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A Laboratory Scale Production Method of Raw Manganese (II) Sulphate from Waste used Alkaline Batteries

M. Sathyamoorthy ^a, Ayesha Jasim Alhammadi ^a & Somaya Ibrahim Alhammadi ^b

Abstract- This experimental project deals with the laboratory scale production method of raw manganese (II) sulphate from waste used alkaline batteries. The Batteries have wide range of applications which includes automobile, household, industrial, electronics, mobile gadgets etc. There are many types of Batteries like alkaline battery, zinc carbon battery, lead acid battery, nickel cadmium battery, lithium battery etc. In UAE, millions of products using the lead acid batteries and alkaline batteries. The batteries are exhausted, after many recharge cycles. These waste used batteries are disposed to atmosphere and makes many environmental pollutions. This experimental research project explains how to synthesis Manganese (II) sulphate from these waste batteries by simple method in lab scale with step by step. Because, $MnSO_4$ has lots of uses and can be produced from these waste batteries. It is one of the great business idea for Chemical Engineers in the present and future UAE industrial sectors.

Keywords: batteries, manganese sulphate, manganese dioxide, used batteries, alkaline batteries, lead acid batteries.

I. INTRODUCTION

Battery is a device consisting of one or more electrochemical cells with external connections provided to power electrical device such as flash light, smart phones and electric cars. When a battery is supplying electric power, its positive terminal is the cathode, and its negative terminal is the anode. The present method is to prepare manganese (II) sulfate from manganese dioxide which is extracted from the waste used batteries. Mainly alkaline batteries are used for this purposes. The product produced is the raw and impure. It has to be further purified.

a) Types of batteries

Primary (single-use or "disposable") batteries are used once and discarded; the electrode materials are irreversibly changed during discharge. Common examples are the alkaline battery used for flashlights and a multitude of portable electronic devices. Secondary batteries can be discharged and recharged multiple times using an applied electric current;

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Secondary (rechargeable) batteries can be discharged and recharged multiple times using an applied electric current; the original composition of the electrodes can be restored by reverse current. Examples include the lead-acid batteries used in vehicles and lithium-ion batteries used for portable electronics such as laptops.

Batteries come in many shapes and sizes, from miniature cells used to power hearing aids and wristwatches to small, thin cells used in smart phones, to large lead acid batteries used in cars and trucks, and at the largest extreme, huge battery banks the size of rooms that provide standby or emergency power for telephone exchanges and computer data centers.

Reuse of the recovered materials from solid wastes is the other principal mode of energy conservations. Therefore attention has been focused in the utilization of industrial wastes and low grade ores for the recovery of metals due to increased mining costs and depletion of mineral wealth. During the last decade a great increase in environmental awareness took place and legislation on wastes developed. It is estimated that in India alone, about 115 million of urban population produces nearly 15 million tons of solid waste causing chronic pollution of land and water.

Recent developments have allowed successful commercial introduction of rechargeable zinc alkaline and manganese dioxide batteries. But dry Lechlanche cell once discharged cannot be recharged again. Household batteries contribute many potentially hazardous compounds to the municipal solid waste stream, including zinc, lead, nickel, alkaline, manganese, carbon-zinc, mercuric oxide, zinc-air, silver oxide, and other types of button batteries.

Higher levels of manganese are toxic and cause brain damage. Very little or no information appeared in the literature on estimation of manganese and its utilization for different analytical applications.

i. Primary cell

Primary batteries, or primary cells, can produce current immediately on assembly. These are most commonly used in portable devices that have low current drain, are used only intermittently, or are used well away from an alternative power source, such as in alarm and communication circuits where other electric

power is only intermittently available. Disposable primary cells cannot be reliably recharged, since the chemical reactions are not easily reversible and active materials may not return to their original forms. Battery manufacturers recommend against attempting to recharge primary cells. In general, these have higher energy densities than rechargeable batteries, but disposable batteries do not fare well under high-drain applications with loads under 75 ohms (75Ω). Common types of disposable batteries include zinc–carbon batteries and alkaline batteries.

ii. Secondary battery

Secondary batteries, also known as secondary cells, or rechargeable batteries, must be charged before first use; they are usually assembled with active materials in the discharged state. Rechargeable batteries are (re)charged by applying electric current, which reverses the chemical reactions that occur during discharge/use. Devices to supply the appropriate current are called chargers.

The oldest form of rechargeable battery is the lead–acid battery, which are widely used in automotive and boating applications. This technology contains liquid electrolyte in an unsealed container, requiring that the battery be kept upright and the area be well ventilated to ensure safe dispersal of the hydrogen gas it produces during overcharging. The lead–acid battery is relatively heavy for the amount of electrical energy it can supply. Its low manufacturing cost and its high surge current levels make it common where its capacity (over approximately 10 Ah) is more important than weight and handling issues. A common application is the modern car battery, which can, in general, deliver a peak current of 450 amperes.

iii. Life time

Battery life (and its synonym battery lifetime) has two meanings for rechargeable batteries but only one for non-chargeable. For rechargeable, it can mean either the length of time a device can run on a fully charged battery or the number of charge/discharge cycles possible before the cells fail to operate satisfactorily. For a non-rechargeable these two lives are equal since the cells last for only one cycle by definition. (The term shelf life is used to describe how long a battery will retain its performance between manufacture and use.) Available capacity of all batteries drops with decreasing temperature. In contrast to most of today's batteries, the Zamboni pile, invented in 1812, offers a very long service life without refurbishment or recharge, although it supplies current only in the nano amp range. The Oxford Electric Bell has been ringing almost continuously since 1840 on its original pair of batteries, thought to be Zamboni piles.

Today, batteries are all around us.

The power our wristwatches for months at a time. They keep our alarm clocks and telephones working, even if the electricity goes out. They run our smoke detectors, electric razors, power drills, mp3

players, thermostats and the list goes on. If you're reading this article on your laptop or smartphone, you may even be using batteries right now! However, because these portable power packs are so prevalent, it's very easy to take them for granted. This article will give you a greater appreciation for batteries by exploring their history, as well as the basic parts, reactions and processes that make them work. So cut that cord and click through our informative guide to charge up your knowledge of batteries.

iv. Waste batteries

Waste batteries that are classified as hazardous waste can be collected under the streamlined collection standards for universal waste. These universal waste standards were created in an attempt to make it easier to collect the waste batteries and send them for recycling (or proper treatment and disposal). The requirements specific to batteries are described below.

Batteries and accumulators play an essential role to ensure that many daily-used products, appliances and services work properly, constituting an indispensable energy source in our society. Every year, approximately 800.000 tons of automotive batteries, 190.000 tons of industrial batteries, and 160.000 tons of consumer batteries enter the GCC.

Not all these batteries are properly collected and recycled at the end of their life, which increases the risk of releasing hazardous substances and constitutes a waste of resources. Many of the components of these batteries and accumulators could be recycled, avoiding the release of hazardous substances to the environment and, in addition, providing valuable materials to important products and production processes in gulf region.

To achieve these objectives, the Directive prohibits the marketing of batteries containing some hazardous substances, defines measures to establish schemes aiming at high level of collection and recycling, and fixes targets for collection and recycling activities. The Directive also sets out provisions on labelling of batteries and their removability from equipment.

It also aims to improve the environmental performance of all operators involved in the life cycle of batteries and accumulators, e.g. producers, distributors and end-users and, in particular, those operators directly involved in the treatment and recycling of waste batteries and accumulators. Producers of batteries and accumulators and producers of other products incorporating a battery or accumulator are given responsibility for the waste management of batteries and accumulators that they place on the market

v. Battery recycling

Battery recycling is a recycling activity that aims to reduce the number of batteries being disposed as municipal solid waste. Batteries contain a number of heavy metals and toxic chemicals and disposing them by the same process as regular trash has raised concerns over soil contamination and water pollution.

Most types of batteries can be recycled. However, some batteries are recycled more readily than others, such as lead-acid automotive batteries (nearly 90% are recycled) and button cells (because of the value and toxicity of their chemicals). Other types, such as alkaline and rechargeable, e.g., nickel-cadmium (Ni-Cd), nickel metal hydride (Ni-MH), lithium-ion (Li-ion) and nickel-zinc (Ni-Zn), can also be recycled.

vi. Alkaline batteries

Alkaline batteries are a type of primary battery dependent upon the reaction between zinc and manganese dioxide (Zn/MnO_2). Another type of alkaline batteries are secondary rechargeable alkaline battery, which allows reuse of specially designed cells. Compared with zinc-carbon batteries of the Leclanché or zinc chloride types, alkaline batteries have a higher energy density and longer shelf-life, with the same voltage.

The alkaline battery gets its name because it has an alkaline electrolyte of potassium hydroxide, instead of the acidic ammonium chloride or zinc chloride electrolyte of the zinc-carbon batteries. Other battery systems also use alkaline electrolytes, but they

use different active materials for the electrodes. Alkaline batteries account for 80% of manufactured batteries in the Asia and over 10 billion individual units produced worldwide. In Japan alkaline batteries account for 46% of all primary battery sales. In Switzerland alkaline batteries account for 68%, in the UK 60% and in the EU 47% of all battery sales including secondary types. Alkaline batteries are used in many household items such as MP3 players, CD players, digital cameras, pagers, toys, lights, and radios.

The alkaline battery is an advanced form of zinc-manganese dioxide batteries and thus of the Leclanché element. It shows a better performance due to three times higher capacity compared to conventional batteries. The active material of the negative electrode is zinc in powder form to reach a high specific surface. The powder is held by a synthetic gel. The positive electrode consists of manganese dioxide as active material and graphite as conducting additive, both also in powder form. A solution of potassium hydroxide with a mass fraction of 30 % to 45% is used as electrolyte and not used in reaction.

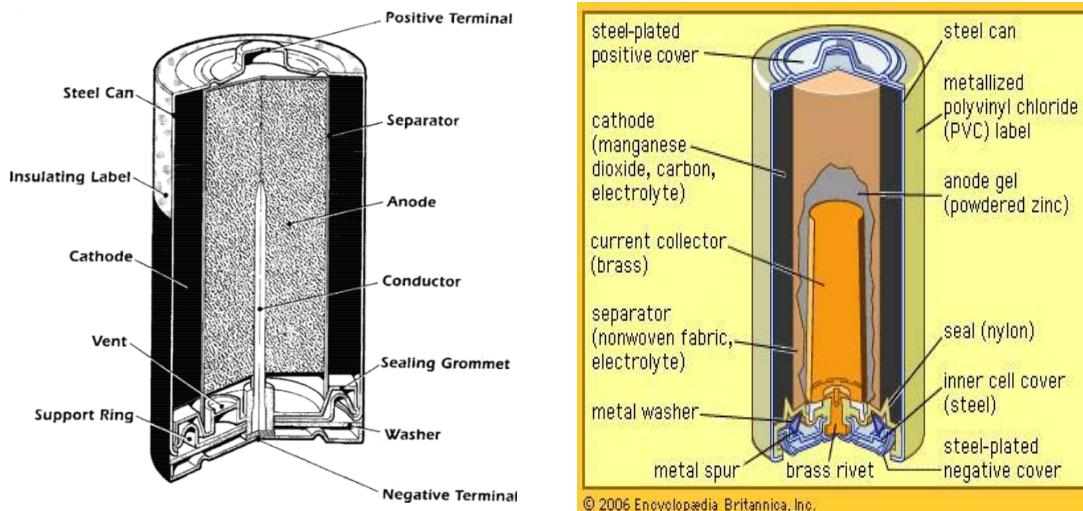


Figure 1: Alkaline battery components

The positive and the negative electrodes are separated by a material, which has to be permeable for hydroxide ions, since equal amounts of them are consumed and produced in both half cells.

b) Manganese sulphate

Manganese (II) sulfate usually refers to the inorganic compound with the formula $MnSO_4 \cdot H_2O$. This pale pink deliquescent solid is a commercially significant manganese (II) salt. Approximately 460 thousand tonnes of manganese (II) sulfate were produced worldwide in 2015. It is the precursor to manganese metal and many other chemical compounds. Mn-deficient soil is remediated with this salt.

Like many metal sulfates, manganese sulfate forms a variety of hydrates: monohydrate, tetra hydrate, pentahydrate, and heptahydrate. The monohydrate is most common. All of these salts dissolve to give faintly pink solutions of the aquo complex $[Mn(H_2O)_6]^{2+}$. The pale pink color of Mn (II) salts is highly characteristic.

Typically, manganese ores are purified by their conversion to manganese (II) sulfate. Treatment of aqueous solutions of the sulfate with sodium carbonate leads to precipitation of manganese carbonate, which can be calcined to give the oxides MnO_x . In the laboratory, manganese sulfate can be made by treating manganese dioxide with sulfur dioxide.



It can also be made by mixing potassium permanganate with sodium hydrogen sulfate and hydrogen peroxide. Manganese sulfate is a by-product of various industrially significant oxidations that use manganese dioxide, including the manufacture of hydroquinone and anisaldehyde. Electrolysis of manganese sulfate yields manganese dioxide, which is called EMD for electrolytic manganese dioxide. Alternatively oxidation of manganese sulfate with potassium permanganate yields the so-called chemical manganese dioxide (CMD). These materials, especially EMD, are used in dry-cell batteries.

Plants use manganese (Mn) for enzyme activity involved in carbohydrate metabolism. They also use it for making fatty acids in every transfers during photosynthesis. Manganese Sulphate supplies manganese, which is used to alleviate manganese deficiencies. These are most common in peat mixes. A manganese sulphate solution is used to correct and prevent manganese deficiency in a wide range of agricultural and horticultural crops.

Manganese sulphate is also applied to mixes or as a foliar application for crop production where a history of Mn deficiency exists. If applied as a foliar, ensure Manganese Sulphate Soluble is requested. Foliar sprays are the most effective way of applying manganese sulfate solution. If applied directly to the soil the manganese can become "locked up" especially in calcareous high pH soils.

Manganese deficiency occurs mainly in high pH conditions, sandy soils that are low in organic matter, organic miss (peats) and in over-limed soils. Uptake of manganese decreases with increased soil pH and is adversely affected by high levels of available iron (Fe). Cereal crops, potatoes, vines and fruit crops grown on high pH conditions are particularly sensitive to manganese deficiency.

i. Properties

Compound Chemical Formula	: MnSO ₄
Molecular Weight	: 169.02
Melting Point	: 700°C; 1292°F
Boiling Point	: 850°C; 1562°F
State at Room Temperature	: Grey/Pink Crystalline Powder
Ionic Compound	
Molecular Geometry	: Octahedral

Uses of MnSO₄: Manganese Sulfate is used in fertilizers, feed additives, paints, varnishes, ceramic, textile dyes, medicines, and fungicides.

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 be produced from manganese dioxide, performing a direct chemical

reaction between gaseous sulfur dioxide and solid MnO₂. Another process relates to the use of ferromanganese for the production of MnSO₄-solution for the electrolytic or chemical precipitation of manganese dioxides. In an alternative technology, MnO₂ 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 (H₂SO₃) will react with MnO₂ to form final product.

Any other useful information: Health Hazards for Manganese Sulfate if swallowed, it may cause gastro intestinal irritation with nausea, vomiting, and diarrhea. If contact with eyes, it may cause a mild eye irritation. If contact with the skin, it may cause skin irritation. If inhaled it may cause a respiratory tract irritation. Manufacturing of manganese sulfate (fertilizer grade) and Manganese dioxide (battery grade) were frequently the objectives of the many 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.

II. MATERIALS AND METHODS

Batteries contain cadmium, mercury, copper, zinc, lead, manganese, nickel and lithium, which may create a hazard when disposed incorrectly. The most important non metallurgical use of manganese is in the form of manganese dioxide, which is used as a depolarizer in dry cell batteries. Simply the black powder in the alkaline battery is the raw manganese dioxide powder. Our first objective is to separate this manganese dioxide powder from the battery then it is used to produce manganese (ii) sulphate.

a) Materials required

- Used alkaline batteries
- Mechanical tools
- Personal protective equipment
- Glass wares
- Sulphuric acid 98%
- Oxalic acid

i. Battery dismantling & pretreatments

House hold disposed dry batteries from different suppliers and places were collected. These batteries were manually dismantled. The steps were shown in the below figures one by one.



Figure 2: Battery dismantling

The outer shell of the battery is removed first. Then the zinc thin cover is also removed. The metallic scraps and plastic/paper films were removed if any. There is a mixture of cathodic (Manganese dioxide and graphite) and anodic (zinc and electrolytic solution) materials. That paste has 55% of the total battery weight. The graphite electrode in the center of the battery is pulled out from the cell.



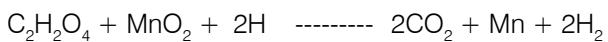
Figure 3: Battery outer cover removal



Figure 4: Battery graphite cathode removal

III. EXPERIMENTAL SETUP & PROCEDURE

The manganese sulphate is produced from the reaction between manganese dioxide and sulphuric acid in the presence of oxalic acid. The reaction of MnO_2 in the low manganese ore with oxalic acid could occur as follows:



The leaching experiments should be 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 should have two entrances used for feeding of reactants and temperature measurement. A reflux condenser may be erected on the 3rd neck to capture any escaped vapors. So that it

has very good control of the process which may yield the pure product.

But this project was carried out manually in the laboratory with different samples. In the leaching experiment the solution were prepared using distilled water, sulphuric acid and oxalic acid. The temperature of the reaction mixture were manually measure using thermometer.

When Manganese dioxide is reacting with 98% concentrated sulphuric acid in the presence of oxalic acid and yields manganese (II) sulphate. During the reaction carbon dioxide gas is evolved. The different reactions takes place during the process are

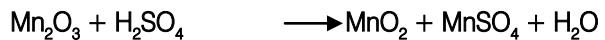
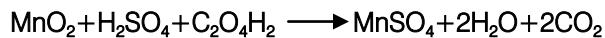


Figure 5: Manganese oxide washing

The step by step production methods are given in the below figures one by one. The battery paste (Manganese dioxide & manganese oxide) which is

collected from the batteries are washed with distilled water for many times and then filtered.

Normally the battery paste contain many impurities like the outer paper cover and other light materials. That's why it is washed so many time in order to remove those impurities. During washing with water the glass rod is continuously stirred in the battery paste so that it will be evenly distributed.

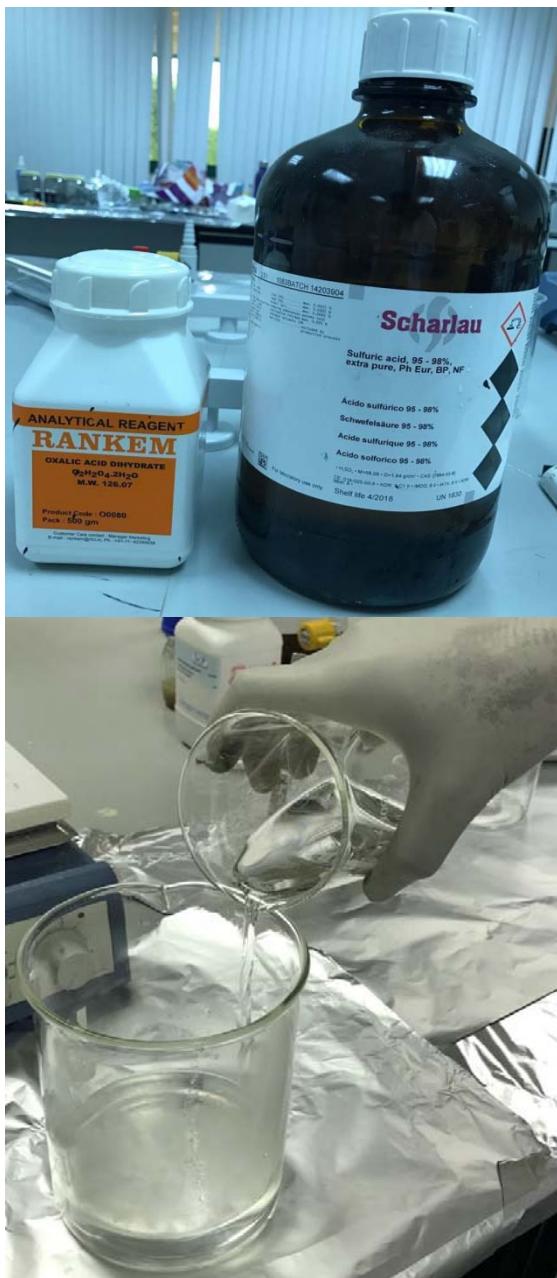


Figure 6: Sulphuric acid & Oxalic acid

The 98% sulphuric acid and oxalic acid salt were taken in different beakers. First the oxalic acid salt is dissolved in suitable amount of water. Then it is mixed with 98% concentrated sulphuric acid gently.

Now the battery paste (manganese dioxide) is kept on the magnetic stirrer hot plate and it is gently heated.



Figure 7: Manganese dioxide paste heated

The mixture of sulphuric acid and oxalic acid solutions are slowly added to the manganese dioxide paste. The reaction is carried out with evolution of carbon dioxide. The solution should be added very very slowly so that there should not be more fumes.

After adding the solution keep the mixture 30 minutes in order to complete the reaction. Then keep the solution at room temperature for 2-3 hours for cooling. The clear supernatant liquid is the manganese sulphate solution and the bottom precipitate is the reacted and unreacted manganese oxides with water.



Figure 8: Reaction



Figure 9: Reaction mixture

Then the supernatant liquid is filtered in the Whatmann filter paper in order to get the manganese sulphate solution. The solution is light pink in color and the black paste can be discarded.



Figure 10: Manganese sulphate solution filtered

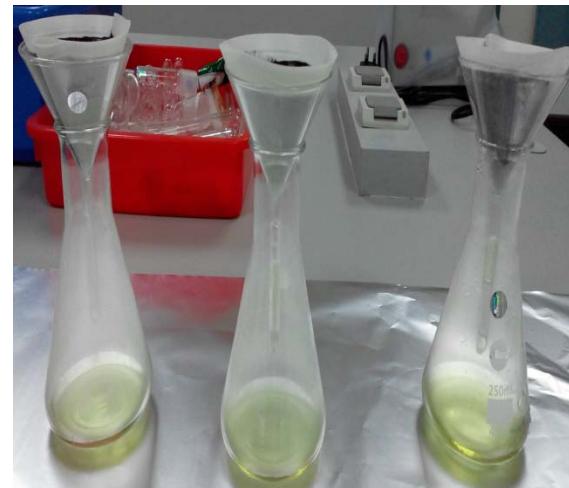


Figure 11: Manganese sulphate solution

The above manganese sulphate solutions are heated to evaporate the water and then it is crystallized by vacuum in order to get the manganese sulphate crystals.

The crystals which is formed from the solution is dried in the oven at 600C to get the dry manganese sulphate powder. This Manganese sulphate is analyzed in spectrophotometer to find the percentage is Manganese in the salt. This percentage determines its market value cost.



Figure 12: Manganese sulphate crystals



Figure 13: Manganese sulphate final product

IV. CONCLUSION

This experiment was carried out to produce manganese (II) sulphate from manganese dioxide which is extracted from waste used alkaline batteries. In UAE, the uses of alkaline batteries are vast. These batteries are simply makes the lots if environmental pollution after it is disposed to environment. Firstly this project eliminates this type of pollution. And secondly the production of Manganese (II) sulphate. Because of lots of uses of manganese sulphate, which is imported in larger quantities every year. It is one of the great business idea for chemical engineers in the present and future UAE industrial sectors. The product produced needs some more purification in order to improve the manganese content in the salt. The future studies are proposed for the quality improvement and also extracting manganese metal from the waste used batteries.

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Figure 14

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