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Process Development for the manufacturing of selected manganese compounds from Egyptian manganese ores in Sinai.

A.F. Shaaban*, I.A. Khattab, E.H. Khater, and Sh.A. El-Rafie.

Chemical Engineering & Pilot Plant Department National Research Centre, Cairo, Egypt,

ABSTRACT

The research project aimed to develop reliable process technologies capable for the production of selected manganese products by utilizing Sinai Mn-ores deposits. Assessment of optimum process machinery and grinding of Mn-ores used to prepare ore concentrate applying both magnetic (10000→17000 Gauss) - and electrostatic (up to 25kV) separation technologies, resulting in increasing MnO_2 concentration from 62.03%→ 82.24 ; while reducing the iron content from 15.85%→ 3.80% that improve dramatically the economics of the project. The ore-concentrate was used to prepare hydrated manganese sulfate together with cumulative screen analysis have been carried out. The grinded product was (fertilizer and commercial grades) by either: (i)reacting with concentrated sulfuric acid(98%) at elevated temperatures (550→650°C) for 2h. The % conversion to manganous- and ferric sulfate exceeds 90%, with almost 100% utilization of sulfur, and minor contamination of iron; or(ii) by reacting with sulfuric acid and using oxalic acid as reducing agent at 75→85°C reaching > 80% reaction conversion. Synthesis of 32% Mn-2-ethyl-hexanoate has been carried out using formerly prepared $MnSO_4$ and applying double decomposition process at 85→ 90°C. The product has proved its practical reliability as an environmentally safe Co-substituent paint drier, preventing yellowing effect of alkid-paints even upon storage, and reducing drying time. Manganese dioxide , used in energy storage dry batteries, was also successfully carried out by electrolyzing a solution of the originally prepared $MnSO_4$ solution. All necessary instrumentation and chemical analysis needed for Mn-ores and final products characterization have been executed including elemental chemical analysis, X-ray diffraction, X-ray fluorescence, energy dispersive X-ray analysis, scanning electron microscope, high performance liquid chromatography, and Fourier transform infrared spectroscopy.

Keywords: manganese ore, manganese sulfate, electrolytic manganese dioxide, manganese drier, process development.

**Corresponding author*

INTRODUCTION

The aim of this research work is to develop reliable processes for the production of some selected manganese compounds through utilizing Egyptian manganese ores in Sinai. The economic deposits of Mn-ores are Um-Bogma in central Western Sinai and Elba in South Eastern desert. The reserves of these ores in UM-Bogma exceeds 1.7 million tons. Most of the ore is exported, while only a small portion is used in the ferro- and silicon-manganese alloys production to cover demands of steel industries [1].

Manganese is one of the most important elements used in industry. It is ranked fourth after iron, aluminum and copper[2]. In reality, this metal has no acceptable substitute in its important applications in metallurgical processes.

Commercial grades of manganese ore exist in many places such as Sinai, Australia, Brazil, China, Gabon, India, South Africa and Ukraine.These ores are usually classified according to its Mn content; ranked as high grade (Mnwt%> 44), medium grade (44 >Mnwt%> 40), low grade (40 >Mnwt%> 35), and steel mill grade (35 >Mnwt%>28) [3]. The lower grade ores of manganese are subjected to various processes for concentrating pure manganese salts. Manganese ores are also classified, according to the end use of manganese, into metallurgical grade (38-55 wt % Mn), chemical and battery grade, often categorized by their MnO_2(pyrolusite) content, typically contain 70-85 wt % MnO_2; i.e. (54- 66wt % Mn) [2].

Manganese ores, as mined, always contain other constituents other than manganese mineral. To get high quality products from an ore, it is not only required, but often obligatory, to remove, as far as practicable, these constituents. For instance, chemical-grade manganese concentrate should contain no more than 8% by weight of iron oxides [4]. For upgrading or beneficiation of an ore, various processes are known but the suitability of a method depends on the nature of impurities in the ore; these processes involve: (a) mechanical concentration including gravity, flotation, magnetic and electrostatic methods; (b) hydrometallurgical extraction in which chemical leaching is needed; (c) Pyro-metallurgical extraction employing some form of smelting technique. Of these processes, mechanical concentration methods expected to have lower operating costs compared to the other two.

Manufacturing of manganese sulfate (fertilizer grade) and Manganese dioxide (battery grade) were frequently the objectives of the project. Preliminary techno-economic feasibility studies together with profitability analysis were the basis of products assessment. The project strategy will fulfill the establishment of native Mn-chemical industries and diminish export potentials, and partially cover local market demands.

Manganese sulfate is used in dying, for glazes on porcelain, boiling oils for varnishes, in feeds, and in fertilizers. Crops with high manganese requirements include beans, oat, soybean, sorghum and wheat. Those with medium relative manganese needs are barley, beet, cabbage, potato and tomato.

Manganese sulfate can also produced from manganese dioxide (pirolusite), performing a direct chemical reaction between gaseous sulfur dioxide and solid MnO_2 [5]. Such process comprises basically two stages: The 1st consists of generating SO_2 by ustulating sulfated minerals, or by burning elementary sulfur. The 2nd stage comprises the absorption of the gassy SO_2 generated in MnO_2, percolating the gas in counter-current through MnO_2-pulp with concentration, pH and density controlled, in 3 absorption columns in series.

Another process relates to the use of ferromanganese for the production of $MnSO_4$-solution for the electrolytic or chemical precipitation of manganese dioxides [6]. In an alternative technology [7] , MnO_2 ore powder (80-100 mesh size) is mixed with water (30%w),then the slurry is fed counter-currently to an absorption column to sulfur-containing fumes at a temperature of 60°C. The sulfurous acid formed (H_2SO_3) will react with MnO_2 to form final product.

A new process is also described for $MnSO_4$ production by treatment the ore firstly with calculated amount of concentrated sulfuric acid at 200→220°C to form manganic and ferric sulfates. The product mixture is then heated at 500→640°C , where the percentage conversion to manganous sulfate reaches 80%, with almost 100% utilization of sulfur, and low contamination with iron [8].

A leaching process to extract Mn from a low-grade manganese ore was investigated using sulfuric acid and oxalic acid as a reducing agent [9]. The optimum conditions under which Mn and Fe recoveries were the highest and the time and temperature were the lowest were determined .The results showed that Mn and Fe recoveries were 93.44% and 15.72% under optimum conditions, respectively. The amount of sulfuric and oxalic acid were obtained to be 7% and 42.5 g/L in optimum conditions , and the best time and temperature were 60 min and 65°C respectively.

Among the environmental challenges concerning the substitution of suspected toxic components in common organic coatings , the search for acceptable alternatives to toxic chemical additives in alkyd paints , especially the anti-skinning agents and cobalt drier catalysts, has recently become a subject of intense industrial and academic interest [10,11]. Manganese 2-ethyl hexanoate is the most important primary drier after cobalt. It is a promising, environmentally safe drier, having excellent auto-oxidation and catalytic properties [12,13,14,15,16], promotion surface and through drying [17,18].

Manganese dioxide is also an important Mn-compound. It is used in manufacturing of manganese steel, oxidizer in alkaline batteries(dry cells), for making amethyst glass, paintaing of porcelain, printing and dying of textiles. Mn-sulfate , originally prepared from Mn-ores, was used for the synthesis of Manganese dioxide used in dry batteries. There is high demand for using MnO_2 as a cathode material for energy storage devices; e.g. the well-known Leclanchecell, alkaline, lithium and other modern batteries. Manganese dioxide occurs naturally in many manganese ores but mostly in a form which is not sufficiently electrochemically active to be used in such devices. Synthesis of electrolytic manganese dioxide (EMD) can be done via chemical [19] or electrochemical [20] routes. Although the two routes use the same main reactant, $MnSO_4$, the electrochemical one is known to be superior to chemical synthesis methods, as control over the properties of the deposited material is possible [20]. It must be emphasized that the synthesized EMD must be free from metals electropositive to zinc; i.e. antimony, arsenic, cobalt, copper and nickel; as their presence decreases the depolarization capacity of the oxide [21].

The aim of the present work was to develop a series of successive unit operations/processes to synthesize manganese compounds having commercial importance from Egyptian manganese ore through fulfilling : (i) full characterization of the ore, (ii) ore concentrate production by shaking table, magnetic separation, and electro-static separation techniques, (iii) synthesis of $MnSO_4$ via two routes, namely thermal method that based on ore reduction by ferric sulfate formed, and using oxalic acid as a reducing agent. The produced manganese sulfate was used in the synthesis of both: (i) Mn-2-ethyl-hexanoate which is an important drier for alkyd paints, and (ii) synthesis of electrolytic manganese dioxide.

MATERIALS AND METHODS

Beneficiation of manganese ore

Manganese ore, brought from Um-Bagma (Egypt) mines was analyzed by XRD and XRF techniques. The ore was crushed, milled and classified as fractions by screen analysis. The resulted fractions were then subjected to shaking table, magnetic and electrostatic separation techniques; each technique was either applied alone or in sequence with other techniques. Representative samples from the processed fractions were the analyzed by XRF for determining the weight percentages of Mn and Fe; as MnO_2 and Fe_2O_3.

Preparation of hydrated manganese sulfate ($MnSO_4.H_2O$)

Pure $MnSO_4$ is of high economic and commercial importance as its application in fertilizing agricultural products, its use in paints and ink industries, manufacturing of ceramics, acid-resisting bricks and paper. Two manufacturing technologies have been practiced for the preparation of hydrated manganese sulfate mainly are:

The Thermal Process

In which the ore-concentrate is first treated with calculated amount of concentrated sulfuric acid at a temperature of 200 → 220°C to form magnetic and ferric sulfates, and then heating the reaction products at 500 → 640°C in an electric furnace for 2h. The percentage conversion to manganous sulfate exceeds 90%, with almost 100% utilization of sulfur, and low contamination with iron.

Experimental procedure

The process involved : (1) treatment with sulfuric acid (98%) at 200→ 220 °C. (2) heating of the acid treated sample at higher temperature (500→ 640°C), and (3) extraction of the soluble iron and manganese salts.

A certain weight of the ore (10→15 g) was triturated with the required amount of 98% sulfuric acid and heated at 200→ 220 °C until sulfur trioxide fumes ceased. The solid mass obtained was ground and transferred to the reaction tube and heated at the desired temperature for the required time. At the end of the experiment, the charge was weight, and a portion was extracted with 0.01 N-sulfuric acid at 80°C. After filtration and washing, total iron and manganese were determined in the filtrate, and the filter cake was dried, weighed and analyzed.

Preparation of manganese sulfate using oxalic acid as a reducing agent

The study showed that oxalic and sulfuric acids can be suitable for leaching of low grade manganese ores. The reaction of MnO_2 in the low manganese ore with oxalic acid could occure as follows :

$$C_2H_2O_4 + MnO_2 + 2H^+ = 2CO_2 + Mn^{+2} + 2H_2O$$

Apparatus and experimental procedure

The leaching experiments were carried out in a 1000 mL three-neck flask (reactor). A magnetic heater stirrer was used to heat and agitate the reaction mixture. The reactor had two entrances used for feeding of reactants and temperature measurement. A reflux condenser was erected on the 3rd neck to capture any escaped vapors.

In the leaching experiments, the solution was prepared using distilled water, sulfuric acid (H_2SO_4), and oxalic acid ($C_2H_2O_4$). After the desired temperature of the reactor was reached (80°C), the predetermined amount of ore concentrate (65 g, 52% Mn) was added to 500 ml leaching solution. Size fraction of the sample was -200 → +125 µm. Samples were taken out at pre-determined intervals and were filtered. The filtrate solution was analyzed for Mn and Fe to calculate the fractions reacted, while the following equation was used :

$$\boldsymbol{R = \frac{c * L}{f * 500}}$$

Where:
R = is the recovery of Mn or Fe .
C and f = are the concentrations of the element (Mn or Fe) in the leaching solution and the original sample, respectively.
L = is the volume of the leaching solution after filtration.

Four factors were considered in conducting experimental studies , mainly are : time, temperature, amount of sulfuric and oxalic acid. The following ranges were experimentally designed : sulfuric acid dosage of 1%→9%; oxalic acid dosage of 27.5→57.5 g/L; temperature of 55→ 95°C; and time of 45→ 105 min.

The optimum conditions under which the Mn and Fe recoveries were the highest and the time and tempertaure were the lowest were determined. The results showed that Mn and Fe recoveries were 94% and 16% under the optimum conditions, respectively. Also, sulfuric acid concentration was the most effective parameter affecting the process. The amounts of sulfuric acid and oxalic acid were obtained to be 7% and 42.5 g/L at optimum condition and the best corresponding time and temperature were 60 min and 65°C respectively.

Preparation of manganese 2-ethyl hexanoate

The precipitation (double decomposition) process was practiced for the preparation of manganese 2-ethyl hexanoate using the formerly prepared $MnSO_4$.

Process chemistry:

$$C_8H_{16}O_2 + NaOH \rightarrow C_8H_{15}O_2Na + H_2O$$
$$2C_8H_{15}O_2Na + MnSO4 \rightarrow (C_8H_{15}O_2)Mn + NaSO_4$$

Process description

A 3 L reaction vessel is charged with 781 g white spirit, 390 g 2-ethyl hexanoic acid, and 175 g process water in a consecutive manner under through stirring conditions. The reaction mixture is heated at 75°C. 46% sodium hydroxide solution (108 g NaOH + 125 g H_2O) is fed as one shot. The whole reacting mass is continuously heated at 80°C for 30 minutes. 34% manganese sulfate solution (185 g $MnSO_4$ + 370 g H_2O) is fed continuously to react with the formed sodium 2-ethylhexanoate under continuous stirring for 15 minutes while the temperature is maintained at the level of 80°C.The whole reaction mixture is kept under total reflux to condense and recycle the distilled white spirit vapors.

After reaction completion , heating and stirring is stopped, and the organic product layer is separated by decantation. The latter is thoroughly washed twice with water under agitation followed by decantation. The whole product mass is continuously heated to distill off the residual white spirit.

95% ethanol, amounted to 5 times the product mass, is added to the product residue under continuous stirring, while the temperature is raised gradually and carefully till the level of 60°C for 20 minutes. The ethanol-product solution is mixed with a controlled amount of process water while maintaining agitation. A brown precipitate is continuously formed and the formed slurry is fed to a vacuum filter to separate impurities.

The clear product-solution is recycled to the main reaction vessel, where it is deeply cooled to a temperature of -6°C. The product crystals are separated in a vacuum filter, dried and subjected to analysis.

Preparation of electrolytic manganese dioxide (EMD)

EMD was prepared from electrolysis of a solution of the previously produced $MnSO_4$.Electrolysis was performed in a glass container of 1L capacity. The power was supplied by a regulated D.C. power source (Lodestar +8203).The manganese dioxide was deposited on a graphite anode spaced one inch on either side from two chemical lead cathodes. The graphite anode size was 1.5 x 6 x 10 and the lead cathode was 0.16x 4 x 10; dimensions are given in cm. The cell was placed in a hot-water bath and supplied with water condenser, fixed at the top of the cell, so as to return back any evaporated water. The temperature of the electrolyte was monitored through a thermometer, which was properly positioned in the cell.

Electrolysis was conducted for two hours under the conditions shown in Table 8.After electrolysis, the deposit on the anode was removed, thoroughly washed with distilled water and dried before being investigated by XRD using Cu K_α radiation (1.54059 Å).

RESULTS AND DISCUSSION

Ore characterization

In order to determine the mineralogical and chemical composition of - as received- ore, X-Ray Diffraction (Fig. 1) and X-Ray Fluorescence analysis were done; the results are shown in Tables 1,2 respectively. The XRD analysis indicated that major constituents are pyrolusite ($Mn^{4+}O_2$) and hausmannite ($Mn^{2+}Mn^{3+}{}_2O_4$). The XRF results indicated, as well, that MnO_2 is major compared to hematite which is minor. The obtained results are compliant with previously published paper on Egyptian manganese ore [1]. Scanning electron microscope (SEM) was used to produce images of different 6Mn- ore samples (-0.5mm, -0.5+0.25 mm, -

0.25+0.20mm, -0.20+0.125 mm, -0.125+0.063mm, -0.063mm) by scanning them with a focused beam of electrons (Fig. 2) .

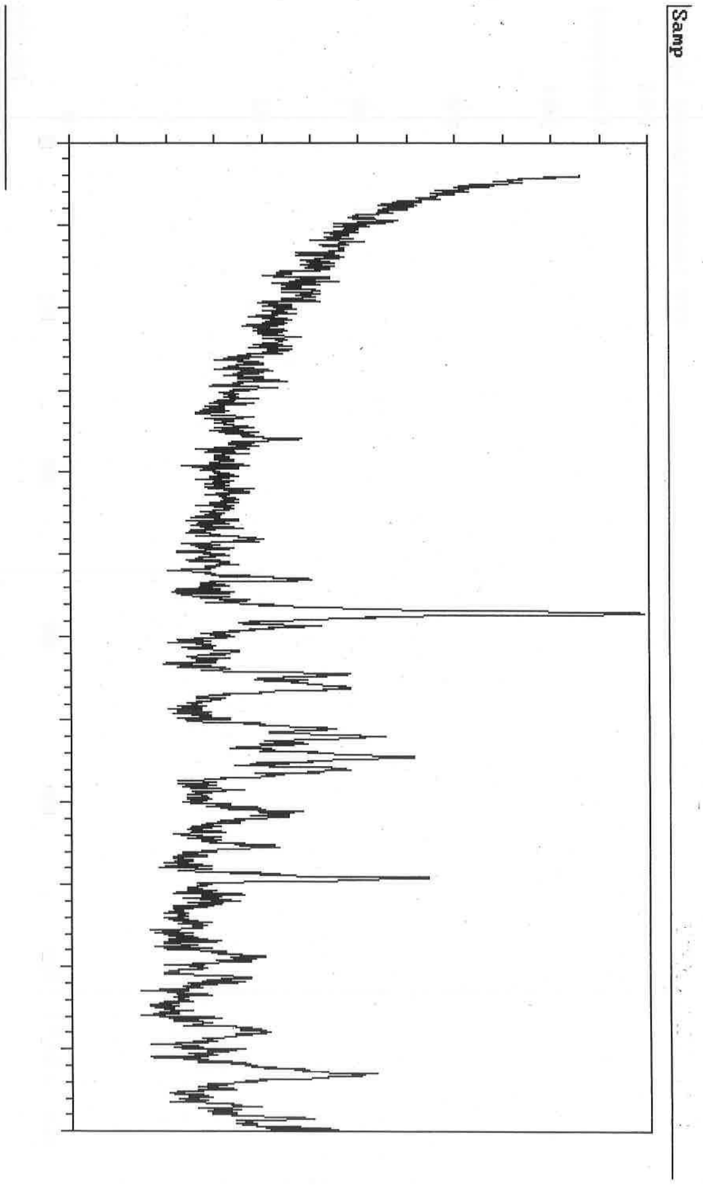

Fig. 1 : X-Ray diffraction pattern of a typical manganese ore sample

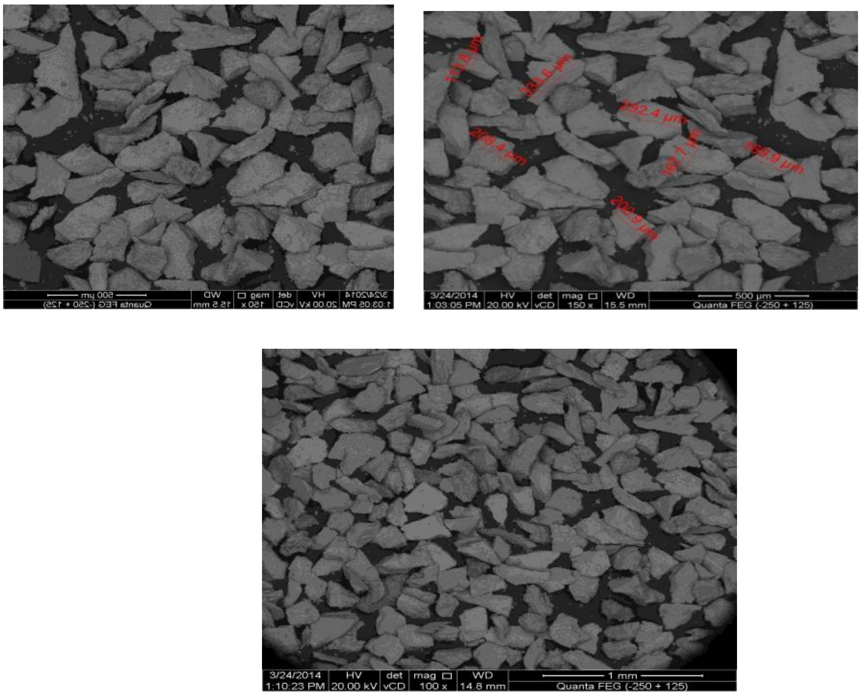

Fig. 2 : Scanning electron microscope of typical manganese ore samples (-250+125µm)

According to the composition depicted in Tables 1,2 the ore might be classified as low grade ore; as it contained 62.03 % MnO_2 (39.2 % Mn) [3]. The chief impurity is hematite and to upgrade the ore, to be suitable for production of manganese chemicals and EMD, it must be removed.

Table 1 : XRD analysis of main manganese ore

Major	Minor	Trace
Pyrolusite and Hausmanite	Hematite	Quartz and Calcite

Table 2 : XRF analysis of main manganese ore sample

Component	SiO_2	Al_2O_3	TiO_2	Fe_2O_3	MnO_2	K_2O	MgO	CaO	L.O.I.
%Composition	5.45	0.25	0.06	15.85	62.03	0.12	0.12	3.55	9.22

Beneficiation of the Ore

The XRF results of different fractions after being subjected to shaking table, magnetic and electrostatic beneficiation techniques are shown in Table 3. It should be addressed that the electro-magnetic and electro-static beneficiation techniques were applied on dry fraction; this is because Mishra et al. [22] reported that “The dry magnetic method gives better grade and recovery of Mn-values than the wet separation methods”.

Table 3: XRF results of beneficiation of different manganese ore fractions

Concentration Separation Technology	- 0.5 mm		- 0.5 mm + 0.25 mm		- 0.25 mm + 0.20 mm		- 0.20 mm + 0.125 mm		- 0.125 mm + 0.063 mm		AA- 0.063 mm	
	MnO_2	Fe_2O_3	MnO_2	Fe_2O_3	MnO_2	Fe_2O_3	MnO_2	Fe_2O_3	MnO_2	Fe_2O_3	MnO_2	Fe_2O_3
ST											**77.72**	**4.51**
EMS (1tesla)											**73.12**	**5.55**
EMS (1.5 tesla)							**77.74**	**4.78**				
EMS (1.6 tesla)							**81.10**	**4.67**				
EMS (1.7 tesla)											**74.05**	**5.85**
ESS 25 kV					**79.22**	**4.05**	**78.99**	**3.58**				
ST +EMS (1tesla)	**76.14**	**5.47**	**78.02**	**3.70**								
ST +EMS (1.5 tesla)			**80.25**	**3.72**					**78.23**	**4.15**		
ST + ESS 25 kV									**78.23**	**4.15**		
EMS (1.5 tesla) + ESS 25 kV					**80.01**	**4.12**	**82.24**	**3.80**	**79.36**	**4.60**		
ST + EMS (1.5 tesla) + ESS 25kV			**81.27**	**4.50**								

ST: Shaking Table. EMS: Electro –Magnetic Separation. ESS: Electro – Static Separation.

The obtained results revealed that the content of MnO_2 could be increased from 62.03 % to 82.24 % and Fe_2O_3 could be decreased from 15.85% to as low as 3.58 %. Among the different modes of beneficiation processes applied, the combination of EMS (1.5 tesla)and ESS (25 kV) gave the best result (82.24 % MnO_2 and 3.80 % Fe_2O_3) for the size fraction – 0.20 mm+ 0.125 mm.

The representative sample of manganese dioxide ore (82.24% MnO_2) containing 52% Mn was used in this investigation. The XRF analysis of the manganese ore concentrate sample is given formerly in Table 4.

Table 4 : XRF analysis of manganese ore concentrate

(size : -200 + 125 µm; 15000 gauss; 25kV)

Component	SiO_2	Al_2O_3	TiO_2	Fe_2O_3	MnO_2	K_2O	MgO	CaO	L.O.I.
%Composition	1.31	0.28	0.15	3.80	82.24	0.55	0.25	0.07	8.05

Production and characterization of manganese sulfate

Production of manganese sulfate

Natural pyrolusite was used to conduct experimental studies. The results revealed that treatment with sulfuric acid at 220°C converts 95% of the total manganese to manganic sulfate. Extraction of the product with 0.01N-sulfuric acid results in conversion of half of the Mn^{3+} to Mn^{2+}, probably due to disproportionation :

$$2Mn^{3+} = Mn^{2+} + Mn^{4+}$$

On the other hand, when the acid-treated product mixture is heated at 640°C, almost complete conversion of the Mn^{3+} to Mn^{2+} takes place.

$$Mn_2(SO_4)_3 = 2MnSO_4 + SO_3 + 1/2\ O_2$$

When the pyrolusite is heated with ferric sulfate at 640°C partial conversion to manganous sulfate is effected, the percentage conversion decreasing with decrease in the percentage of unchanged manganese dioxide in the reaction mixture. Maximum conversion was brought about when the acid treated material was heated at 640°C in the presence of ferric sulfate.

The conversion brought about above 420°C up to 640°C may be attributed to the effect of ferric sulfate on the residual manganese oxides, and may be explained by two alternate mechanisms:

$$\begin{array}{ll}
\text{(a)} & Fe_2(SO_4)_3 + 2MnO_2 = Mn_2(SO_4)_3 + Fe_2O_3 + 1/2\ O_2 \\
 & Fe_2(SO_4)_3 + Mn_2O_3 = Mn_2(SO_4)_3 + Fe_2O_3 \\
 & Mn_2(SO_4)_3 = 2MnSO_4 + SO_3 + 1/2\ O_2 \\
\text{(b)} & Fe_2(SO_4)_3 = Fe_2O_3 + 3\ SO_3\ ; \quad SO_3 = SO_2 + 1/2\ O_2 \\
 & SO_2 + MnO_2 = MnSO_4
\end{array}$$

It is possible that under these conditions the dissociation of sulfur trioxide is catalyzed by ferric oxide. Thermal treatment above 640°C decreased considerably the amount of ferric sulfate, but manganous sulfate was stable up to 850°C, and only above 950°C did it decompose to Mn_2O_3 and Mn_3O_4 which were identified by X-ray examination.

The effect of duration of heating was studied at 640°C, 680°C, and 850°C after pretreatment with excess acid. Maximum conversion to manganous sulfate was attained at 640°C after heating for 1½ h. Further heating up to 25 h, resulted in the decomposition of about 1→ 3% of the manganous sulfate, while the percentage of ferric sulfate started to decrease after heating for 10 h until it reached a negligible amount after

20 h. At higher temperatures the decomposition of ferric sulfate complete after heating for 8 h at 780°C , or 4 h at 850°C.

Characterization of prepared manganese sulfate

Hydrated manganese sulfate was prepared through the direct reaction between manganese concentrate (82.24% MnO_2) and concentrated sulfuric acid (98%) using electric furnace to reach a temperature of 640°C. Product analytical techniques are :

- Product chemical analysis summarized in Table 5 proves that the %conversion of Mn in the ore to $MnSO_4$ exceeds 92% with the absence of Pb and As that allows its use in agricultural fertilizing.

Table 5 : Chemical analysis of thermally prepared hydrated manganese sulfate

Component	**Hydrated $MnSO_4$ product sample**	**Anhydrous MnSO4 product sample**	**Fertilizer grade $MnSO_4.H_2O$**
Manganese(Mn), %	30.01	33.60	31.8
Sodium(Na),%	1.43	1.60	NA
Potassium(K),%	1.08	1.21	NA
Iron(Fe),%	0.003	0.0034	NA
Sulfate($SO4^{-2}$),%	56.32	63.054	56.1
Chloride (Cl^{-1}),%	0.36	0.403	0.005
Loss at 105°C, %	10.68	-	10.65
Fineness(pass 250µ),%	-	91	95
Lead(Pb),	-	-	0.001 max
Arsenic(As),%	-	-	0.0005 max

- Fig. 3 presents the results of Energy- Dispersive X-Ray Spectroscopy analytical technique used to characterize the product compositional analysis that ensure oxygen, sulfur and manganese as basic elements limiting Na, K and Mg as main impurities.
- Scanning electron microscope (SEM) was used to produce images of $MnSO_4$ solid sample by scanning it with a focused beam of electrons. Fig. 4 presents various signals that contain information about surface topography and composition.
- X-ray diffraction analytical technique, Figs. 5, 6, was used for phase identification of $MnSO_4$ crystalline material (as prepared thermally and using oxalic acid as reducing agent) providing information on unit cell dimensions.

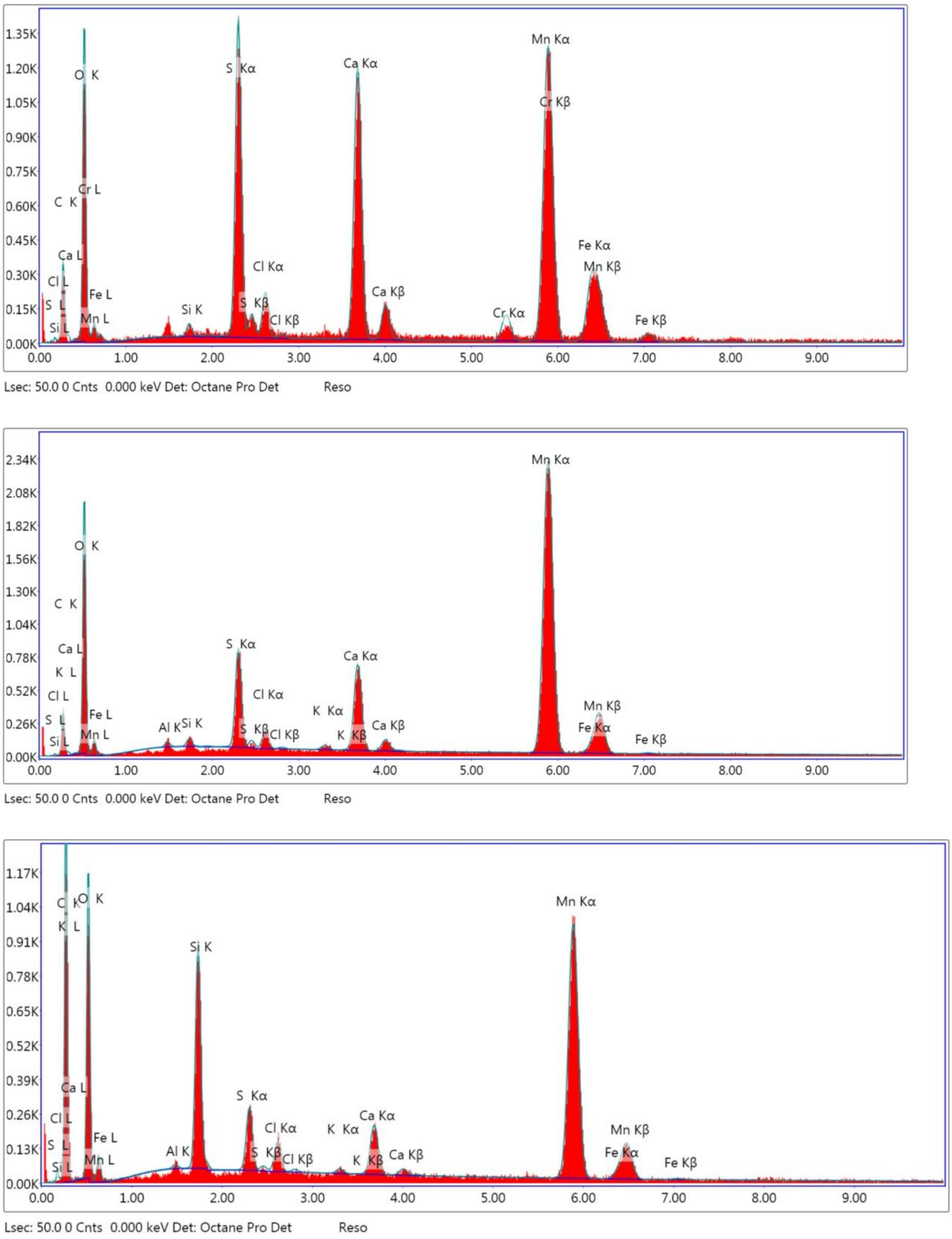

Fig. 3 : Energy dispersive X-Ray spectroscopy of a thermally prepared manganese sulfate sample

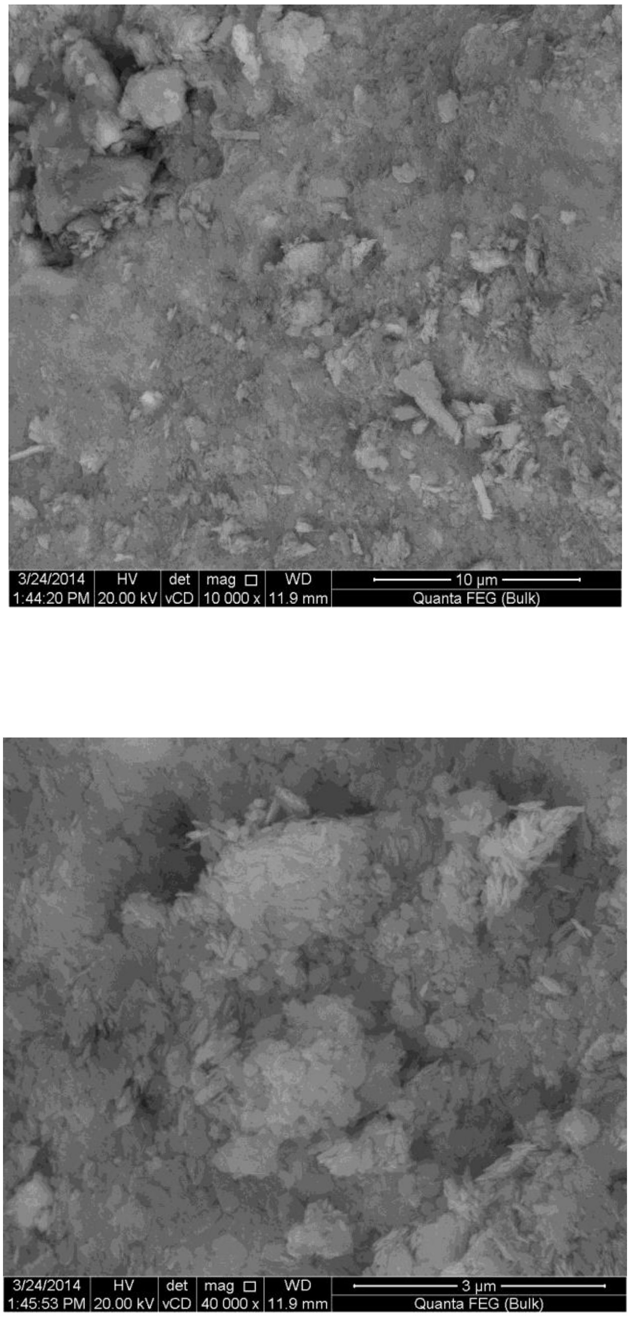

Fig. 4 : Scanning electron microscope of $MnSO_4$ surface topography and composition

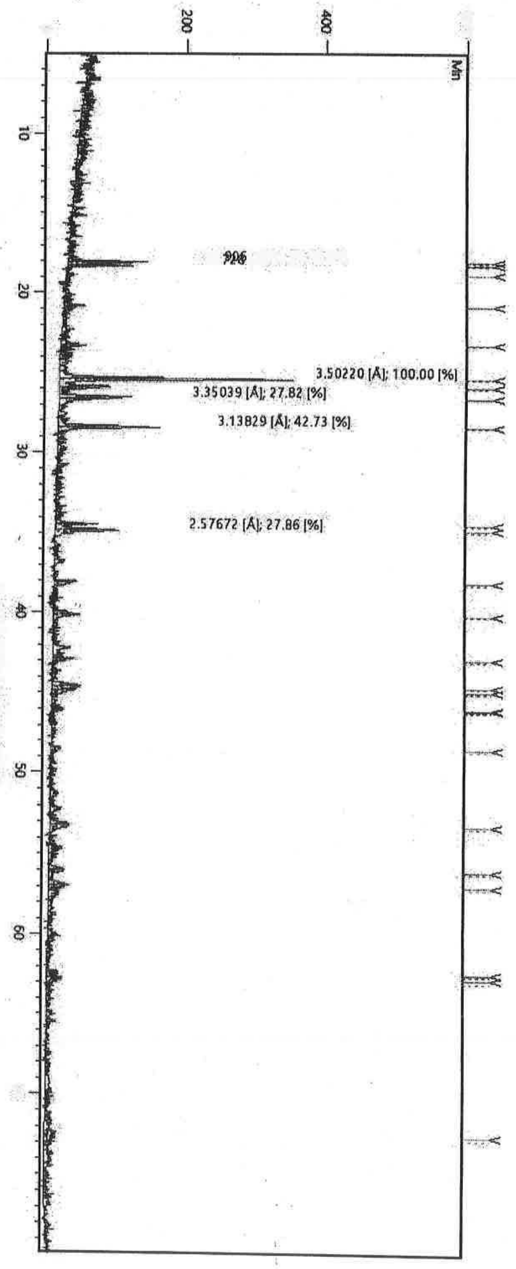

Fig. 5 : X-Ray diffraction pattern of a typical thermally prepared manganese sulfate sample

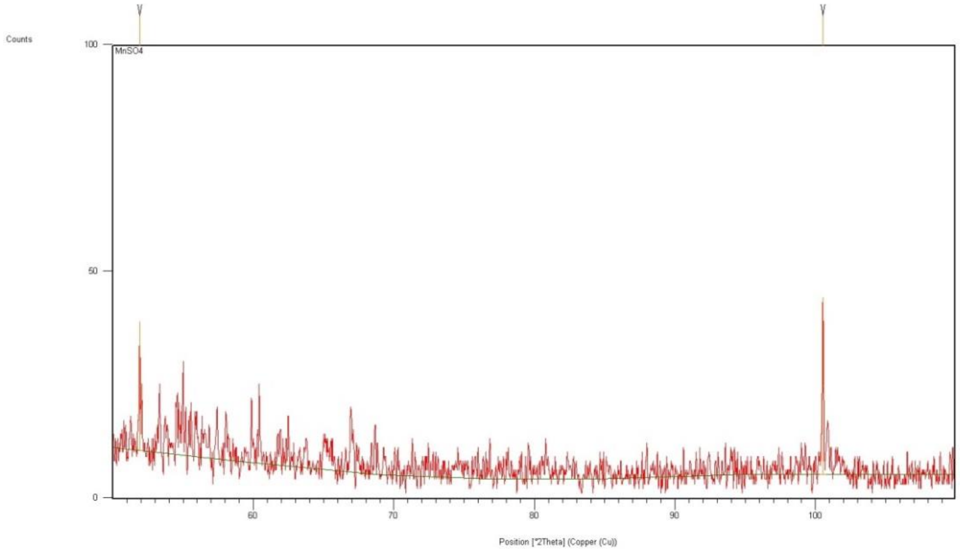

Fig.6 : X-Ray diffraction pattern of a typical manganese sulfate sample

prepared using oxalic acid as reducing agent

Assay analysis and specifications of Mn-2-ethyl hexanoate product

The following instrumentation analyses have been carried out to identify the final product specifications and assess its quality assay:

- Elemental analysis: The results conform exactly with the expected elemental percentages that are based on product chemical structure(C=56%, H=8%).
- Fourier transform infrared spectroscopy : The FTIR monograph of final product, Fig.7, proves exact with published documented Mn-2-ethylhexanoate finger print.

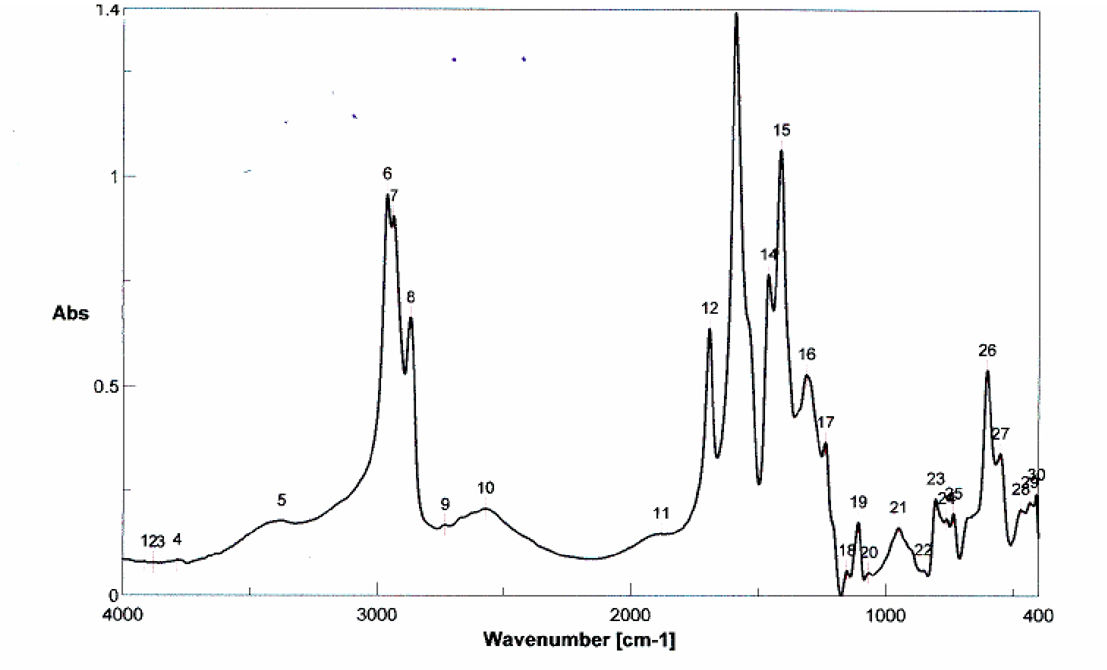

Fig. 7 : Fourier transform infrared spectroscopy of Mn-2-ethyl hexanoat

- XRD-spectrum illustrated in Fig. 8 reflects the amorphous state of product nano molecules. The 1st and 2nd peaks correspond to associated organic impurities, while the major sharp peak belongs to the major product.

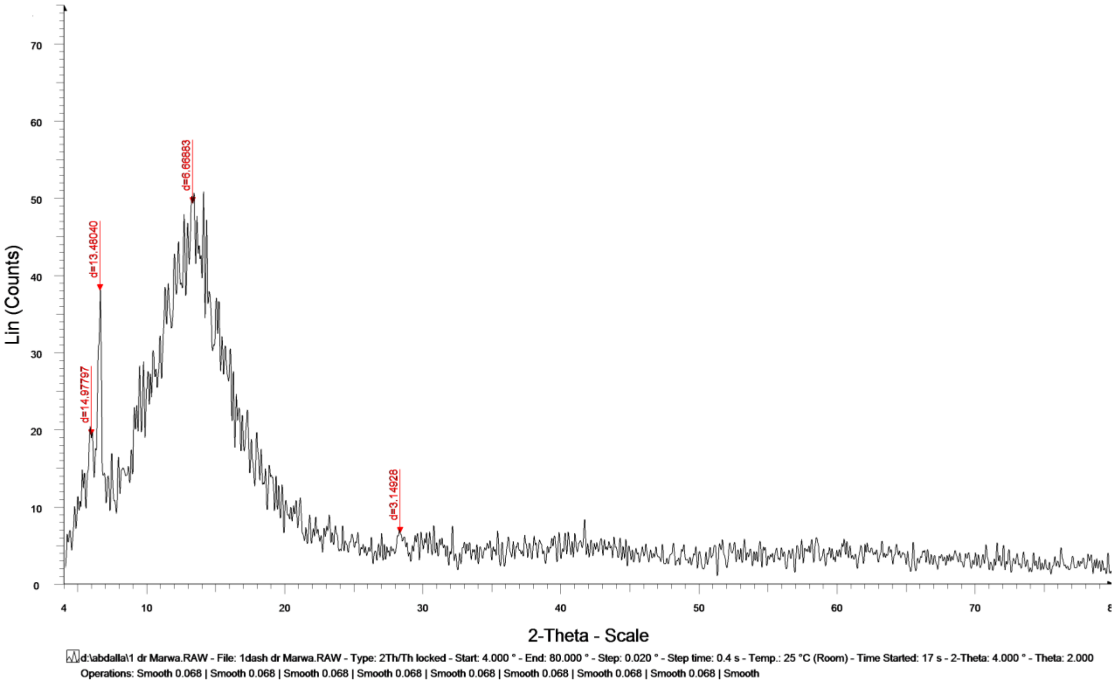

Fig. 8 : X-Ray diffraction spectrum of Mn-2-ethyl hexanoate crystals

- HPLC was used to conduct qualitative and quantitative concentration measurements of formed product, Fig. 9. The major sharp 3rd peak (retention time=3.149 min) corresponds to main product, while the 2nd peak (retention time = 2.482 min) belongs to associated impurities.
- Chemical analysis: Table 6 presents the chemical analysis of a drier 5.1% Mn-concentration.

Table 6: Chemical Analysis of the Prepared Manganese 2-ethyl hexanoate

Component	Concentration
Manganese (Mn) , %	5.1
Iron (Fe) , ppm	90
Sodium (Na) , ppm	850
Zinc (Zn), ppm	7.5

Product importance : Such drier is of high practical and economic importance and is superior in: (i) reducing drying time of paint driers and printing inks., (ii) absence of yellowing phenomena of paint even upon storage for a long time, (iii) Mn-drier can be used as a substituent for Co- and Pb- driers which are environmentally forbidden according to international regulations.

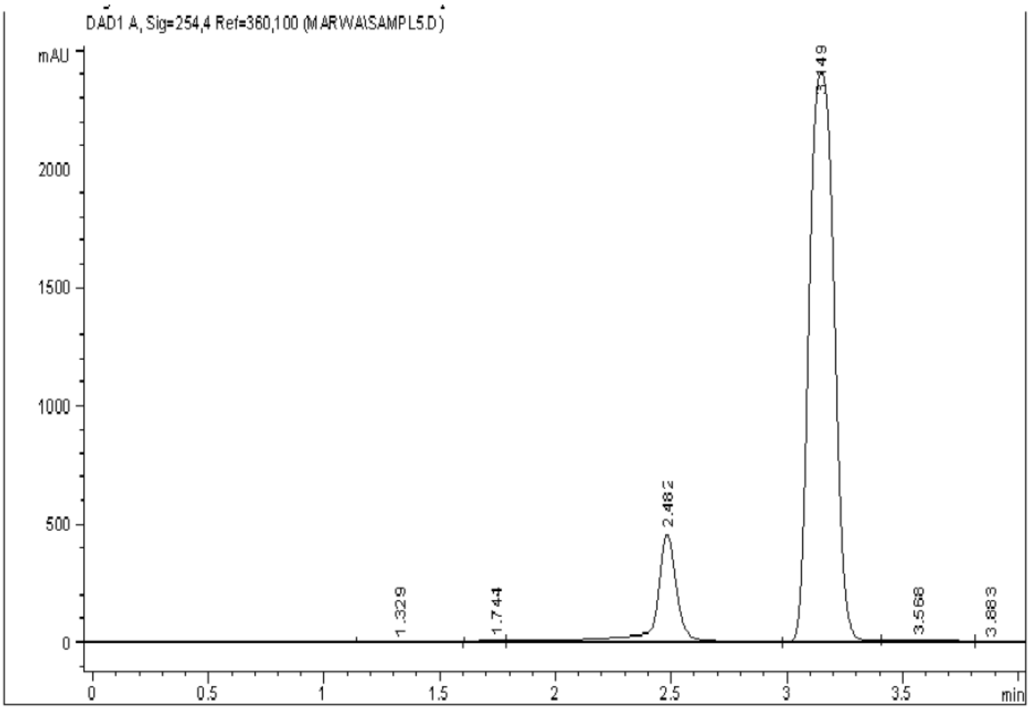

Fig. 9 : High performance liquid chromatography of Mn-2-ethyl hexanoate solution in petroleum ether

Identification of the product on the anode

Fig. 10 presents a comparison between the XRD pattern of the product deposited on the anode (lower) and the XRD pattern of EMD (upper) presented by Shim et al. [23]. There is a close correspondence between the two patterns and can be, at best, described as a small number of broad peaks on top of an undulating background; suggesting a highly defective structure [24]. Such defected structure has been thought to be the origin of the electrochemical activity of EMD [25].

MnO_2 has various polymorphs, among which γ- and ε- MnO_2 contribute to its electrochemical activity [24]. In Table 7 the values of 2 Ө angles and the corresponding phase/s of the patterns illustrated in Figure (XRD pattern) are given. It is worth noting thatγ- and ε- MnO_2 have four identical peaks. Simon et al. [25] reported that the weight ratio of γ- and ε- MnO_2 is approximately 1:1.

Based on this observation, we can claim that EMD could be electrochemically synthesized as per the following reactions.

Anode: $Mn^{2+} + 2H_2O \rightarrow MnO_2 + 4H^+ + 2e^-$
Cathode: $2H^+ + 2e^- \rightarrow H_2$
Overall reaction: $Mn^{2+} + 2H_2O \rightarrow MnO_2 + H_2 + 2H^+$

The most appropriate conditions for electrolytic cell operation are shown in Table 8.

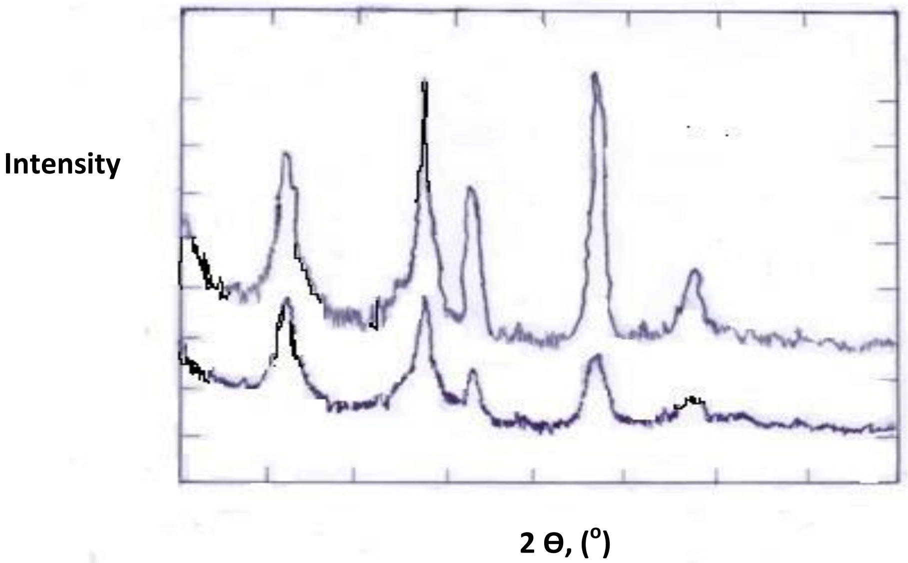

Fig. 10 : X-Ray diffraction of electrolytic manganese dioxide

Table 7 : Values of 2θ —angles and the phase/s of the p

Peak Number	2θ , degrees	Phase/s
(1)	22.2	γ- MnO_2
(2)	36.6	γ- and ε - MnO_2
(3)	41.7	γ- and ε - MnO_2
(4)	55.6	γ- and ε - MnO_2
(5)	66.1	γ- and ε - MnO_2

Table 8 : Appropriate Conditions for Electrolytic Cell Operation

Parameter	Value
Voltage , V	1.95
Current density , Am^2	72
Temperature , °C	95
H_2SO_4concentration , g/L	95
$MnSO_4$ concentration , g/L	150

CONCLUSION

Utilizing Egyptian manganese ores in Sinai is frequently the objective of this research study. Magnetic- and electrostatic separation techniques were successfully used as in producing a superior manganese concentrate. The beneficiated ore is used as a raw material for Mn-compounds synthesis. New process technologies are developed for the production of selected manganese compounds proving both technical and economic feasibility. Reliable processes are presented for the production of fertilizer grade manganese sulfate. The latter was used in the production of both manganese-2-ethyl hexanoate and electrolytic manganese dioxide. The former is used as an effective cross linking and environmentally safe alkyd paint drier while the latter is used in the commercial production of commercial dry-cell batteries such as alkaline – and zinc-carbon batteries. Full characterization of all developed products were accomplished through practicing a variety of instrumental and chemical analysis.

REFERENCES

[1] Fahim MS, El-Faramawy H., Ahmed AM, Ghali SN, Kandil AT. J of Minerals and Materials Characterization and Engineering 2013; 1: 68-74.

[2] Malayoglu U., Asian Journal of Chemistry 2010; 22: 3292-3298.

[3] Gao Y., Olivas-Martinez M., Sohn HY, kim HG, Kim CW. Metallurgical and Material Trans. B 2012; 43B: 1465 – 1475.

[4] IS 11895 (2006): Classification of manganese ore; Bureau of Indian Standards.

[5] Santos JRD, WO 2010096887 A2, Sep. 2, 2010.

[6] Samonides J., US Patent 3,227,520, Jan. 4, 1966.

[7] Zhiguang J., Dong H., Fei W., European Patent Application, EP 2 487 137 A1, Aug. 15,2012.

[8] Razouk RI, Tobia SK, Messiha MA, J. Appl. Chem., 1964;14: 105-108.

[9] Azizi D., Shafaei SZ, Noaparast M., Abdollahi H., Trans. Nonferrous Met. Soc. China, 2012; 22: 2295-2305.

[10] Bieleman JH, Polym. Paint Color J., 1998; 188: 28-31.

[11] Van Haveren J., Oostveen EA., Micciche F, Weijnen JGJ, Eur. Coat. J., 2005; 1-2: 16-19.

[12] Liu Z., Kooijman H., Spek AL, Bouwman E., Prog. Org. Coat., 2007; 60: 343-349.

[13] Van Gorkum R., Bouwman E., Reedijk J., Inorg. Chem., 2004; 43: 2456-2458.

[14] Hoogenraad M., Ramkisoensing K., Kooijman H., Spek AL, Bouwman E., Haasnoot JG, Reedijk J., Chim. Acta, 1998; 279: 217-220.

[15] Erich SJF, Laven J., Pel L., Huinink HP, Kopinga K., Prog. Org. Coat., 2006; 55: 105-111.

[16] Erich SJF, Van der Ven LGJ, Huinink HP, Pel L, Kopinga K., J. Phys. Chem. B, 2006; 110: 8166-8170.

[17] Van Gorkum R., Berding J., Tooke DM, Spek AL, Reedijk J., Bouwman E., J. Catal., 2007; 252: 110-118.

[18] Van Gorkum R., Berding J., Mills AM, Kooijman H., Tooke DM, Spek AL, Mutikainen I., Turpeinen U., Reedijk J., Bouwman E., Eur. J. Inorg.Chem., 2008; 2008: 1487-1496.

[19] Kanungo SB, J. Chem. Tech. Biotechnol., 1991; 50: 91-100.

[20] Biswal A., Tripathy BC, Sanjay K., Subbaiah T., Minakshi M., RSC Adv., 2015; 5: 58255-58283.

[21] IS 11153 (1996): Manganese dioxide for dry batteries; Bureau of Indian Standards.

[22] Mishra PP, Mohapatra BK, Mahanta K., Journal of Minerals & Materials Characterization & Engineering, 2009; 8: 47-56.

[23] J. Shim, H. Choi and Y.Tak, “Electrochemical Activities of Electrolytic Manganese Dioxide (EMD) as a Cathode Electrode for Lithium Air Batteries”, Int. J. Electrochem. (2015), Sci., Vol. 10, p. 7091 – 7102.

[24] Rus ED, Moon GD, Bai J., Steingart DA, Erdonmez CK, J. of the Electrochemical Society, 2016; 163: A356-A363.

[25] Simon DE, Morton RW, Gislason JJ, International Centre for Diffraction Data (2004), Advances in X-ray Analysis, 2004; 47: 267-280.