The European Journal of Mineral Processing and Environmental Protection
Vol.3, No.2, 1303-0868, 2003, pp. 208-214

Influence of fabric on aqueous SO_2 leaching of manganese ore

P.K. Naik*, B.K. Mohapatra, S.C. Das, V.N. Misra

Regional Research Laboratory (CSIR), Bhubaneswar, India

Received 4 October 2002; accepted 15 June 2003

ABSTRACT

Extraction of manganese value through SO_2 leaching from three different grade of manganese ores, viz. high grade, medium grade and low-grade from Nishikhal deposit of Orissa (India) have been undertaken. The influence of mineral fabric and variable rate of SO_2 consumption on extraction of Mn and K from these ores were established. Recovery of metal values is best achieved in low-grade siliceous variety showing granular texture and devoid of any ferruginous minerals. This was followed by high-grade ore that exhibits massive texture, rich in pyrolusite and paucity of gangue constituents. The leaching in case of medium grade ore is least favoured for intimate intergrowth of Mn-phases with iron minerals. Consumption of higher quantity of SO_2 in medium grade ore further attests the role of mineral fabric in metal recovery.

Keywords: Manganese ore; Fabric; Sulphur dioxide; Leaching

1. INTRODUCTION

Manganese dioxide is stable in acid or alkaline oxidising conditions. Hence, extraction of manganese is carried out in reducing condition. Aqueous SO_2 has proven to be an effective leachant for Mn from manganese dioxide ore, because of rapid rate of dissolution, room temperature operation, relative ease of purifying leach liquors and elimination of solution disposal problem. Studies have been carried out on synthetic MnO_2 to understand leaching mechanism (Basset and Parker, 1951; Herring and Ravitz, 1965; Miller and Wan, 1983). Aqueous SO_2 dissolves manganese oxides by reducing Mn^{4+} and Mn^{3+} metal centers to stable water soluble Mn^{2+} (Cotton and Wilkinson, 1988) and oxidises SO_2 to SO_4^{2-} or dithionate $S_2O_6^{2-}$. The overall reaction can be given as follows.

$$MnO_2 + SO_2 \rightarrow Mn^{2+} + SO_4^{2-} \quad (1)$$
$$MnO_2 + 2SO_2 \rightarrow Mn^{2+} + S_2O_6^{2-} \quad (2)$$
$$2MnOOH + SO_2 + 2H^+ \rightarrow 2Mn^{2+} + SO_4^{2-} + 2H_2O \quad (3)$$
$$2MnOOH + 2SO_2 + 2H^+ \rightarrow 2Mn^{2+} + S_2O_6^{2-} + 2H_2O \quad (4)$$

SO_2 leaching of manganese ore (Abbruzzese, 1990; Abbruzzese *et al.*, 1990; Grimanelis *et al.*, 1992; Naik *et al.*, 2000) and manganese nodules (Khalafalla and Pahlman, 1981; Kanungo and Das, 1998) have been studied by some authors. But the effect of mineral fabric on SO_2 leaching of manganese ore has not been given due emphasis in any such earlier study. This paper reports the influence of mineral fabric/characteristic on winning of metal values from manganese ore.

2. MATERIALS AND METHODS

Three different types of manganese ore namely, low-grade, medium-grade and high-grade were collected from Nishikhal deposit, Rayagada dist., Orissa, India for the said investigation. Polished surfaces of different ore types were studied under Leitz microscope and powdered samples were exposed under Philips X-ray Diffractometer to find out the mineralogical and textural characteristic of these three ore types. The samples were ground to below 72μm for chemical analysis. Small blocks of 3 cubic cm were made from all the three varities of Mn-ore to find out their bulk density and porosity.

* Corresponding author. E-mail: pradyumnanaik@yahoo.co.in

The leaching experiments were carried out on three different powdered Mn-samples, varying the stoichiometric quantity of SO_2 added. The SO_2 solution provided by Merck (India) was used for leaching experiments. The stoichiometric calculation was done using the equation (1). The concentration of SO_2 solution was measured by titrating against $KMnO_4$ after addition of a few mL of H_2SO_4. The effect of duration of leaching was studied for each type of ore at twice the stoichiometric quantity of SO_2 added. For each experiment, a 500ml conical flask was charged with 10g of ore and required volume of 3% SO_2 solution was added into it. The slurry was continuously stirred at a rate of 1000min^{-1} using a mechanical stirrer. All the experiments were carried out at room temperature. 5ml samples were withdrawn at selected time intervals and analysed for Mn, Fe and K in an Atomic Absorption Spectrophotometer after required dilution with acidified distilled water.

3. RESULTS AND DISCUSSIONS

3.1. Characteristics of Mn-ore

The manganese ores of Nishikhal in general, are pitch black in colour, show massive to botryoidal form and soils the hand. The low-grade appears spotted and has a grey look. The characteristic difference in physical properties of these three varieties of ore samples is given below (Table 1).

Table 1
The physical characteristics of different Mn-ore types

Property	High-grade ore	Medium-grade ore	Low-grade ore
Hardness	Soft, soils the hand	2 - 3	6 - 7
Bulk density	4.07	3.09	2.85
Porosity, %	3	12	20

Texturally, the high-grade ore is massive while medium-grade ore is laminated and low-grade spotted/disseminated. Cryptomelane ($KMnO_2$), pyrolusite (MnO_2) and microcline are identified from the XRD pattern of high-grade manganese ore (Figure 1). In addition to the above minerals goethite is recorded in the medium-grade ore (Figure 2).

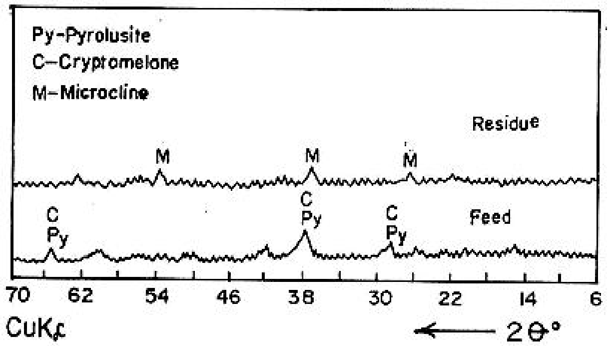

Figure 1. X-ray diffraction pattern of high-grade manganese ore (Bottom - Feed, Top – Residue)

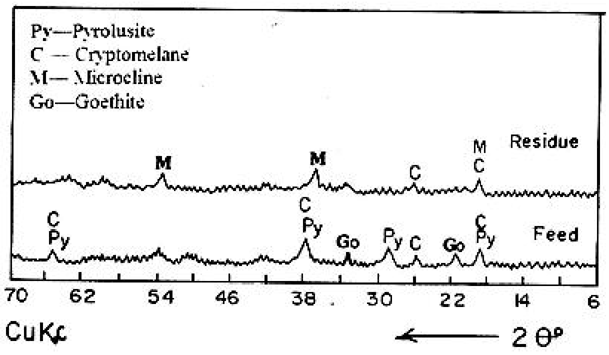

Figure 2. X-ray diffraction pattern of medium-grade manganese ore (Bottom - Feed, Top – Residue)

The minerals present in low-grade ore are cryptomelane, quartz (SiO_2), microcline and kaolinite [$Al_4Si_4O_{10}(OH)_8$] (Figure 3). The other minerals namely romanechite ($BaMnO_2$), lithiophorite (LiMnOH) appear in subordinate amount and recorded only under microscope. The lower Mn-oxide minerals like jacobsite ($MnFe_2O_4$), hausmannite (Mn_3O_4) and manganese silicate phase such as spessartite [$MnAl_2(SiO_4)_3$], and braunite ($3Mn_2O_3.MnSiO_3$) are of minor significance. Besides microcline identified in XRD patterns (Figures 1 - 3) gangue minerals like quartz, sillimanite (Al_2SiO_5), biotite [$K(Mg, Fe)_3 Si_3O_{10}(OH, F)_2$], muscovite [$KAl_2 (AlSi_3O_{10})(OH)_2$], graphite (C) and zircon ($ZrSiO_4$) are also recorded. Phosphorous is present either as minute apatite grains or in adsorbed state with manganese phase.

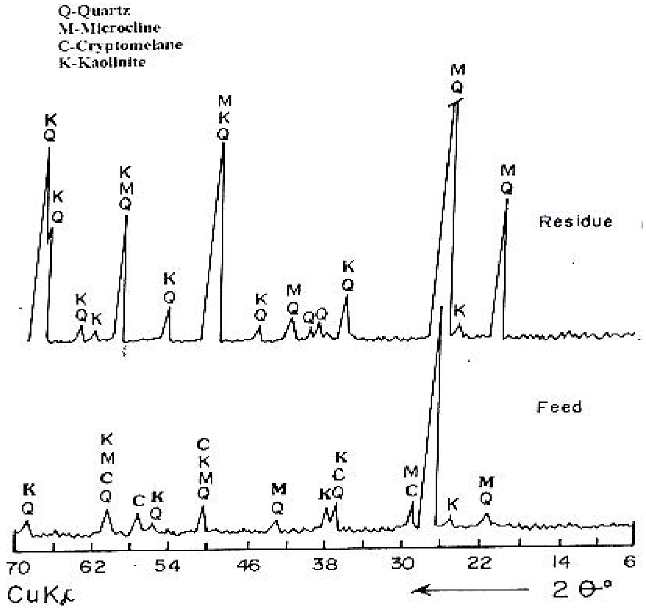

Figure 3. X-ray diffraction pattern of low-grade manganese ore (Bottom - Feed, Top – Residue)

The high-grade ore, enriched in pyrolusite and cryptomelane layers, often contains small inclusion of clay minerals (Figure 4). In medium-grade type the goethite occurs in fine layers/colloform bands alternatively with cryptomelane (Figure 5). Small oolites of goethite is also noticed as inclusion within cryptomelane. The low-grade ore constitutes abundant granular quartz and cryptomelane (Figure 6).

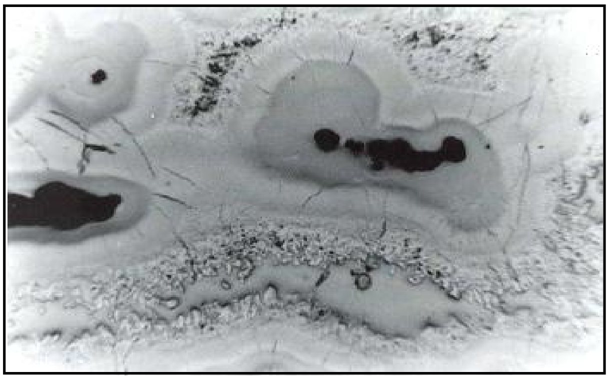

Figure 4. Thin layers of Mn-oxide phases (bright – pyrolusite, grey- cryptomelane) in high grade ore. Note the small inclusions of clay materials (black) x 100

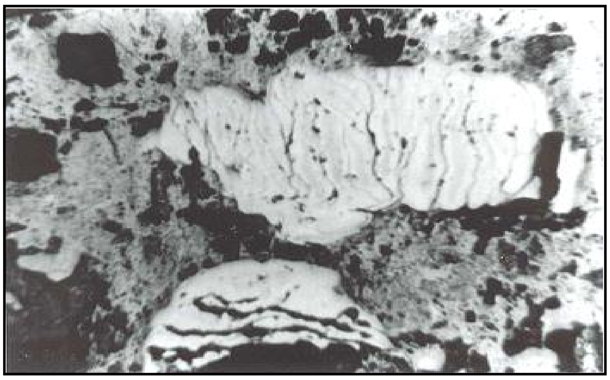

Figure 5. Elongated patches of Mn-oxide phases (cryptomelane + goethite intergrown) with mixed iron alumina rich area in medium grade ore x 200

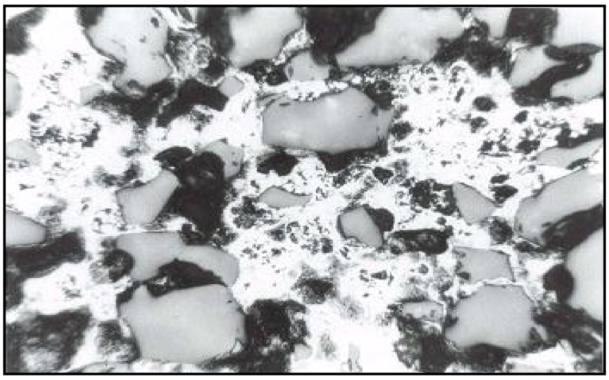

Figure 6. Large silica grains (quartz) floating within Mn-oxide matrices (cryptomelane – white), in low-grade ore x 100

The major and minor element analyses results of the ore samples are given in Table 2. The high-grade sample is rich in manganese with poor iron content while the medium grade ore has high iron and low manganese values relative to the former type. In contrast, the siliceous low-grade ore has very high silica, low manganese and negligible iron. Both high and low-grade samples have comparable phosphorous in contrast to the medium grade type that shows higher value.

Table 2
Major and minor element distribution pattern in three different Mn-ore types

Elements (wt%)	High-grade	Medium-grade	Low-grade
$MnO_2^{(t)-}$	81.07	55.44	39.55
$Fe_2O_3^{(t)-}$	06.72	23.06	01.69
Al_2O_3	02.95	03.19	03.50
SiO_2	01.42	02.36	41.29
K_2O	02.95	01.87	01.08
P_2O_5	01.43	02.11	01.24

3.2. Leaching characteristics

3.2.1. Effect of stoichiometric quantity of SO_2

In general, the extraction of manganese increases with the increase in stoichiometric quantity of SO_2 added. But in the present case a minor deviation is recorded. In high-grade ore 94.40% of Mn is extracted with 1.5 stoichiometric quantity of SO_2 after which it increases slowly and reaches 99.55% at 2.0 stoichiometric quantity of SO_2 (Figure 7). In medium-grade ore 90.88% of Mn is extracted with 1.75 stoichiometric quantity of SO_2. The Mn extraction further increases with higher quantity of SO_2 and attains 97.17% at 2.5 stoichiometric quantity of SO_2 (Figure 8). In low-grade ore almost all (99.29%) manganese values are extracted with 1.5 stoichiometric quantity of SO_2 (Figure 9). More than stoichiometric quantity of

SO_2 may be attributed to the fabric pattern of individual ore types. The extraction of K follows similar trend to that of Mn, the reason being its intimate association with the manganese phase, cryptomelane ($KMnO_2$). The extraction of iron is initially slow but after a particular quantity of SO_2 added it shoots up (Figures 7-9). This is because of the fact that the leaching of Fe is slower than Mn (Khalafalla and Pahlman, 1981) and the extraction of former is activated after the extraction of later is slowed down.

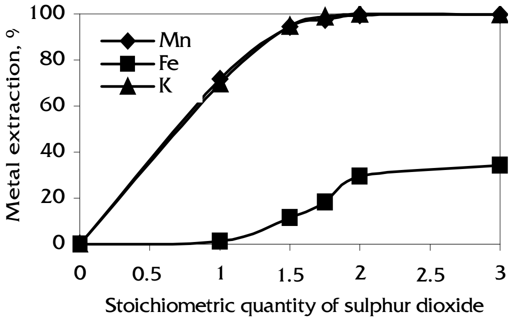

Figure 7. Effect of quantity of SO_2 on extraction of metals from high grade ore; size of ore -150µm, duration of leaching 30min, stirring speed $1000 min^{-1}$

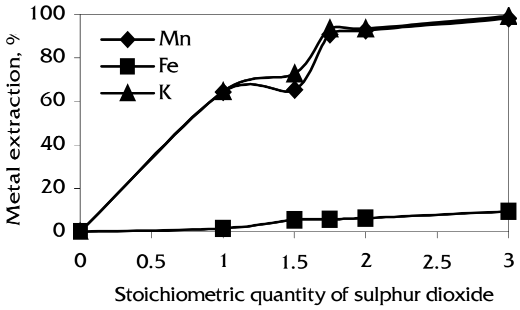

Figure 8. Effect of quantity of SO_2 on extraction of metals from medium grade ore; size of ore -150µm, duration of leaching 30min, stirring speed $1000 min^{-1}$

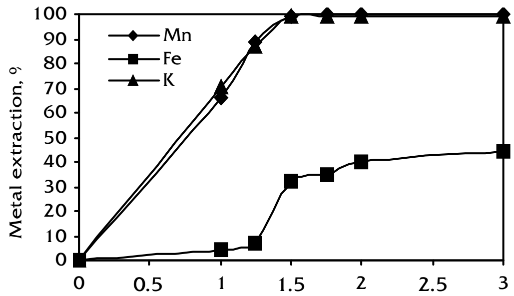

Figure 9. Effect of quantity of SO_2 on extraction of metals from low grade ore; size of ore -150µm, duration of leaching 30min, stirring speed $1000 min^{-1}$

3.2.2. Effect of duration on leaching

The leaching of Mn is fast in low-grade manganese ore in which the extraction is complete in 5 minutes followed by high grade and medium grade ore (Figures 9-12). This may be explained due to simple textural pattern of low-grade siliceous ore. In low-grade ore the Mn phase and the major impurity quartz occur as discrete grains which is again an advantage for fast reaction. Better leaching in low-grade ore could also be due to its higher degree of porosity over other ore types (Table 1). The slow leaching of manganese in high and medium-grade ore may be due to its complex textural pattern and intimate association with iron/clay phase. The chemical analysis (Table 2) shows that the quantity of iron in the low-grade ore is least followed by high-grade ore and medium-grade ore.

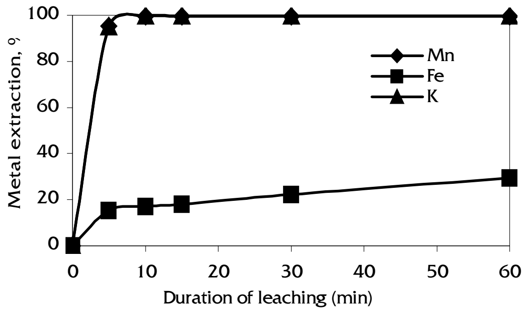

Figure 10. Effect of duration of leaching on extraction of metals from high-grade ore; size of ore -150μm, quantity of SO_2 2.0 stoichiometric, stirring speed $1000 min^{-1}$

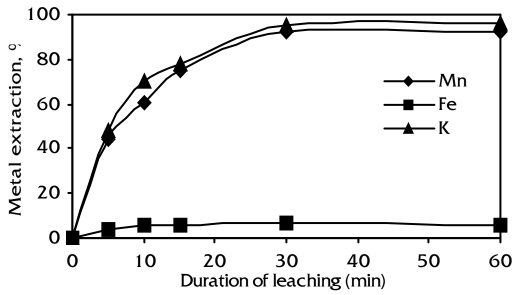

Figure 11. Effect of duration of leaching on extraction of metals from medium-grade ore; size of ore -150μm, quantity of SO_2 2.0 stoichiometric, stirring speed $1000 min^{-1}$

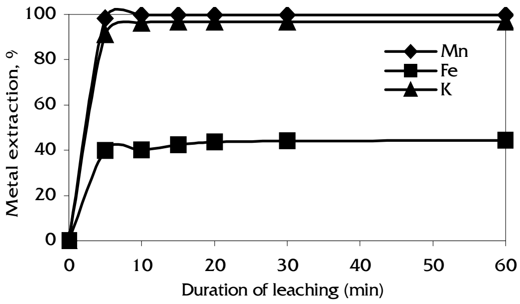

Figure 12. Effect of duration of leaching on extraction of metals from low-grade ore; size of ore -150μm, quantity of SO_2 2.0 stoichiometric, stirring speed $1000 min^{-1}$

3.2.3. Influence of ore characteristics/fabric pattern on leaching

The high-grade ore is more oxidised and contains pyrolusite mineral in abundance (Figure 4). The higher oxide minerals are formed in highly oxidising condition and very unstable in reducing condition. The Mn extraction in high-grade ore is above 99.5% because the major phase is manganese and the chances of entrapment of the same in gangue minerals is less.

In medium-grade ore, cryptomelane (higher oxides of manganese) phase dominates which is unstable in reducing condition. The ore contains lot of goethite (iron oxyhydroxide), which is present in intimate association with (as alternate bands) cryptomelane (Figure 5). Large patches of mixed iron + alumina rich phases also reduces the manganese recovery to below 98%.

On the contrary, the siliceous ore contain large grains of quartz, microcline within the cryptomelane matrices (Figure 6). Here both quartz and microcline grain occur as discrete grains and are free from any manganese inclusion. Hence, even the ore is of low-grade type, paucity of clay and iron rich phases in general, absence of manganese silicate phase and granular microfabric in particular has resulted better extraction (99.99%) as compared to other two ore types.

In the residue of medium grade sample, a small peak dignostic of Mn-phase (cryptomelane) indicates minor remnants of primary manganese phase that escaped leaching (Figure 2). The rest of materials were identified as microcline (K-aluminium silicate). However, in case of high and low-grade variety lack of any reflection peak characteristics of manganese mineral clearly indicates its absence in the leached residue. The other silicate minerals identified in the residue of low-grade ore are quartz, microcline and kaolinite (Figure 3). Only microcline was identified in the residue of high grade ore (Figure 1).

4. CONCLUSIONS

From the leaching studies undertaken on three different grades of manganese ores the following conclusions have been made:

1. The high grade ore is rich in pyrolusite (MnO_2) phase and shows massive texture while the medium grade ore is laminated and contains both cryptomelane ($KMnO_2$) and pyrolusite intimately associated with goethite (FeOOH). In low-grade ore cryptomelane occurs as free grains in association with quartz.
2. The fabric pattern influences the degree of Mn extraction from these ores to a great extent. It is highest in low-grade ore followed by high and medium grade ores.
3. Normally stoichiometric requirement of SO_2 for leaching is Mn-dependant. But deviation in the present case is due to their mineral characteristics and fabric pattern. The stochiometric requirement is least in ore showing granular fabric (1.5 in low-grade ore) and highest in laminated type (2.5 in medium grade ore).

ACKNOWLEDGEMENTS

The authors are thankful to Dr. R.P. Das Advisor, Chemical Metallurgy Division for his valuable suggestion from time to time during the course of work. The authors are also thankful to the Director, RRL, Bhubaneswar for permitting to publish the paper.

REFERENCES

Abbruzzese, C., Percolation leaching of manganese ore by sulfur dioxide. Hydrometallurgy, 1990, **25**, 85-97.

Abbruzzese, C., Duarte, M.Y., Paponetti, B., Toro, L., Biological and chemical processing of low-grade ores. Minerals Eng., 1990, **3**(3-4), 307-318.

Basset, H. and Parker, W.G., The oxidation of sulfurous acid. J. Chem. Soc., Part II, 1951, 1540-1560.

Cotton, F.A. and Wilkinson, G., Advanced inorganic chemistry. 5th ed., Wiley Interscience, 1998, New York.

Grimanelis, D., Neou-Syngouna, P., Vazarlis, H., Leaching of rich Greek manganese ore by aqueous solution of sulphur dioxide. Hydrometallurgy, 1992, **31**, 139-146.

Herring, A.P. and Ravitz, S.F., Rate dissolution of manganese dioxide in sulfurous acid. Transaction of SME/AIME, 1965, **231**, 191-195.

Khalafalla, S.E. and Pahlman, J.E., Selective extraction of metals from Pacific Sea nodules with dissolved sulfur dioxide. J. Met., 1981, **33**, 37-42.

Kanungo, S.B. and Das, R.P., Extraction of metals from manganese nodule of Indian ocean by leaching in aqueous solution of sulphur dioxide. Hydrometallurgy, 1998, **20**, 135-146.

Miller, J.D. and Wan, R.Y., Reaction kinectics for leaching of MnO_2 by sulfur dioxide. Hydrometallurgy, 1983, 10, 219-242.

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.