different types of manganese ores using such reductants has recently been reviewed by Zhang and Cheng¹¹.

Some of the reducing agents used, such as SO₂, may be harmful to the environment. Hence, many past investigators had focused on reductive leaching of manganiferrous ores using organic reductants mainly carbohydrates like glucose¹¹⁻¹³, sucrose¹⁴, lactose¹⁵, oxalic acid¹⁶ etc. Carbohydrates are non-hazardous and low cost reducing agents that may be used either in pure form or as industrial wastes¹⁷⁻¹⁹. The reported studies¹¹ show that the

carbohydrates are effective reductants under mild temperature conditions (<90°C).

Ligno-cellulose based waste materials such as saw dust and bagasses are potential reductants for acid leaching of manganese ores. However, waste paper which is another lingo-cellulose based material has not been used as the reducing agent. Looking into the composition of waste papers which contain lignin, cellulose and hemicelluloses, it was thought that it may work as a good reductant for manganese ore in the temperature range of 30 to 90°C. Besides systematic studies on dissolution of manganese ore using paper as a reductant, attempts were made for enrichment and purification of leach solution to obtain pure MnSO₄.H₂O from medium grade manganese ore of Gujarat Mineral Development Corporation, India. The potential importance of the process is represented by mild experimental conditions.

Experimental Procedure

Material

The manganese ore used for the study was collected from Gujarat Mineral Development Corporation, Ahmedabad. The ore contained: Mn 38.22, Fe 4.9, Cu, Co and Zn 0.01 (each), Ni 0.02 and acid insoluble 25.4%. The ore was crushed, ground and screened to obtain material with a particle size of -100 µm. X-ray diffraction pattern of the sample showed that all the major peaks correspond to silica

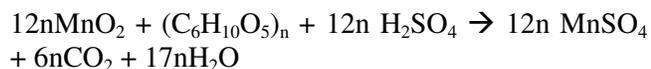
and pyrolusite phases. Waste news papers were cut into tiny pieces and used as reducing agent. TrueSpec CHNS analyzer supplied by LECO Corporation, USA, was used to do the ultimate analysis of charred news paper. It contained 37.1% fixed carbon, 12.7% moisture, 7.4% ash, 42.8% volatile matter. All other reagents used were of analytical grade.

Procedure

Experiments were carried out in a 250 mL glass reactor kept over a ceramic hot plate with magnetic stirring system. The reactor was fitted with a reflux condenser. Initially required amount of concentrated sulphuric acid was mixed thoroughly with weighed amount of shredded newspaper and that pulp was transferred to the ore slurry of fixed pulp density. The total mixture was heated to predetermined temperature and stirred for 8 h. Samples were collected at different time intervals. Manganese analysis was carried out volumetrically by EDTA titration using thymolphthalein indicator. The minor elements were analysed by atomic absorption spectrophotometer.

Results and Discussion

The used newspaper after charring had a fixed carbon content of 37%. The major structural components of paper are lignin, hemicellulose and cellulose which makes it a good source of sugars²⁰. Cellulose, a linear polysaccharide of β -1,4 linkages is susceptible to acid catalyzed hydrolysis releasing soluble sugars such as glucose. Concentrated H_2SO_4 disrupts the hydrogen bonding of cellulose making it amorphous in nature. Decrystallisation of cellulose results in gelation with acid. This gelatinous mass hydrolyses under dilution. Considering total manganese in the ore present as MnO_2 overall reaction can be represented by:



$(C_6H_{10}O_5)_n$ indicates that cellulosic part of paper consists of α -D glucose units.

Effect of reductant to ore ratio

The reductant to ore ratio was varied from 1 to 0.4 by varying the amount of ore from 5 to 12.5 g keeping the reductant (newspaper) weight constant at 5 g. Temperature ($90^\circ C$) and H_2SO_4 concentration (5% v/v) were kept constant. It is observed from

Fig. 1 that with the decrease in reductant to ore ratio leaching becomes slower and after a ratio of 0.5 final recoveries also decreased quite significantly which may be due to inadequate amount of available reducing agent. When 1 g reductant/g of ore is used Mn extraction is 98% in 4 h whereas for 0.5 g reductant/g ore 93% Mn is achieved after 8 h.

Effect of temperature

Leaching temperature was varied from 60 to $90^\circ C$ keeping other parameters constant at: H_2SO_4 5%(v/v), ore 10 g, newspaper 5 g, $-100 \mu m$ ore particles. Results on the effect of leaching temperature on manganese extraction are shown in Fig. 2. Extraction of manganese increased with increase in temperature.

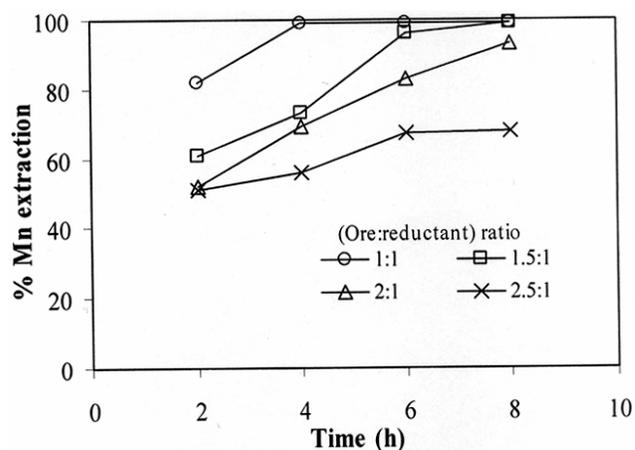


Fig. 1— Effect of reductant to ore ratio on Mn extraction. [Conditions: 5% H_2SO_4 (v/v), $90^\circ C$, $-100 \mu m$ ore size, 5 g newspaper].

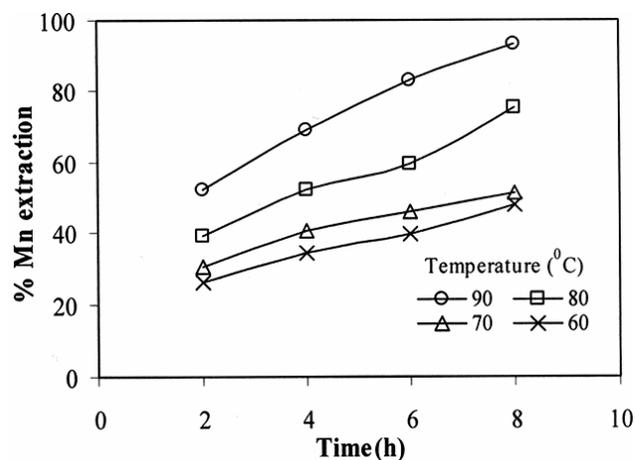


Fig. 2— Effect of temperature on Mn extraction. [Conditions: $-100 \mu m$ ore size, 10 g ore, 5 g newspaper, 5% H_2SO_4 (v/v), 10% pulp density].

With the increase in leaching temperature from 60 to 90°C, manganese extraction (after 8 h) increased from 47.87 to 93%.

Effect of particle size

In order to study the effect of particle sizes of ore, the ore was sieved into different narrow size fractions in the range of (-300 +250) μm to (-63 + 53) μm and leaching experiments were conducted under standard conditions of 90°C and 10% pulp density. The average particle diameter has been calculated from the geometric average as:

$$d_p = (f_1 \times f_2)^{1/2}$$

where d_p is the diameter and f_1, f_2 are upper and lower size of particular fraction. The results given in Fig. 3 show that the smaller the size of ore particles, greater is rate of reaction in a certain period of time due to greater exposed surface area for the reaction.

Effect of acid concentration

Amount of sulphuric acid for saccharification as well as leaching was varied from 2 to 5 mL which can also be expressed in terms of percentage (v/v) considering total volume of slurry to be 100 mL. Other parameters were kept constant: ore 10 g, reductant 5 g, temperature 90°C and time of leaching 8 h. The results of acid variation are shown in Fig. 4. With lower amount of acid the rate of hydrolysis is slower and the release of carbohydrate subunits would be less resulting in lower recovery of manganese. By increasing the acid concentration from 2 to 5%, manganese extraction increased from 29 to 93%. The XRD of leach residue obtained from maximum

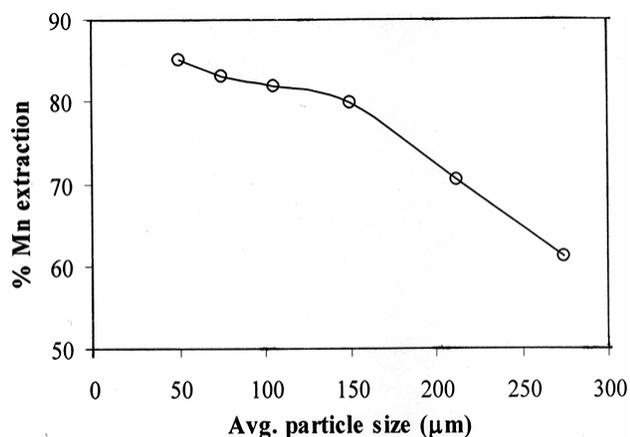


Fig. 3— Effect of particle size on Mn extraction. [Conditions: 90°C, 10 g ore, 5 g newspaper, 5% H_2SO_4 (v/v), 8 h, 10% pulp density].

manganese extraction showed very sharp peaks for quartz with a totally diminished peak corresponding to pyrolusite.

Comparison of reducing action of newspaper and processed paper

In this study a comparison had also been made for evaluating reducing action of highly processed paper like white office paper vis-à-vis news print paper which is made from mild chemical treatment of pulp. During manufacturing of white papers several chemicals are used with the paper pulp to give whiteness. Due to the presence of excess chemicals these type of papers may be less reactive. Fig. 5 shows the comparative results. The maximum manganese recovery using white office paper was 82.29% whereas with that of news paper was 93.07% in 8 h.

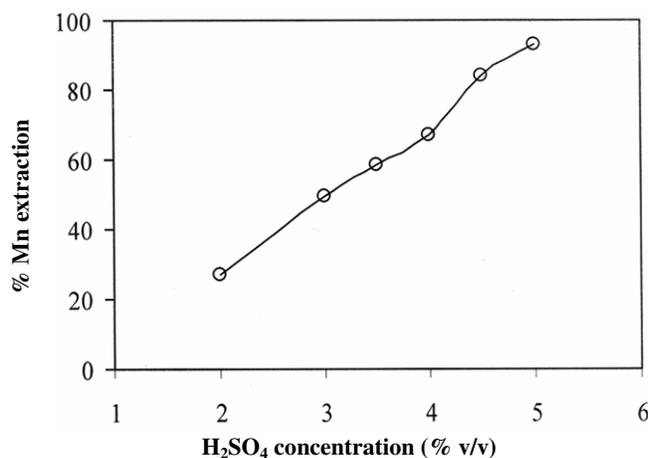


Fig. 4— Effect of acid concentration on Mn extraction. [Conditions: 90°C, 10 g ore, 5 g newspaper, -100 μm ore size, 8 h, 10% pulp density].

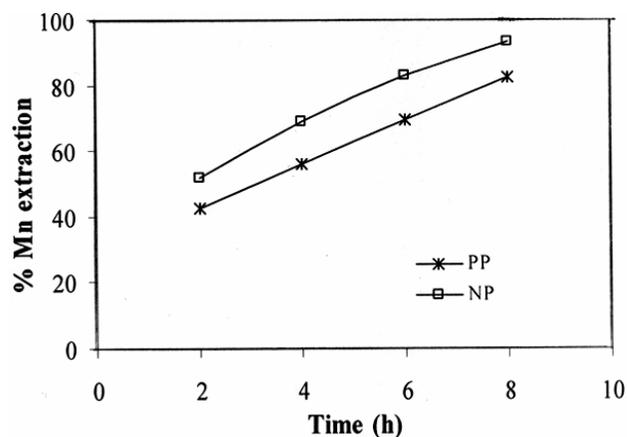


Fig. 5— Comparison of office paper and newspaper as reducing agent. PP: Processed paper, NP: Newspaper [Conditions: 90°C, 10 g ore, 5 g reductant, 5% H_2SO_4 (v/v), -100 μm ore size and 10% pulp density].

Leaching of low grade manganese ore

A typical low grade Mn ore containing 15.83% Mn, 3.52 % Fe and 57.17 % acid insoluble was also tested for its response to leaching using paper as the reductant. Effect of leaching time under the following conditions: pulp density 10%, acid concentration 2.5 % (v/v), amount of paper 2.5 g/10 g of ore, temperature 90°C, is shown in Fig. 6. Almost quantitative extraction of manganese was obtained under the above conditions.

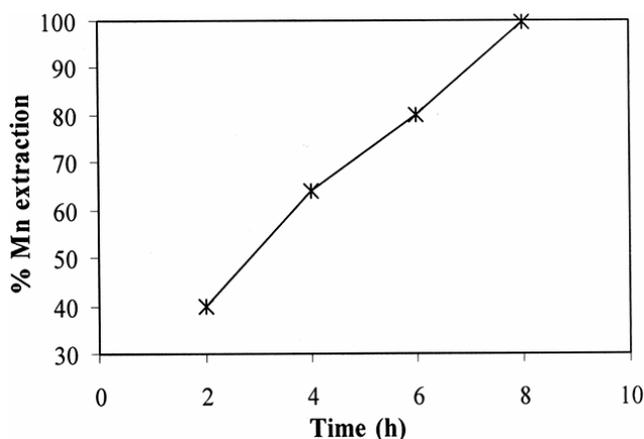


Fig. 6— Effect of leaching time on Mn extraction from low grade ore. [Conditions: 90°C, 10 g ore, 2.5 g newspaper, 2.5% H₂SO₄ (v/v), 10% pulp density, -100 μm ore size].

Enrichment of leach solution by recycling, its purification and crystallization of MnSO₄.H₂O

The leach solution obtained under optimum conditions was enriched by recycling for further processing to recover Mn as MnSO₄.H₂O. Leaching experiments were carried out in 100 g scale and the leach liquor was recycled using fresh ore, reductant and acid. After three cycles leach solution composition was: Mn 87, Fe 5.1, Co 42, Ni 62 and Cu 21 mg/L. The end pH of the solution was 0.5.

Iron was the major impurity in the leach solution with other metal ion impurities in ppm level. To meet the specifications of manganese sulphate monohydrate, iron had to be removed. This was achieved by pH adjustment using lime slurry. The pH was adjusted to 4.7 using 20% lime slurry. No manganese loss was observed in this pH range. The composition of purified solution was: Mn 78.97, Fe 20, Co 38, Ni 58 and Cu 19.0 mg/L. The lower manganese content in purified solution is due to the dilution effect caused by addition of lime slurry to adjust the pH. The purified solution was evaporated and manganese sulphate monohydrate was crystallized. The chemical composition of the salt was: Mn 32, Cu 0.017, Ni 0.01, Co 0.02, Zn 0.02, Fe 0.01, Ca 0.04 and Mg 0.05%.

The XRD patterns of manganese sulphate prepared from manganese ore and chemical grade MnSO₄.H₂O (BDH) are given in Fig. 7 and the XRD data are

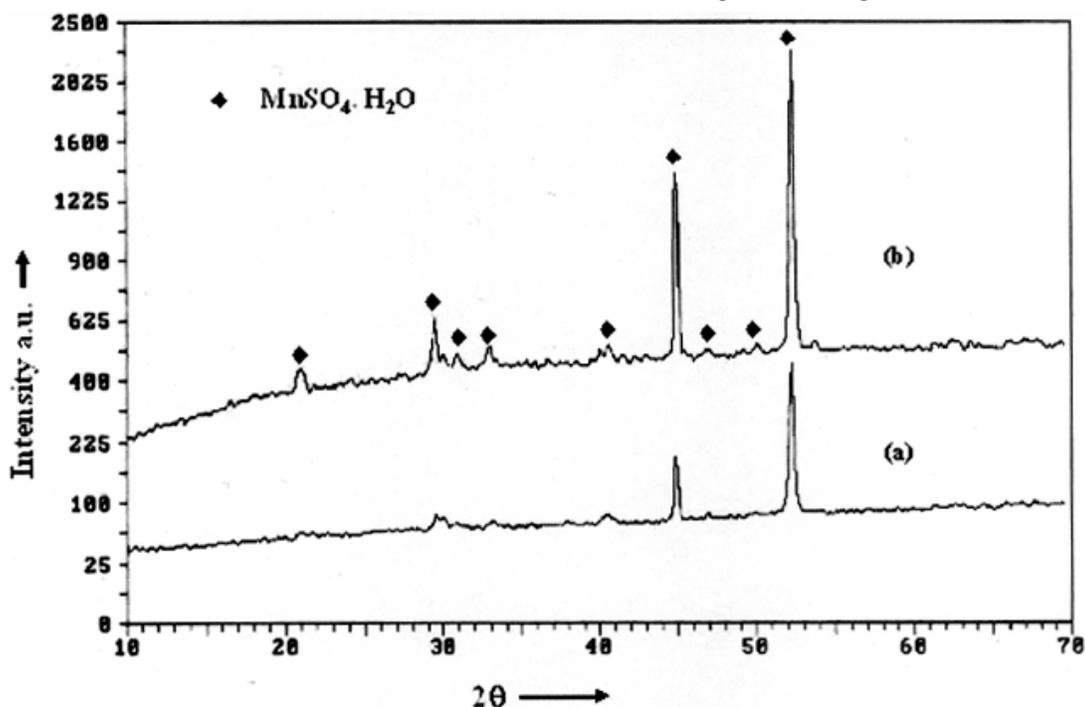


Fig. 7— XRD patterns of (a) manganese sulphate prepared from Mn ore and (b) BDH MnSO₄.H₂O.

compared in Table 1. It is observed that the manganese sulphate monohydrate prepared from Mn ore is similar to the chemical grade $\text{MnSO}_4 \cdot \text{H}_2\text{O}$ (BDH). The schematic flow-sheet for preparation of manganese sulphate monohydrate from manganese ore is shown in Fig. 8.

Table 1— XRD data for $\text{MnSO}_4 \cdot \text{H}_2\text{O}$ of reagent grade and prepared from the ore

d-values of chemical grade $\text{MnSO}_4 \cdot \text{H}_2\text{O}$	% Relative intensity	d-values of $\text{MnSO}_4 \cdot \text{H}_2\text{O}$ prepared from ore	% Relative intensity
4.229	2.1	4.244	4.4
3.019	4.4	3.030	13.0
2.975	2.8	2.892	3.1
2.704	1.8	2.716	4.2
2.225	2.4	2.222	2.8
2.019	40.0	2.017	62.9
1.936	1.7	1.938	1.0
1.749	100	1.747	100

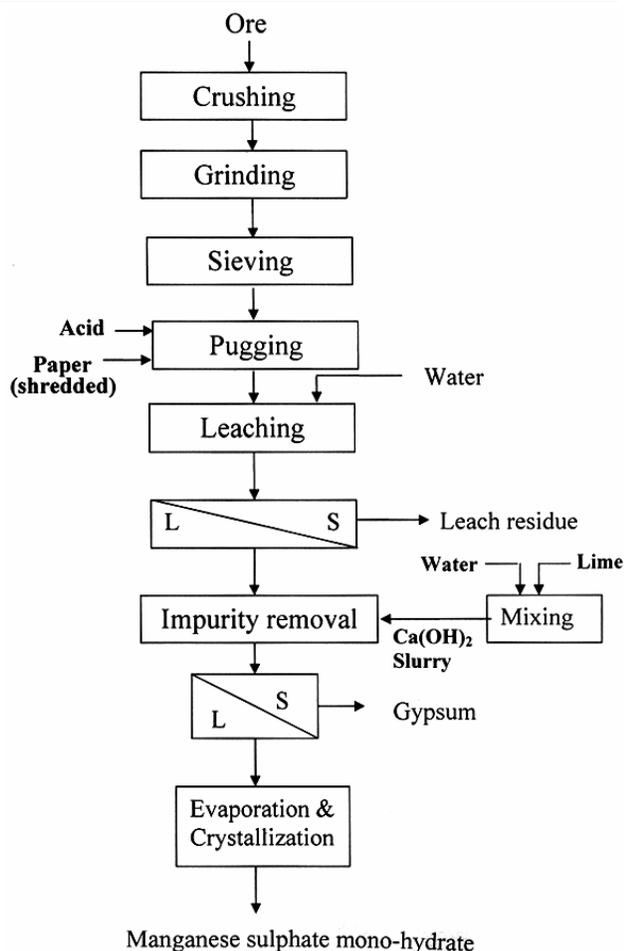


Fig. 8— Schematic flow-sheet for preparation of manganese sulphate from Mn ore.

Conclusion

Used news paper can act as a very good reducing agent for extraction of manganese from low/medium grade ores. Manganese extraction of > 90% can be obtained by leaching the ore at 90°C for 8 h in sulphuric acid medium. With the variation of temperature the rate of leaching increased. With the increase of ore to news paper ratio manganese recovery decreased. The increase in acid concentration increased manganese recovery. High manganese extraction (93.1%) was obtained under the following conditions: pulp density 10%, time 8 h, sulphuric acid 5% (v/v), temperature 90°C and reductant to ore ratio 0.5. The leach solution was enriched through recycling, purified and evaporated to obtain high pure $\text{MnSO}_4 \cdot \text{H}_2\text{O}$.

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