Extraction of Manganese Through Baking-Leaching Technique from High Iron Containing Manganese Sludge

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ABSTRACT

The growing demand for manganese and environmental regulations had made it increasingly important to develop process for the recovery of manganese from manganese sludge before dumping. This article explores the possibility of extracting manganese from manganese sludge containing 10% manganese and 15.5% iron. Detailed physico-chemical characterization was carried out by using X-ray diffraction (XRD), Scanning electron microscopy (SEM), X-ray fluorescence (XRF), Atomic absorption spectrometer (AAS) and conventional analytical tools. The manganese present in the form of Mn^{+4} is stable in acid or alkaline oxidizing condition so the recovery of manganese must be carried out under reducing condition. Sulfation roasting in the presence of proper reductant followed by water leaching process was developed to recover manganese. Different processes parameters such as roasting temperature, roasting time, reductant mass, sulfuric acid concentration, leaching time and temperature were studied and optimized to give more than 98% dissolution of manganese with almost complete rejection of iron in the residue. The leached solution is purified further and precipitated as manganese carbonate (>95%) in the presence of ammonium carbonate. The precipitate was dried and calcined at 350°C to produce chemical manganese dioxide (CMD). The products were characterized by XRD and SEM.

Keywords: *Chemical manganese dioxide; dissolution; manganese sludge; precipitation; sulfation roasting*

1. Introduction

Manganese is an important strategic metal, which is widely used in alloy steel production, batteries production, fertilizer, colorants and medicines. Due to growing demands for manganese, it is important to develop the process for recovery of manganese from low grade ore as well as manganese containing wastes [1-4] in the form of their salts/oxides. Manganese carbonate is widely used as a fertilizer whereas chemical manganese dioxide (CMD) and electrolytic manganese oxide (EMD) is used as cathode material for both primary and secondary batteries [5]. The Manganese extraction from manganese ores is mainly carried out by reducing the ore in the first stage to manganese (II) oxide followed by leaching with sulfuric acid [6-7] or direct sulfuric acid leaching of the ore in the presence of proper reductant. In direct leaching process different types of inorganic and organic reductant were studied [8-14]. During leaching of manganese ore, other impurities associated with the ore such as iron also report to leach liquor. To avoid iron in the leach liquor, industries mainly restrict the leaching pH to 2.5-3.5. This process leads to generation of sludge which contains considerable amount of manganese and high amount of iron. Several recent studies were carried out for the recovery of manganese from different types of manganese containing wastes [15-17]. In the present study we explored the process of sulfation roasting in presence of saw dust as reductant followed by water leaching. Effect of different process parameters such as the amount of sulfuric acid and saw dust, roasting temperature, dissolution temperature and time. This paper mainly aims to achieve quantitative recovery of manganese with minimum dissolution of iron. The sulfate solution obtained was purified by precipitation followed by production of high value products in the form of manganese carbonate and chemical manganese dioxide.

2. Material and methods

The manganese sludge sample used in this study was obtained from Rang Sarjan chemicals, Gujarat (India). The sludge was mixed properly and a representative sample was collected by conning and quartering method for physical and chemical characterization studies. The obtained sample was first dried at 105°C for 12 h and the dried sample (1 gm) was digested in aqua-regia followed by perchloric fuming. After complete digestion, the dissolved sample was extracted by 5% HCl and filtered. A clear pale yellow solution was obtained and the volume makeup was performed by double distilled water. This solution was used for analysis of manganese content and other impurities by using Atomic absorption spectrometer (AAS) of Thermo S-series and ICP-OES of Agilent make. The residue was analyzed for silica by using gravimetric method. The phases present in the Mn-sludge and the valuable product obtained after treatment was studied by X-ray diffraction technique (Bruker diffractometer model D8 discover) using Ni filtered Cu Kα radiation. The powder morphology was investigated by scanning electron microscopy by using Hitachi S-3400N.

Analytical reagent grade sulfuric acid 98.07% (AnalaR) was used for direct acid leaching as well as for sulfation roasting followed by water leaching. The Mn-sludge sample was moisten with little amount of distilled water as mixed with concentrated sulfuric acid and saw dust to ensure homogeneous mixture. After mixing, samples were roasted in muffle furnace at different temperature between 200 - 400°C. The roasted sample was water leached to dissolve manganese. All the leaching experiments were carried out with 10% pulp density by using a three necked closed type glass reactor placed on ceramic top hot plate, having arrangements for continuous monitoring of temperature and pH. After leaching, the leach liquor was analyzed for their composition. The saw dust used during sulfation roasting is obtained from timber plant. It was processed by pulverizer for size reduction below 150µm. All the experiments were performed in duplicate and the results reported are their average values.

3. Results and Discussion

3.1. Chemical and physical characterization of Mn sludge.

The complete chemical composition of manganese sludge sample in weight percent of their oxide are reported in Table 1. The sample contains SiO_2-41.4%, Fe_2O_3-22.1%, MnO- 13.8% and Al_2O_3-6.6% as major components.

Table 1. Chemical constituents of Mn-sludge in weight (%) of oxide.

Components:	SiO_2	Fe_2O_3	Al_2O_3	MnO	K_2O	CaO	SO_3	BaO	LOI
Weight (%):	41.4	22.1	6.6	13.8	1.8	1.2	8.6	1.6	2.2

The saw dust is mainly composed of cellulose, hemicelluloses and lignin. The XRD patterns of Mn-sludge exhibit different phases like SiO_2, MnO, MnO_2 and Fe_3O_4 with predominance of the quartz phase. The fully indexed XRD analysis of the sample is shown in Fig. 1.

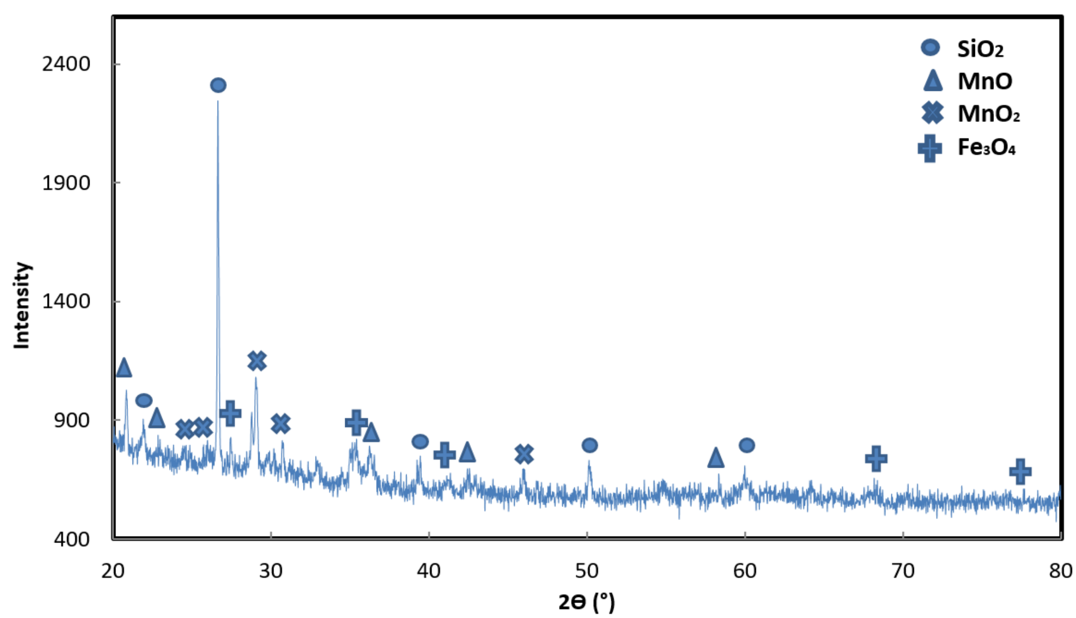


Fig. 1. XRD pattern of Mn-sludge.

The manganese sludge sample was scanned in secondary electrons (SE) to study the morphology as shown in Fig. 2.

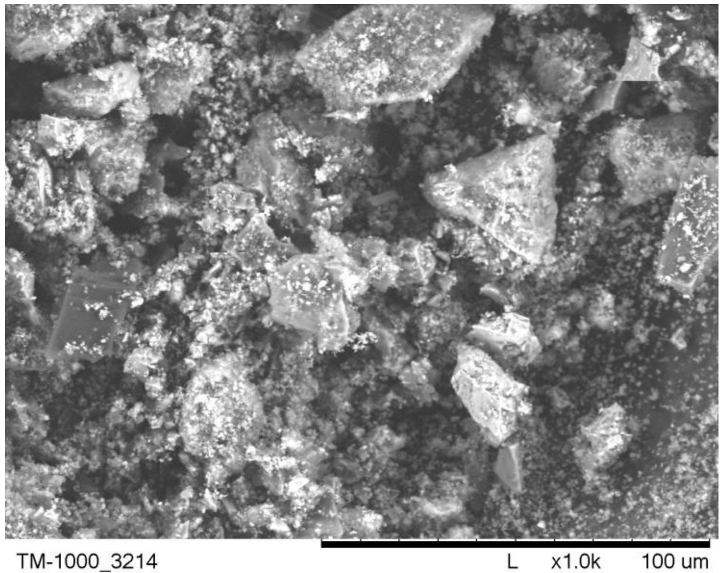


Fig. 2. SEM analysis of Mn-sludge.

3.2. Direct Dissolution Studies

To bring manganese in leach solution for further treatment for its recovery in the form of carbonate salt, direct H_2SO_4 leaching studies was carried out. Effect of concentration H_2SO_4 within the range of 1-10% (v/v) and leaching temperature was varied between 30°C to 85°C

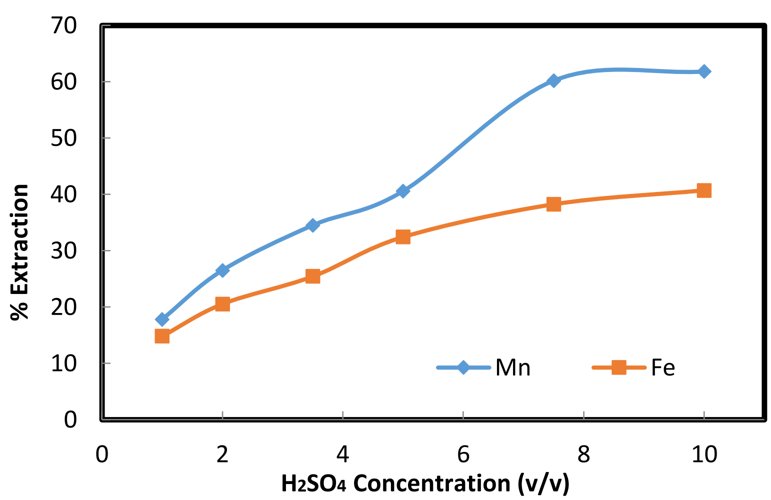


Fig. 3. Dissolution of manganese & iron against H_2SO_4 concentration.

was studied, keeping pulp density and leaching duration constant at 10% and 2 h respectively. Fig. 3 shows the effect of H_2SO_4 concentration on the dissolution of manganese and simultaneous dissolved iron. Increasing the sulfuric acid concentration from 1-10% (v/v) increased the recovery of manganese from 17.81% to 61.83% and iron from 14.85% to 40.73% at 30ºC. The dissolution of manganese is function of H_2SO_4 upto 7.5% only after that there is no significant dissolution was observed. The dissolution of iron still continues to increase. In order to investigate the effect of leaching temperature, experiments where performed for 2% H_2SO_4 in temperature range 30-85ºC keeping other parameters constant as shown in Fig. 4. With increase in dissolution temperature the extent of dissolution of both the manganese and iron increased. The Mn leaching efficiency was found to increase from 26.52% to 47.32 % and iron dissolution from 20.56% to 26.75%.

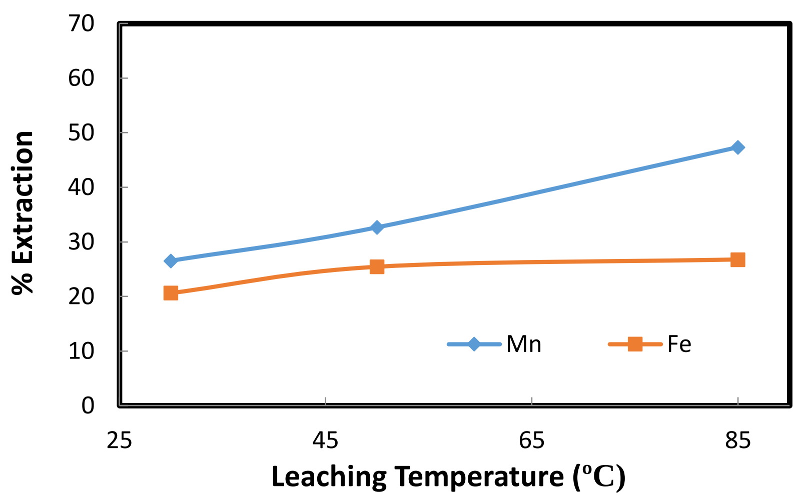


Fig. 4. Dissolution of Manganese & iron against leaching temperature.

With increase in temperature leaching kinetics increases. So, further leaching experiments were carried out at fixed leaching temperature of 85ºC. However, the maximum manganese dissolution achieved under the above condition was not satisfactory from the process point of view. Therefore, to increase the recovery of manganese with minimum dissolution of iron by using very low acid concentration, a combined sulfation roasting– water leaching process in presence proper reductant (saw dust) was studied.

3.3. Sulfation roasting in presence of saw dust

The sulfation roasting was carried out by mixing Mn-sludge with saw dust and concentrated sulfuric acid followed by roasting at different temperature for 2 h. The concentration of saw dust varied from 0-3gm, sulfuric acid was varied from 1-3 mL for 10 gm of the sample and roasting temperature between 200 to 400 °C. During sulfation roasting most of the oxides are converted to sulfates which are water soluble.

3.3.1 Effect of Saw dust dosage

The dosage of saw dust is required for conversion of unreduced Mn^{4+} to Mn^{2+} for complete leaching of manganese after reduction. It is an important factor for this roasting process. The effect of saw dust is presented in Fig. 5. Other conditions include 300ºC of roasting temperature, 1mL of H_2SO_4, 2h of roasting and leaching time at 85ºC of leaching temperature.

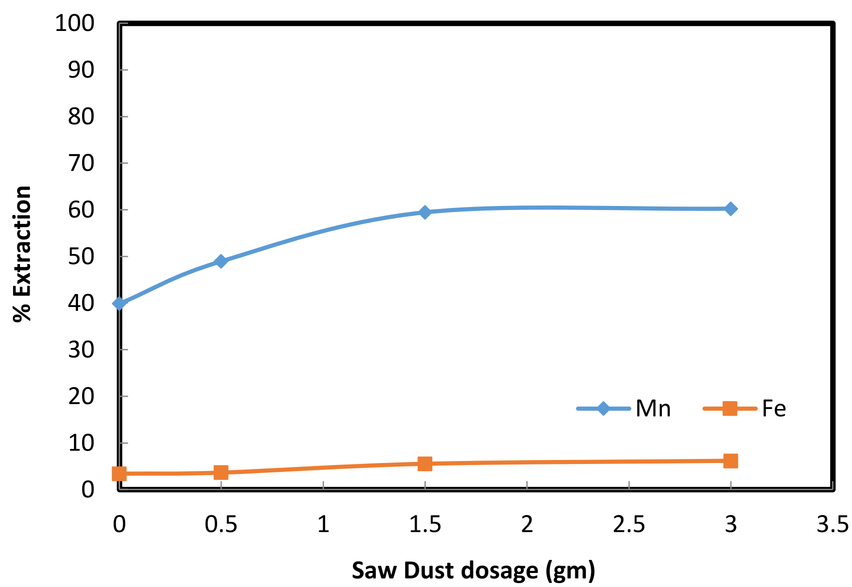


Fig. 5. Effect of saw dust dosage on leaching of metals.

It is shown in the Fig. 5 that the leaching of manganese and iron increased with saw dust dosage and reached a plateau after 1.5gm. This dosage is consequently chosen for all subsequent experiments.

3.3.2 Effect of roasting temperature

The effect of roasting temperature in the range of 200-400ºC on the behavior of manganese and iron leaching were investigated with saw dust dosage of 1.5gm, 2 mL of H_2SO_4 concentration, roasting and leaching time of 2 h at 85ºC of leaching temperature as shown in Fig. 6. With increase in roasting temperature from 200-400ºC, the leaching of manganese increased from 80.11% to 88.64% and iron shows slight decrease from 27.98% to 23.76%. Roasting temperature of 300ºC is from 27.98% to 23.76%. Roasting temperature of 300ºC is chosen as optimized temperature for further experiments.

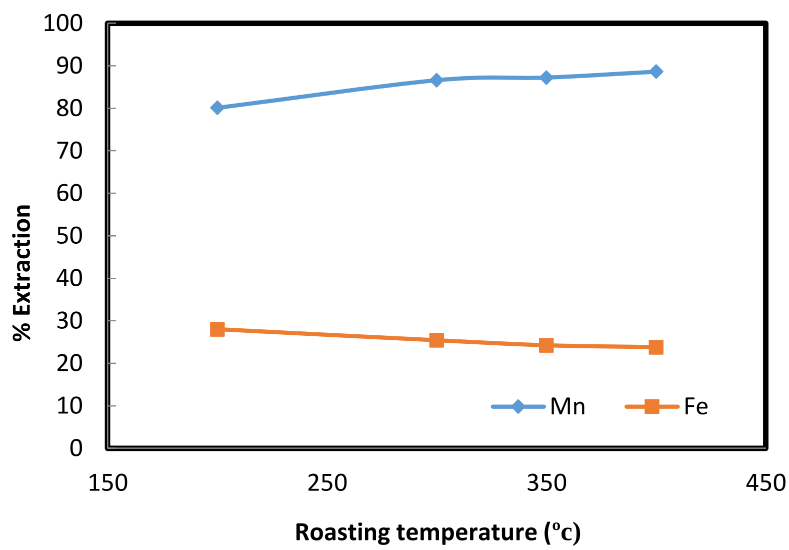


Fig. 6. Effect ofroasting temperature on leaching of metals.

3.3.3 Effect of sulfuric acid amount on leaching

A series of experiments were carried out by varying the H_2SO_4 concentration for the sludge roasted at 300ºC. The other parameters such as roasting and leaching time is constant for 2h, with 1.5gm of saw dust at 85ºC of leaching temperature as shown in Fig. 7. As it can be seen, increasing the H_2SO_4 concentration from 1mL to 2.5mL increased the recovery of manganese from 59.44% to 98.75%. Further increase in the H_2SO_4 concentration (3mL) shows only marginal increase in manganese recovery with large dissolution of iron (49.26%).

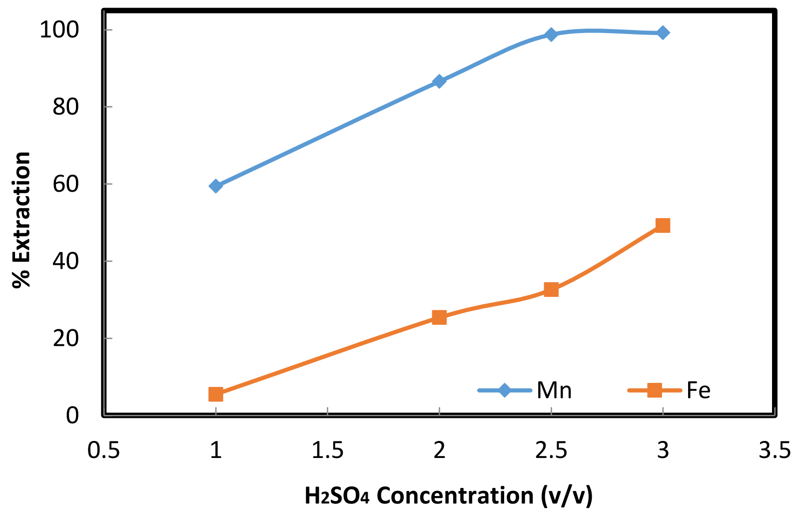
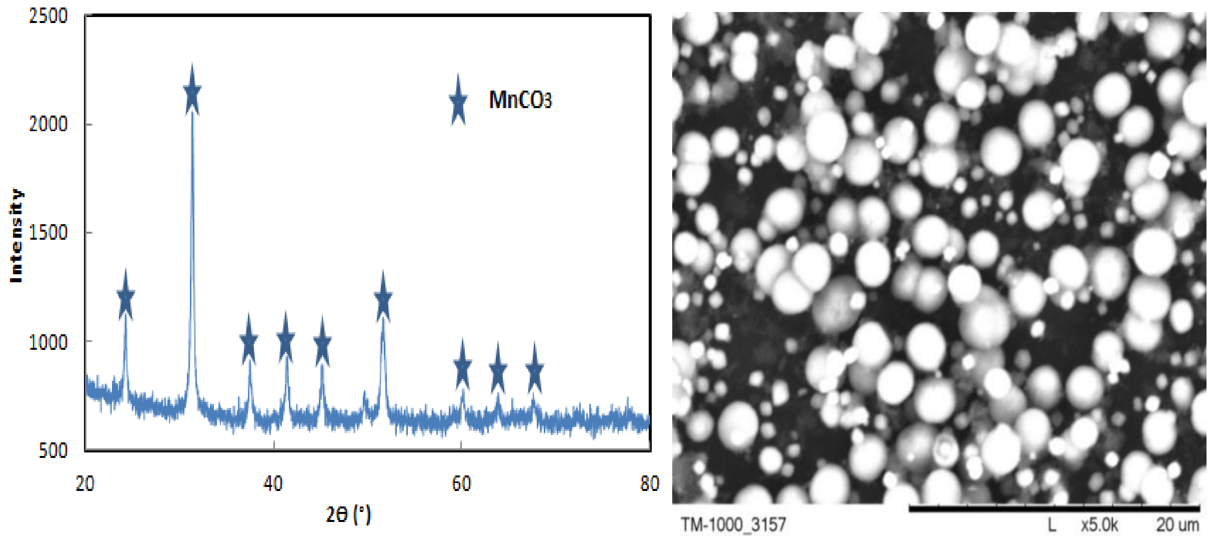


Fig. 7. Effect of sulfuric acid concentration on leaching of metals.

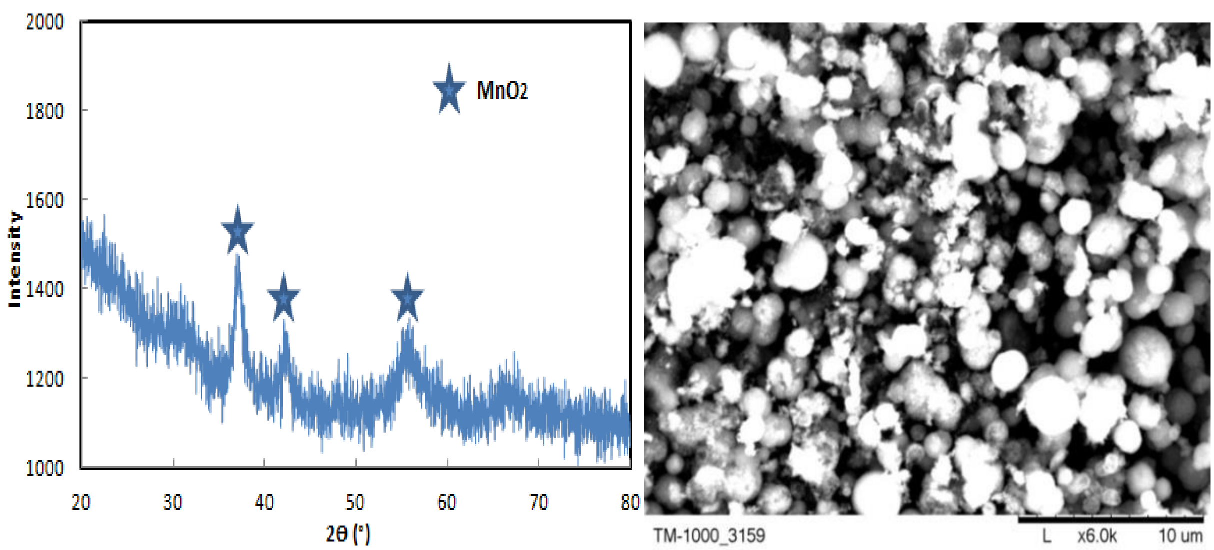
3.4. Manganese carbonates and CMD recovery from roasted Mn-sludge

The roasted mass was further water leached at a fixed pulp density of 10% with stirring speed of about 300rpm at 85°C. Effect of various parameters such as sulfuric acid concentration, roasting temperature and dissolution temperature etc were optimized to maximize manganese recovery. The manganese concentration in the leach solution in a single stage leaching is about 10.5 g/L, which was increased to about 42 g/L by fourtimes recycling of the leach liquor. The leach liquor was further treated for removal of impurity (iron and aluminum) through precipitation by adding lime to raise the pH to about 5.5. After precipitation the slurry was filtered and the manganese sulfate solution was further precipitated as manganese carbonate at pH of 8-9.5 by adding ammonium carbonate solution at 70ºC. The precipitate was filtered and washed with distilled water and dried. The dried manganese carbonate was further calcined at 350ºC to produce chemical manganese dioxide. Thus the obtained products manganese carbonate and chemical manganese dioxide were analyzed by XRD and SEM as shown in Fig. 8 (a, b) and Fig. 9 (a, b).



(a) (b)

Fig. 8. XRD (a) and SEM (b) pattern of $MnCO_3$.



(a) (b)

Fig. 9. XRD (a) and SEM (b) pattern of MnO_2.

4. Conclusion

Following conclusions can be drawn from the detail investigation carried out for the recovery of manganese from Mn-sludge obtained during processing of lean grade manganese ore.

(1) The XRD analysis shows that SiO_2, MnO, MnO_2 and Fe_3O_4 are the major phases present in the Mn-sludge.

(2) Recovery of manganese and iron increased with increase in H_2SO_4 concentration with incomplete dissolution of manganese.

(3) A sulfation roasting in the presence of saw dust as reductant followed by water leaching process was developed to dissolve manganese.

(4) It was possible to recover 98.75% of manganese value by sulfation roasting at 300°C using 2.5mL sulfuric acid, 1.5gm saw dust and leaching at 85°C for 2 h of roasting and leaching time.

(5) Manganese sulfate was further treated to produce high value product as manganese carbonate and chemical manganese dioxide.

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References

[1] Zhang, W.S., Cheng, C.Y., 2007a. Manganese metallurgy review. Part 1: leaching of ores/secondary materials and recovery of electrolytic/chemical manganese dioxide, Hydrometallurgy 89, 137-159.

[2] Zhang, W.S., Cheng, C.Y., 2007b. Manganese metallurgy review. Part II: Manganese separation and recovery from solution, Hydrometallurgy 89, 160-177.

[3] Zhang, W., Cheng, C.Y., Pranolo, Y., 2010. Investigation of methods for removal and recovery of manganese in hydrometallurgical processes, Hydrometallurgy 101, 58-63.

[4] Dwivedi, D., Randhawa, N.S., Saroj, S., Jana, R.K. An Overview of Manganese Recovery by Hydro and Pyro-Metallurgical Routes, J.Inst. Eng. 2017, 98, 147–154.

[5] Biswal, A., Barsha, D., Tripathy, B.C., Subbaiah, T., Shin, S.M., Sanjay, K., Mishra, B.K., 2013. Influence of alternative alkali reagents on Fe removal during recovery of Mn as Electrolytic Manganese Dioxide (EMD) from Mn sludge, Hydrometallurgy 140, 151-62.

[6] Atlam, A., 1997. Hydrometallurgical treatment of Egyptian lowgrade manganese ore, Metall. (Heidelberg) 51, 486.

[7] Darmane, Y., Cherkaoui, M., Kitane, S., Alaoui, A., Sebban, A., Touhami, M.E., 2008. Preparation of chemical manganese dioxide from Moroccan pyrolusite mine waste, Hydrometallurgy 92, 73–78.

[8] Sahoo, R.N., Naik, P.K., Das, S.C., 2001. Leaching of manganese from low-grade manganese ore using oxalic acid as reductant in sulphuric acid solution, Hydrometallurgy 62, 157-163.

[9] Ismail, A.A., Ali, E.A., Ibrahim, I.A., Ahmed, M.S., 2004. A comparative study on acid leaching of low grade manganese ore using some industrial wastes as reductants, Canadian Journal of Chemical Engineering 82, 1296–1300.

[10] Rodriguez, M., Rivarola, J., Ruiz, M.D., 2004. The effects of carboxylic acid addition on hydrofluoric acid autoclave leaching of a ferrocolumbite, Hydrometallurgy 74, 39-46.

[11] Furlani, G., Pagnanelli, F., Toro, L., 2006. Reductive acid leaching of manganese dioxide with glucose: identification of oxidation derivatives of glucose, Hydrometallurgy 81, 234 240.

[12] Hariprasad, D., Dash, B., Ghosh, M.K., Anand, S., 2007. Leaching of manganese ores using sawdust as a reductant, Min. Eng. 20, 1293-1295.

[13] Su, H., Wen, Y., Wang, F., Sun, Y., Tong, Z., 2008. Reductive leaching of manganese from low-grade manganese ore in H2SO4 using cane molasses as reductant, Hydrometallurgy 93, 136–139.

[14] Tian, X., Wen, X., Yang, C., Liang, Y., Pi, Z., Wang, Y., 2010. Reductive leaching of manganese from low grade manganese dioxide ores using corncob as reductant in sulphuric acid solution, Hydrometallurgy 100, 157– 160.

[15] Mocellin, J., Mercier, G., Morel, J.L., Blais, J.F., Simonnot, M.O., 2015. Factors influencing the Zn and Mn extraction from pyrometallurgical sludge in the steel manufacturing industry, Journal of Environmental Management 158, 48-54.

[16] Mocellin, J., Mercier, G., Morel, J.L., Charbonnier p., Blais, J.F., Simonnot, M.O., 2017. Recovery of zinc and manganese from pyrometallurgy sludge by hydrometallurgical processing, Journal of cleaner production, doi: 10.1016/j.jclepro.2017.09.003.

[17] Mishra, D., Sahu, K.K., Agrawal, A., 2018. Process integration for material synthesis from deactivated catalyst: Studies on the intraction of metal ion between two immiscible phases, Journal of Hazardous Materials 344, 169-178.