

PREPARATION OF MANGANESE NANOPARTICLES AND VALUABLE SALTS FROM SPENT DRY BATTERY CELLS

Mahmoud A. Rabah¹, Taha M.A. Razek², Omar M. Abdel Aziz³

¹Chemical and electrochemical treatment Lab, Mineral Processing Dept. Central Metallurgical R&D Institute, P.O>Box 87 Helwan Cairo Egypt

²Assoc. Prof. Environmental chemistry, Institute for environmental studies and research, Ein Shams University

³Director, Great Cairo Potable water Co.

¹mahmoud.rabah@ymail.com, ¹mrabah010@gmail.com, ²Tahaelsabbagh@yahoo.com, ³Omermhelmy@gmail.com

Abstract- This work shows a method to prepare manganese nanoparticles on carbon substrate and some inorganic and organic salts such as carbonate, nitrate, chloride, citrate and acetate from spent dry battery cells. The method involves dismantling the cell followed by sulfuric acid leaching of the whole contents at temperatures up to 75°C for 3 hours. The leaching products were filtered and the metals went into solution were determined. Metals other than manganese were chemically separated whereby manganese hydroxide was precipitated at pH 8. Nanoparticles of manganese were prepared by direct reduction of the hydroxide using hydrazine hydrate. The hydroxide salt reacted with the respective acid to prepare the required salt. Results revealed that manganese content in the spent battery cell amounts to 22 % by weight. Leaching extent in sulfuric acid increased with the increasing the acid molarity up to 3, temperature of leaching up to 75 °C, leaching time up to 3 hours and stirring conditions. The quality of the products have been characterized by XRD, SEM and FT-IR investigations. The activation energy of the acid leaching of manganese amounts to kJ.mol.

Key words: Manganese, hydrometallurgy, nanoparticles, spent dry cell battery

I. INTRODUCTION

There are four main types of batteries

A. Disposable dry-cell batteries

It includes: 1- Zinc-carbon and zinc-chloride batteries are used in low energy use appliances such as clocks and radios. They are often found in products sold with disposable batteries, as they are cheap. 2- Alkaline batteries are used in equipment such as MP3 players, torches or toys. They are longer lasting and less prone to leaking than zinc carbon and zinc-chloride batteries. 3- Button cell batteries contain mercury, silver, lithium or other valuable heavy metals. Mercuric oxide button cells are used for hearing aids, pacemakers and photographic equipment. 4- Zinc-air batteries are an alternative to mercuric oxide button cells. They may be used in hearing aids and radio pagers. 5- Silver oxide button cells are a type of alkaline battery used in electronic watches and calculators. 6- Lithium button cells are also used in watches and in photographic equipment.

B. Recycling disposable batteries

1- Zinc-carbon, 2- alkaline manganese batteries and 3- button cell

C. Rechargeable dry-cell batteries

1- Nickel cadmium (NiCd) batteries, Nickel-metal hydride (NiMH) batteries Lithium-ion and lithium ion polymer (Li-Ion) Batteries

D. Recycling rechargeable batteries 1- NiMH batteries and 2- NiCd batteries

Spent dry battery cells (DBC) are processed by a variety of methods, including size reduction, screening, magnetic separation, and mechanical and chemical processes for recovering zinc and ammonium salt. [1]. Nicolae [2] developed mechanical separation for Leclanché (ammonium chloride-manganese dioxide-zinc) batteries in which the powdered manganese oxide and other compounds were dissolved in concentrate HCl, then oxidized to obtain MnO₂ and Zn(OH)₂ The mixture was washed with dilute HCl to dissolve Zn(OH)₂ and zinc was recovered as ZnCl₂ Shaoguo [3] also recovered zinc and NH₄Cl from spent DBCs. Studies on the effect of temperature on the recovery process for DBCs was also performed. The powder feed of the spent batteries was leached after shredding and grinding with 1–50 percent H₂SO₄ and/or HCl under inert atmosphere or in the presence of hydrazine sulfate, a reducing agent, to recover zinc and manganese. Zinc was precipitated with oxalic acid and recovered by filtration; manganese was then precipitated in the form of mixed hydroxide and carbonate using Na. Lindermann et al. [4] applied a novel procedure including mechanical separation for steel and plastic casings followed by leaching in H₂SO₄ Zinc has been recovered by solvent extraction or by electrolysis [5,6,7]. The pyro-metallurgical recovery of zinc from DBCs in an oxidation or rotary furnace has been reported [8,9]. Zinc and its compounds were vaporized and entered a bubbling type condenser. The recovery processes were carried out under non oxidizing atmosphere at 1,000–1,150°C, by carbon reduction, by carbon-containing materials, or by vacuum distillation [10]. Rabah and El- Sayed [11] studied the recovery of zinc from zinc-waste materials in which the coarse fraction was heated with 10%NHCl at 600°C to produce a zinc recovery efficiency of about 89%. Several pyro-metallurgical and hydro-metallurgical processes for the recycling of batteries were proposed[12]. Hydrometallurgical processes are usually characterized by different pretreatment stages, followed by leaching and separation of different metals by electrolysis, liquid-liquid extraction, or selective precipitation. The Batenus process treats

all types of batteries (except for button cells); copper, nickel, and cadmium are selectively recovered by ion exchange, whereas zinc and manganese were separated by liquid-liquid extraction and electrodeposited in two cells to obtain metallic zinc and manganese dioxide [13]. In the Recupyl process zinc and manganese are recovered as carbonates or other compounds [14]. Revabat process treats only zinc-carbon and alkaline batteries; after sorting, batteries are dismantled and treated by sulfuric acid solution, from which Mn and Zn are recovered as oxides or salts [15]. Toro et al. [16] developed a patented process for the recycling of alkaline and zinc-carbon spent batteries, where the metals are leached in acid solution in the presence of carbohydrates as reducing agents; after purification of solution, metallic zinc and manganese dioxide are recovered by electro winning. Veloso et al. [17] proposed a process in which metals are leached by H_2SO_4 and H_2O_2 ; after that manganese and zinc are selectively precipitated by KOH. De Souza and Tenório [18] described a similar process performed by an acid leaching, but zinc and manganese are simultaneously recovered as metallic zinc and manganese dioxide by electro winning. Salgado et al. [19] and Devi et al. [20] investigated liquid-liquid extraction separation of zinc and manganese after a leaching step with H_2SO_4 . De Michelis et al. [21] developed a statistical design in leaching of alkaline and zinc-carbon battery paste by using sulfuric acid and oxalic acid as reducing agent. Ferella et al. [22] studied acid leaching of battery paste whereby zinc was recovered by electrolysis and a blend of manganese oxides was obtained by roasting of the leaching solid residue. Sayilgan et al. [23] have studied leaching of battery samples (zinc-carbon, alkaline, and mixture of them) by sulfuric and hydrochloric acid in the presence of oxalic acid as reducing agent. Xi et al. [24] proposed a process for production of Mn-Zn ferrites using spent alkaline batteries: the powder is leached by H_2SO_4 and H_2O_2 as reducing agent, then NaOH is used to adjust the pH value in the range 3–5. Mn and Fe salts are added to have the right molar ratio, and after precipitation with NH_4HCO_3 in pH range 6.0–9.5 the precipitate was calcined at C to obtain ferrite. The process of Nan et al. [25] replaced $(NH_4)_2C_2O_4$ as a precipitating agent. Application of manganese nanoparticles are in magnetic data storage, magnetic resonance imaging and Biosensors, textile and coating, nanowires, plastics and nanofibers. Magnetic resonance imaging (MRI) is a routine diagnostic tool in modern clinical medicine.

The objective of this study is to prepare valuable manganese inorganic and organic salts from spent dry battery cells by applying friendly and cost-effective method. Parameters affecting the efficiency and quality of the end products, such as time, temperature, pH value, and stoichiometric ratio of the leaching solutions, were studied.

II. EXPERIMENTAL

A. Materials

- About ten Kg of the spent dry battery sample were supplied by the waste collection stores, Cairo. The sample was washed with water and left to rinse in normal ambient conditions.
- The carbon substrate for preparation of manganese nanoparticles was prepared from two carbon types. The first type was a thin sheet of artificial graphite cut from a mother plate of Carbon Lorene France. The second type was glassy carbon obtained from the carbon rod of the dry battery after dismantling. Both two types were freed from wax by heating at $300^\circ C$ in normal conditions. The de-waxed samples were washed and cleaned by washing in acetone.
- Chemicals used for leaching, precipitation, separation and salts preparation were chemically pure grade. Sulfuric, nitric citric, formic, acetic acids and ammonium hydroxide 30% were of ADWIC production (Egypt)
- Mono distilled water was used for leaching and precipitation steps.

B. Method of preparation of manganese nanoparticles

Manganese nanoparticles were prepared from the spent black paste of the dry battery cell by acid leaching of the element in sulfuric acid. The sulfate solution was treated with ammonia solution to precipitate manganese hydroxide at pH 8. The precipitate was washed with water and suspended in glucose solution.

C. Measurement of the physic-chemical properties

Determination of metals available in the spent battery sample was conducted applying the standard analytical methods given in the literature. Spectrophotometer U.V visible spectrophotometer type UV 260 (Shimadzu) was used for the determination of manganese content in the samples [26]. Zinc was determined titrimetrically against EDTA using Eriochrome Black T as an indicator [27]

Determination of alkali metals Sodium, Potassium and calcium were determined with the help of photometric analysis applying a flame photometer type Chloride ion was determined gravimetrically by silver nitrate precipitation

2.3 Method of preparation of the manganese salts

Figure 1 shows the conceptual flow sheet of the applied method for preparation of manganese nanoparticles and manganese salts. The dry battery cell type was A, AAA size of energizer production

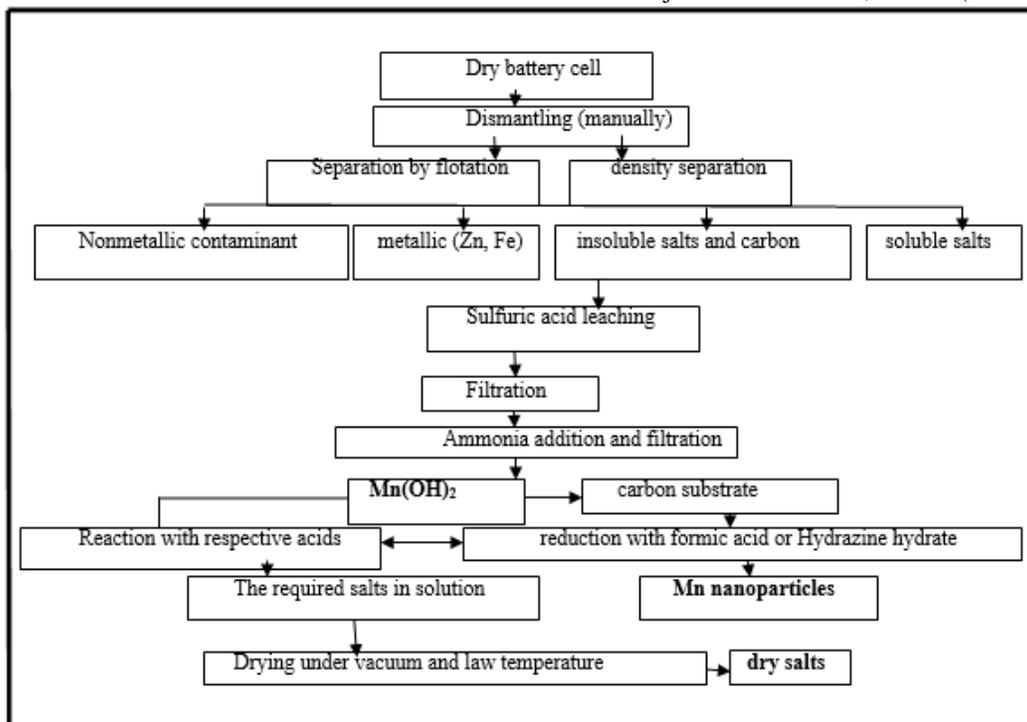


Fig. 1 the conceptual flow sheet of preparation of manganese nanoparticles and valuable salts From spent dry battery cell

III. RESULTS

Table 1 The contents of the spent dry battery cell

material	Weight, g	Basis of determinat ion	Weight % in battery
Stainless cover	1.055		1.56
Cartoon	3.092		4.75
Carbon rod	5.139		7.60
Polymer Insulator	1.403		2.07
Plastic ring	1.796		2.65
metal cup	14.534		21.5
Black paste	30.35	C/MnO ₂	59.99
Water soluble salts	10.20		
Total	67.6		100

Table 1 shows the contents of the spent dry cell batteries of type A and AAA. It can be seen that the black powder (carbon + manganese dioxide) content amounts to 40.55 g out of 67.6 g for the whole battery weight. The net manganese dioxide weight amounts to 25 g

The weight of carbon in black paste amounts to 15.55. It was removed by heating at temperatures up to 1000°C till constant weight. Fig. 2a,b shows the XRD of the black paste.

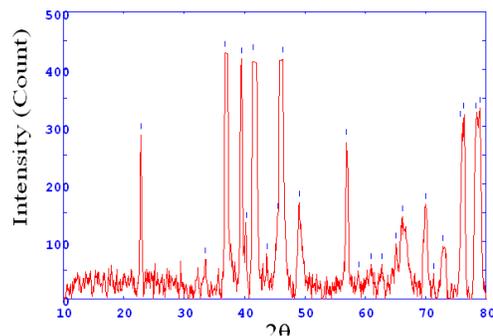


Fig. 2a XRD pattern of black paste before heating

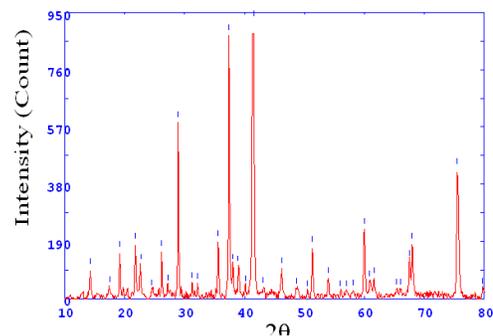


Fig. 2b XRD pattern of black paste after heating

Figure 3a,b shows the weight loss of the black paste as a function of temperature. Figure 4 shows the TGA of this paste after heating at temperatures up to 1000°C.

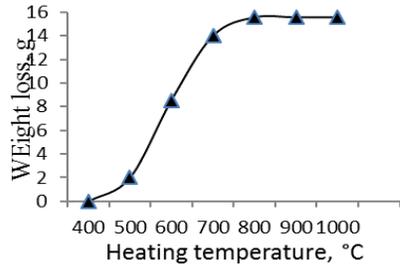


Fig. 3a the weight loss of black paste as a function of temperature

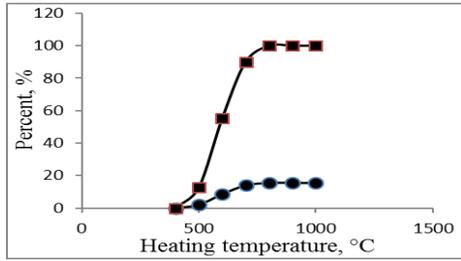


Fig. 3b The effect of temperature on the percent weight loss of black paste

Legend: ■, ● weight, g

Figure 4 shows TGA of the black paste. It can be seen that a significant loss in weight takes place at ≥ 650 °C.

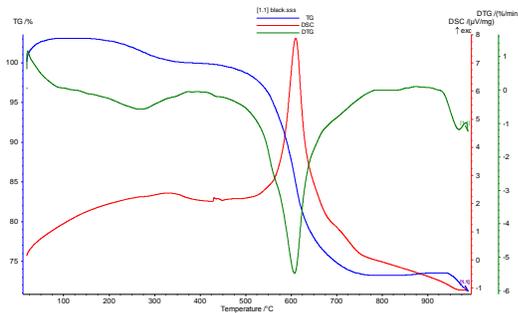


Fig. 4 The TGA curve of this paste after heating at temperatures up to 1000°C.

Figure 5 shows the extent of water soluble salts present in the black paste of spent ever ready battery type. It can be seen that the maximum extent of 0.17 % was attained with boiling water whereas the least extent of 0.08 % took place in cold water.

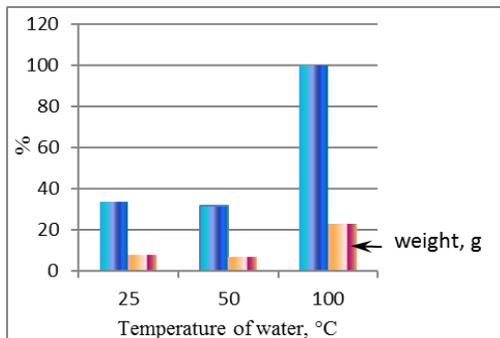
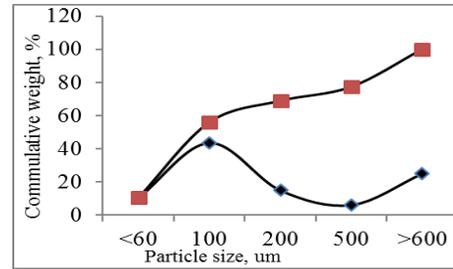


Fig. 5 the extent of water soluble matters in the spent battery as affected by temperature of water washing



Legend: ◆, ■ weight, g, Cumulative weight, %

Fig. 6 the particle size distribution of the black paste of spent dry cell

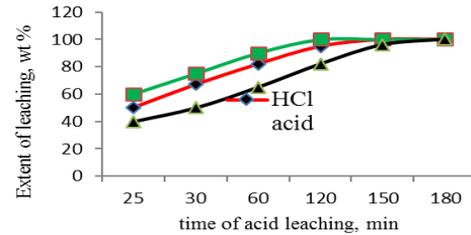


Figure 7 The extent of leaching of Mn metal from the spent dry cell using different mineral acids for 3 hours.

Figure 7 shows the extent of leaching of manganese metal from the spent dry cell using different mineral acids for 3 hours at room temperature. It is seen that the extent of leaching decreases in the order sulfuric > HCl and nitric acid. It is also seen that leaching increases with time whereby the maximum value takes place at 180 minutes.

Figure 8 shows the extent of leaching zinc in nitric acid as affected by the acid normality at room temperature. It is seen that zinc leaching increases with increase in acid normality passing through a maximum with 3 N acid.

Fig.9 shows the leaching results obtained with sulfuric acid. It is seen that leaching decreases with increase in acid normality and temperature. It is seen that the extent of leaching at room temperature overweighs leaching in boiling conditions. It is noted that leaching using dilute acid ($N_{\leq 3}$) is more efficient than using more concentrated acid.

Figure 10 shows the leaching extent of manganese in sulfuric as a function of particle size of the black paste. It is seen that the extent of leaching is inversely proportional to the grain size of the black paste.

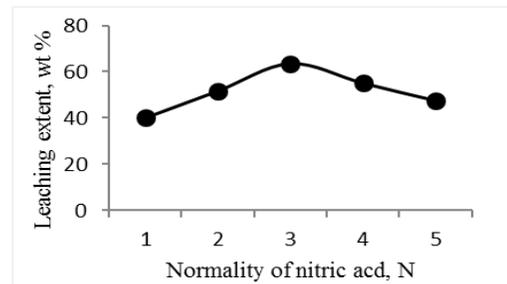


Fig. 8 The extent of leaching zinc in nitric acid as affected by acid normality at room temperature.

IV. DISCUSSION

Recovery of spent dry battery cells has dual benefits. It helps to get rid of the waste of hazardous materials and obtain valuable products of market value. The average quantity of the used dry battery cells in Egypt increases dramatically on basis of the increasing rate of the population development. In this context, studies carried out to recycle the dry battery cells have different issues and objectives. Some studies paid attention to the zinc content alone whereas others paid attention to iron discs. In some cases, agencies had their aim to recover black paste altogether with zinc metal. The present study has its aim to make use of all the contaminants of the dry cell battery in the country. The experimental program started by dismantling the spent cell with the help of a double toothed saw blade. Plate 1 shows a split dry cell.

Table 1 shows the contents of the battery cell. XRD patterns given in Figs 2a,b confirms the presence of these components. Determination of carbon in the black paste was examined by heating the black paste at temperatures up to 1000°C. the initial weight loss taking place up to 400°C can be attributed to the loss of moisture content and volatile salts such as ammonium chloride and ammonia. The slight increase in weight loss taking place within the temperature range 400-500°C is assigned to the escape of zinc chloride. The drastic increase in weight loss at 600°C is due to the oxidation of the available carbon in the black paste to carbon oxides(mono and dioxide)

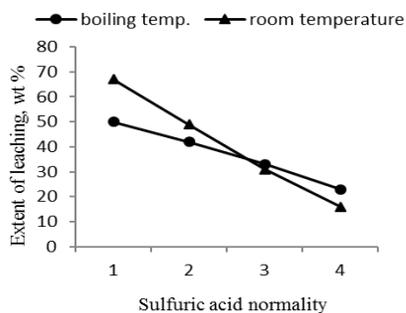


Fig. 9 Leaching of manganese in sulfuric acid having different normality and temperature values

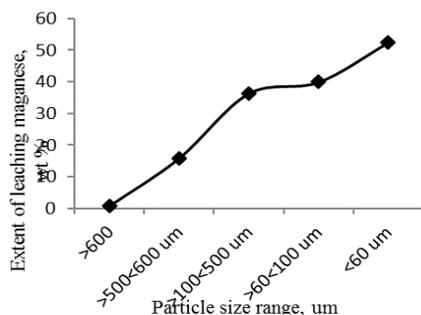


Fig. 10 the effect of particle size of the black paste on the extent of leaching manganese in sulfuric acid

Figure 11 shows the SEM of the nanoparticles of manganese as prepared on carbon substrate

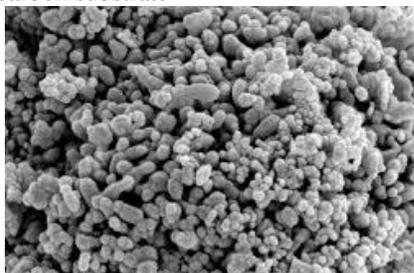
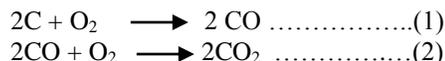


Fig. 11 SEM image of manganese nanoparticles on carbon substrate.

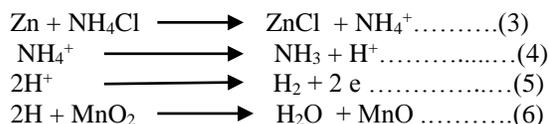
Table 2 shows the data for preparation of some inorganic and organic salts of manganese from its hydroxide salt and the respective acid.

Table 2 Data for the preparation of some manganese salts

Product of Mn	Weight/volume of reagents			Acid conc.
	Mn(OH) ₂	CO ₂	Respective acid	
CO ₃ ²⁻ (rose)	10 g	4.947 g		
(NO ₃) ²⁻ (pink-rose)	10 g		75 ml	3N (HNO ₃)
Cl ⁻ (brown)	10 g		44.8 ml	5N (HCl)
acetate			13.49 ml	Glacial acetic acid
citrate			43.247	In 100 ml water



The humidity detected in the cell upon cutting finds support from the fact that the chemical reactions taking place during discharging the battery generate water as follows:



and the overall reaction is:



The moisture content amounts to about 7.2% in the unused cells. Zinc chloride and ammonia primary used in the manufacture of the dry cells. During discharging of the battery, excessive quantity of water generated and dissolves more zinc chloride. This explains why the total weight of the water soluble salts in the spent battery(22.5 %) is much higher as compared to the new cell (7.2%). Results given in Fig. 5, is in a good agreement with the solubility of zinc chloride in cold water (432g/100g water) and hot water (635g/100 g water) [28]

The particle size distribution analysis of the black paste given in Fig.6 shows that the finer particle size of <60 um helps to enhance the oxidation-reduction reactions (Ox-Re) to take place during the battery discharge at a high performance. This imparts a convenient duty of the battery. On the contrary, if the black paste has a larger grain size, it would decrease the efficiency of the Ox-Re) and the battery duty as well.

Leaching of zinc in different mineral acids (sulfuric, nitric and HCl) showed that the process is time dependent particularly within the first 180 minutes. This phenomenon is ascribed to the passivity action of the generated hydrogen gas evolving during acid attack. Also the more concentrated acid has the same effect. Dilute acids help less quantity of hydrogen gas to build a gas barrier on the zinc surface. The same explanation would be applied to the acid leaching of manganese. Results of fig. 9 confirm this model. The effect of particle size of the paste on the extent of acid leaching of manganese imparts that the surface area of the fine particles are much higher than coarse particles. In other words the surface subjected to acid attack is much more available with fine particles as compared to the coarser one. SEM image shows that the average grain size of the nanoparticles, obtained in this work, amounts to nearly 10-30µm.

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