Extraction of Manganese Sulphate from Local Pyrolusite Ore by Cellulose Reduction Method

Khin Su Su[1] and Kyaw Naing[2]

Abstract

In the present research, manganese ore samples were collected from Popa Mount in Mandalay Region and Pawe Island in Tanintharyi Region. Pyrolusite is a mineral consisting essentially of manganese dioxide and is important as manganese ore. According to EDXRF data, the presence of Mn, Ca and Sr in Popa manganese ore sample and Mn, Fe, Ba, K, Ca, Cu, Zn, Sr, Ni and Zr in Pawe manganese ore sample were found. Manganese dioxide 67.02 and 59.84 % of Manganese dioxide were found in Popa and Pawe manganese ore samples. Among the two samples, according to XRD data, Popa manganese ore sample showed the highest content of pyrolusite (β-MnO_2). Most of the peaks of Popa manganese ore are well matched with library data of JCPDS-81-2261 of pyrolusite (MnO_2). $MnSO_4$ was prepared from Popa manganese ore sample by waste cellulosic reductant method. Prepared $MnSO_4.H_2O$ was characterized by XRD and FTIR techniques. In XRD data for $MnSO_4.H_2O$ product well matched with standard JCPDS 35-0751 of $MnSO_4.H_2O$. According to FT IR data, the peaks related to hydroxyl (moisture), S-O and Mn-O groups were found.

Keywords: Pyrolusite, EDXRF, β-MnO_2, JCPDS, FT IR, XRD

Introduction

Manganese ores

The only forms of manganese occurring in nature with sufficient quantities to be of commercial value are the oxides, the carbonate, and silicate (Deer *et al.*, 1992). Pyrolusite is manganese dioxide, MnO_2, Manganese 63.2 percent, oxygen 36.8 percent (Read, 1976). Sometimes occurs associated with psilomelane in alternating layers. Pyrolusite is secondary mineral (Evangelou, 1998). In Myanmar, manganese ores occurred in Popa, Mogok, Kyaukpadaung, and Tagaung Township (Mandalay Region), Ho-pong and Lawksawk (Shan State) and Pawe Island Bokpyin Township, Tanintharyi Region. Pyrolusite, MnO_2, is also used for a number of purposes such as the decolourization of glass, as a dryer in the manufacture of paint and varnish, and in dry batteries, and very largely for the manufacture of chlorine, bromine and oxygen and permanganates and other manganese compounds. Psilomelane is manganese dioxide with small amounts of other oxides (MnO, BaO, K_2O, H_2O). Manganese content is variable but less than 63.2 percent. Of the oxides, pyrolusite and psilomelane may be nearly identical in chemical composition. Pyrolusite usually contains some impurities and impurities may include one or more of the oxides which in slightly greater amount are characteristic of psilomelane (Pagnanelli et al., 2007).

Extraction of manganese from ore using reducing agent

The hydrometallurgical processing of lower grade material avoids high temperature reduction roasting that is conventionally used in processing high grade material to render the manganese to be acid leachable using sulphuric acid (H_2SO_4). High temperature roasting is energy intensive and would not be economical for lower grade material (Norman et al., 2010).

[1]Associate Professor, Dr., Department of Chemistry, Hinthada University
[2]Pro-Rector, Dr., University of Distance Education, Yangon

The extraction of manganese from such source has to be carried out under reducing conditions (Hariprasad et al.,2009). Several reducing agents have been used previously under different acidic media such as coal, pyrite, ferrous sulphate, aqueous sulphur dioxide and hydrogenperoxide. Some of the reducing agents used, such as sulphur dioxide may be harmful to the environment. Many past investigators had focused on reductive leaching of manganiferous ore, using organic reductants mainly carbohydrates like glucose, sucrose, lactose, oxalic acid etc. Carbohydrates are non–hazardous and low cost reducing agents that may be used either in pure form or as industrial wastes, the carbohydrates are effective reductants under mild temperature conditions (Wenshang, 2007). Ligno-cellulose based waste material such as saw dust and bagasses are potential reductants for acid leaching of manganese ores. Waste paper which is another lingo-cellulose based material that the reducing agent. The composition of waste papers contains lignin, cellulose and hemicelluloses. Solution purification is performed in two stages. In the first stage, the solution pH is adjusted to above 6 to precipitate aluminum (Al), arsenic (As) and most of the iron (Fe) and silica (SiO_2). Air/oxygen sparging during the pH adjustment will improve the iron removal, by oxidizing the ferrous iron to its ferric form. In the second stage, sulphide precipitation will remove the zinc, providing a solution of sufficient purity to process into a saleable product.

Materials and Methods

The ore samples are collected in Popa (Mandalay Region), and Pawe Island near Bokpyin Township (Tanintharyi Region). The sampling was done by the well-mixed material into a flat cone and dividing it into quarters. Opposite quarters were rejected, and the remaining half portion again was treated as mention above and rolling the sample back and forth on a paper. Each of four corners of the paper was lifted in turn to get well-mixed. The sample was treated again by coning and quartering until desired amount of representative sample was obtained. The representative samples were ground by using a sieve shaker to get the size of 200 meshes.

The conventional oven dry method was used to determine the moisture content in pyrolusite ores. Trace elements present in sample were investigated at the Universities' Research Centre, University of Yangon, by using atomic absorption spectrometer. Samples were digested to dryness with aqua-regia and boiled with distilled water. The ppm levels read out from the computer were recorded. The structure of pyrolusites ore samples were characterized by X-ray diffraction (XRD) technique. Pyrolusite ores were also characterized by energy dispersive X-ray fluorescence spectrometer.

Extraction of manganese as manganese sulphate was done from ore by cellulose reductant (wasted newspaper) method. A 100 mL 5% sulphuric acid was added onto 3g of ore-reductant in 250mL round bottom flask. The mixture was refluxed at 90°C for 8 hours (Hariprasad *et al.*, 2009). Before refluxing, the mixture stood for one day to contact thoroughly. There fluxed liquor was obtained by filtering the mixture. Determination of manganese content from refluxed solutions was done by complexometric titration using Eriochrome black T as indicator. Removal of Iron from the refluxed solution with 20% lime slurry solution. A small amount of 20% lime slurry was slowly added each time to the 100 mL leached solution until pH 4.7. The required pH was adjusted by adding dilute sulphuric acid or dilute sodium hydroxide solution. After removing, iron impurities of the solution was filtered to obtain iron free refluxed solution and gypsum as residue. Iron content in refluxed solution was measured with AAS. Manganese sulphate monohydrate was crystallized from the purified refluxed solution by evaporating on the sand bath at 60^oC (Norman, 2010). The crystals were crushed into powder with a motor and pestle. Characterization of prepared

powder manganese sulphate from pyrolusite ore by X-ray diffraction (XRD) measurement and FTIR technique.

Results and Discussion

The aim of this work is to investigate the manganese dioxide content in the ore samples and to determine the suitable ore for further research. The moisture percent of manganese ore samples were determined by oven dry method. The moisture percent for Popa and Pawe ore samples were found to be 0.523 and 0.609 %, respectively. Moisture should be 20 % or lower in the ore at the completion of drying. An average moisture content of 8 % with permitted deviation of 2 % is satisfactory. In this research, percent of manganese dioxide 67.02 % and 59.84 % were found on Popa and Pawe ore samples respectively. The trace amount of calcium, iron and copper percent in Popa and Pawe ore samples were investigated by AAS.

Table 1 Moisture Manganese Dioxide and Total Manganese Contents in Manganese Ore Samples

Name of sample	Moisture* (%)	Manganese dioxide** (%)	Total manganese (%)
A	0.523	67.02	42.35
B	0.609	59.84	37.82

A= Popa manganese ore sample *Oven dry Method
B= Pawe manganese ore sample **Redox titration

Table 2 Calcium, Iron and Copper Contents in Manganese Ore Samples

Name of sample	Calcium (ppm)	Iron (ppm)	Copper (ppm)
A	41.15	0.1325	0.6965
B	2.659	16.59	9.655

A= Popa manganese ore sample
B= Pawe manganese ore sample

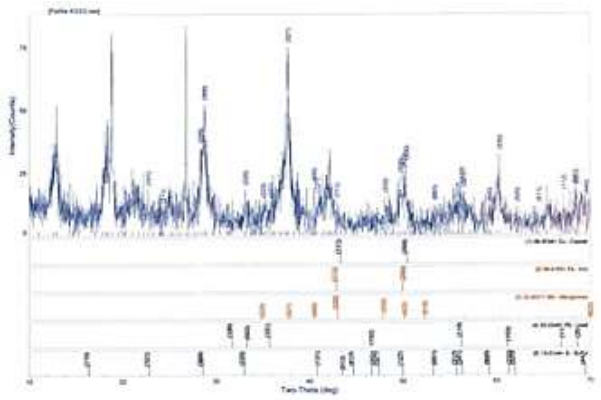

Fig. 1 XRD diffractogram of the Popa manganese ore sample

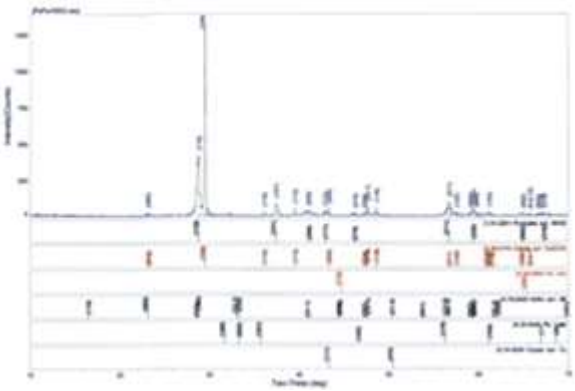

Fig. 2 XRD diffractogram of the Pawe manganese ore sample

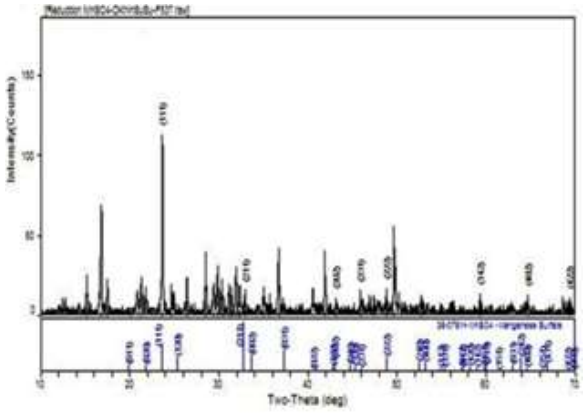

Fig. 3 XRD diffractogram of prepared $MnSO_4.H_2O$

Fig. 4 FTIR spectrum of prepared $MnSO_4.H_2O$

Fig. 5 Photographs of prepared $MnSO_4.H_2O$ from Popa manganese ore

Table 3 Semi-quantitative analysis of manganese ore samples by EDXRF technique

No	Elements		
		A	B
1	Si	-	-
2	S	-	-
3	Fe	-	10.190
4	Ca	18.507	0.435
5	Ti	-	-
6	Mn	81.334	84.346
7	Cr	-	-
8	Cu	-	0.234
9	Ba	-	2.371
10	K	-	1.729
11	Zn	-	0.212
12	Sr	0.159	0.211
13	Ni	-	0.186

A = Popa manganese ore sample
B = Pawe manganese ore sample

Table 4 Manganese Contents of the Popa Ore Sample Before and After Extraction

Sr. No.	Element	Before extract (%)	After extract (%)
1	Manganese	42.35	90.77

Table 5 Iron Contents in the Solution Before and After Removal of Iron

Sr. No.	Element	Before removal (ppm)	After removal (ppm)
1	Iron*	33.26	ND

ND= non detective

Table 6 Comparison of FT IR Data of Prepared $MnSO_4$

No.	$MnSO_4$*	$MnSO_4$**	Literature value	Functional groups****	Interpretation
1	3374	3277	3600-3200	υ_{O-H} OH group	Absorbed water bounded at $MnS0_4$
2	1146 1018	1142 1090 1018	1100-1140	υ_{S-O} S-O group	Stretching vibration of S-O group
3	654	625	650-610	υ_{Mn-O} Mn-O group	Stretching vibration of Mn-O group

* BDH ** Cellulose reduction method *** Guo *et al.,* (2010)

This research, XRD measurements were carried out on two manganese ore samples. XRD diffractograms of Popa and Pawe ore samples were shown in Figures 1 and 2 respectively. Among the two samples, according to XRD data, Popa manganese ore sample showed the highest content of pyrolusite (β-MnO_2). Most of the peaks are well matched with libiary data of JCPDS-81-2261 of pyrolusite (MnO_2). The presence of Mn, Ca, and Sr were found in Popa manganese ore sample by ED-XRF measurement. According to Table 3, Popa ore sample was the highest manganese content and the lowest impurities contents.

Popa manganese ore sample was continuously used for further research work due to the XRD data. Preparations of manganese sulphate were carried by cellulose reduction method. The major structural components of paper are lignin, hemicelluloses and cellulose which make it a good source of sugar (Hariprasad, 2009). Cellulose, a linear polysaccharide of $\beta -1$, 4 linkages is susceptible to acid catalyzed hydrolysis releasing soluble sugars such as glucose. Concentrated H_2SO_4 ruptures the hydrogen bonding of cellulose making it amorphous in nature. Decrystallization of cellulose results in gelatin with acid. This gelatinous mass hydrolyses under dilution. Considering total manganese in the ore present as MnO_2 overall reaction can be represented by:

$12nMnO_2 + (C_6H_{10}O_5)_n + 12nH_2SO_4 \rightarrow 12nMnSO_4 + 6nCO_2 + 17nH_2O$-------- (1)

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

In this research, ore was roasted with ammonium sulphate to evolve ammonia, it was heated in furnace at 200 °C 1 hour which was digested with sulphuric acid to dryness. Silica was left and diluted and boiled the residue. The possible equations are as follows:

$MnO_2 + (NH_4)_2SO_4 + H_2SO_4 \rightarrow 2NH_3 + 2MnSO_4 + 4H_2O$---------- (2)

$Fe^{3+} + (NH_4)_2SO_4 + H_2SO_4 \rightarrow Fe(SO_4)_3 + NH_3 + H_2O$ ---------- (3)

Iron was removed by using 20% lime slurry at pH 4.7. Loss of manganese was not found in this pH range (Hariprasad *et al.,* 2009). In the present research, manganese content was determined in leached solution by complexometric titration. Iron was major impurity in the leached solution with metal ion impurities in ppm level. To meet the specifications of manganese sulphate monohydrate, iron had to be removed. Iron content in solution before and after iron removal was found to be 33.26 ppm and non-detected as determined by AAS technique (cf .Table 5).

The leached liquor was evaporated on sand bath at 60 °C until crystallization was completed. The crystal obtained was dried at 105 -110 °C to a constant mass (Norman, 2010). Photographs of manganese sulphate monohydrate was shown in Figure 3.8. The common pinkish color of the compound is clearly observed. The prepared $MnSO_4$ were characterized by XRD and FT IR techniques. In XRD data of the prepared $MnSO_4$ from ore are well matched with standard JCPDS 35-0751 of $MnSO_4$. The characteristic FT IR peaks of the prepared $MnSO_4.H_2O$ from ore (cf. Figures. 4)at 3394 cm^{-1} to 3277 cm^{-1} confirmed the presence of water molecules, the peaks at 1122 cm^{-1} to 1145 cm^{-1} confirmed the presence of stretching vibration of S-O group and the peaks at 600 cm^{-1} to 654 cm^{-1} confirmed the presence of stretching vibration of Mn-O group (cf. Table 6) (Guo et al., 2010 and Stoilova, 2002).

Conclusion

In this research, the manganese ore samples were collected from Popa Mount (Mandalay Division) and Pawe Island in Bokpyin Township (Tanintharyi Division). Firstly, these samples were analyzed by volumetric titration method and modern instrumental analytical techniques. From the vloumetric titration, XRD and EDXRF data, Popa manganese ore sample also exhibited the highest manganese content and lowest impurities contents. So, Popa manganese ore sample was selected for further study. Manganese sulphate was prepared from Popa manganese ore sample by leaching with cellulose reductant method. The product was characterized by XRD and FT IR techniques and manganese content was determined in leached solution by complexometric titration. Manganese content was found to be 90.77%. The prepared $MnSO_4.H_2O$ was characterized by XRD and FT IR techniques. Thus, the manganes sulphate extraction by cellulose reduction method is of low cost, simple and convenient. Pure product was obtained.

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