

## RECOVERY OF Zn AND MnO<sub>2</sub> FROM SPENT Zn-C DRY CELLS

BY

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### ABSTRACT

*Hydrometallurgical process is used to recover zinc and manganese dioxide (MnO<sub>2</sub>) from spent zinc-carbon dry cell. The process, which involves electroplating of zinc and oxidation of manganese dioxide, allows for easy separation of the components. The design can produce 10kg/day of MnO<sub>2</sub> and zinc, made up of 5.38 kg. of MnO<sub>2</sub> and 4.62 kg. of zinc per day. Other metals, which are recovered in the process, include mercury, nickel and iron. The annual production cost is estimated at about ₦3,088,775 for a total production rate of 3000kg per year, giving a profit of ₦1,651,104.69.*

### INTRODUCTION

A zinc-carbon (Zn-C) dry cell is an electrochemical energy source that converts chemical energy into electrical energy. It contains

- zinc container as the negative plate,
- carbon rod as the positive plate,
- a mixture of MnO<sub>2</sub> and ground carbon as the electrolyte, in paste form. ZnCl<sub>2</sub> is added to keep the paste damp by absorbing moisture from the atmosphere.

The cell is generally used in portable transistorized radio receivers, flash-lights, electric bells, etc.

The raw materials for the chemically active parts of a Zn-C (Zn, MnO<sub>2</sub>, C, NH<sub>4</sub>Cl<sub>2</sub>, etc.) are being imported into the country, despite their availability in Nigeria. However, lack of downstream industries to process the raw materials in their raw form to intermediate stage has made the importation inevitable. In a spent Zn-C dry cell, only 30% of Zn and 33% of MnO<sub>2</sub> are used up during the discharging process, while the remaining is left as waste for disposal [Wiaux and Waeffer, 1995]. With urbanisation and high population growth, however, the disposal of dry cells, like other solid waste, constitutes an environmental hazard. The paper therefore looks at the possibility of recycling spent Zn-C dry cells with the aim of recovering Zn and MnO<sub>2</sub>, which are the two main raw materials

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**Recovery of Zn and MnO<sub>2</sub> From Spent Zn-C Dry Cells** \*Eterigho, E. J. And \*\*Adediran, Y. A. required in the manufacture of the cells and which are being imported, thereby draining the external reserve and leading to the collapse of the battery industry. Such a recovery process is already being achieved in some countries such as Japan that allows the recycling of dry cells since 1984 [Takashi and Toshio, 1995].

Two main processes that can be used in the recycling of Zn-C dry cells are the pyrometallurgy and hydrometallurgy [Wiaux and Waeffler, 1995]. The former is used for the recovery of metals from substances from their ores through the use of heat, after which various purification methods could be used. The latter, hydrometallurgical process, is used for the production of metals or metal-containing substances from different types of ores or from solid waste by means of leaching with aqueous solution, followed by purification steps. The hydrometallurgical approach is adopted here because of its outstanding advantages over the pyrometallurgical process. Its advantages include

- relatively low energy requirements, and
- near-complete recovery of metals,
- high purity products,
- avoidance of effluent emission.

Earlier designs of recycling process applied to spent dry-cells include

- the Raytec process which is successfully operating on a continuous industrial base since 1994 [Pierre, 1995].
- Batrec, operating a plant with a capacity of 3000 tonnes per year, yielding four products: ferromanganese, zinc, mercury and slag; and,
- combination of Sumitomo-Batrec process and Recytec process yielding better recovery of the metals [Mauro et al, 1994].

## PROCESS DESIGN

The hydrometallurgical process employed in this work involves many stages, comprising mainly of grinding, leaching and drying. The block diagram of the process is shown in Fig. 1.

### Kinetics of Reaction

When a cell is connected to a load, it supplies electrical energy which it had stored in chemical form. During this discharge process, chemical energy is converted to electrical energy. The reactions at the positive and negative poles are given in Equations (1) and (2) respectively as:

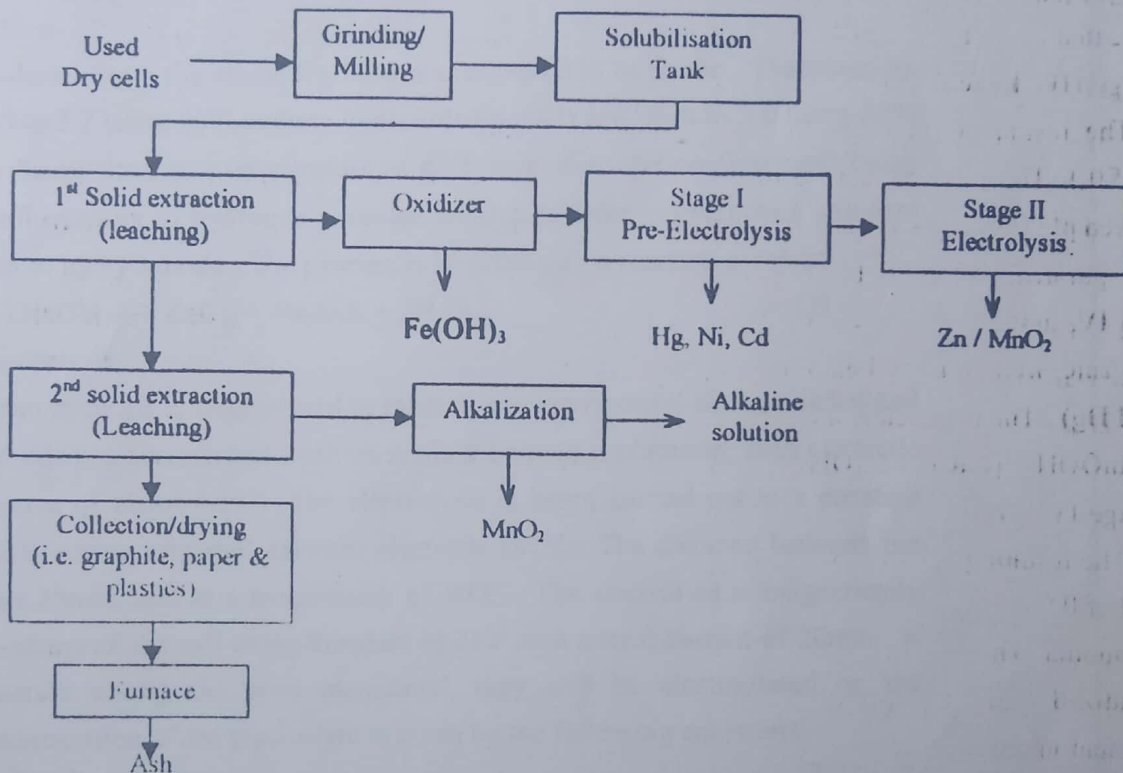
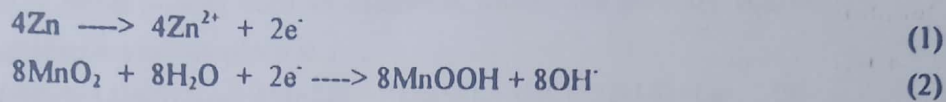
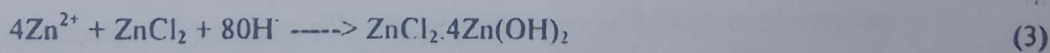
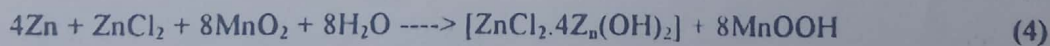


Figure 1: Block diagram of the hydrometallurgical process

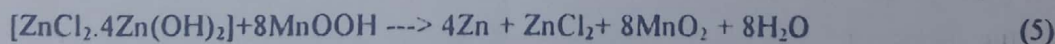
In the electrolyte, the dissociation is,



The net reaction is given as



The main equation of the recovery process is the reverse of Equation(4); that is,



## PROCESS DESCRIPTION

### Stage I - Grinding

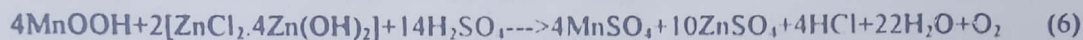
The spent dry cells are collected and dismantled in order to ease the grinding process, after which they are crushed for the same reason. The crushed cells are then ground into a powdery form in order to increase the surface area and, hence, increase the rate of reaction.

### Stage II - Solubilization

The powder from grinding stage is washed in water at a ratio of 5:1 (volume of water to weight of powder) at room temperature, for about one hour. This is to separate any soluble salts that could be in the powder. The solution is separated into filtrate and residue.

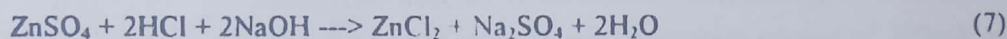
### Stage III - Leaching 1

The residue from stage II is leached using about 32% of tetra-oxosulphate VI acid (H<sub>2</sub>SO<sub>4</sub>). The ratio of residue to the dilute acid is 5:1. The leaching is carried out in a stirred plug flow reactor at a temperature of 50°C for about two hours. The resulting slurry is separated, yielding a brown black paste residue. The residue from the leaching contains Mn IV, graphite, paper etc while the leachate contains little amount of Mn II, Mn III, all the zinc, iron and any heavy metal present such as cadmium, nickel and mercury (Ca, Ni and Hg). The net chemical reaction taking place is



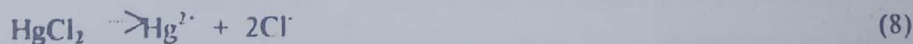
### Stage IV - Oxidation

The resulting solution from the above leaching is discovered to be acidic. Therefore, its pH of 0.9 is raised to 3.7 using 50% sodium hydroxide (NaOH) and then to 5.0 using 32% ammonia. This is being done at a temperature of 60°C with the solution (leachate) being oxidized with small quantity of hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) in order to precipitate any iron present in the form of its hydroxide. The process is an alkalization reaction given by



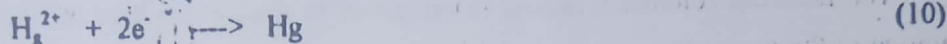
### Stage V - Pre-Electrolysis

The solution from stage IV is electrolysed to remove any heavy metal such as nickel and mercury. The cathode is a commercial steel net while the anode is platinum, each electrode having a surface area of about 6cm<sup>2</sup>. The electrolysis is being carried out at a constant potential of 900mV versus saturated calomel electrode (SCE). The distance between the electrodes is about 35mm, and at a temperature of 50°C. The electrolyte is magnetically stirred, with the voltage of the cell being constant at 25V with a total current of 20mA. If there are any metals among the ones mentioned, they will be electroplated on the electrodes. The dissociation of the electrolyte is given by the following equations:

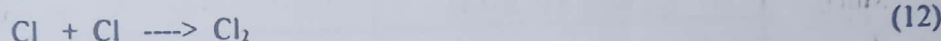


At the cathode, which is a steel net, mercury ion and hydroxide ion will migrate there for discharging; but mercury will preferentially discharge because of its high concentration as

follows:



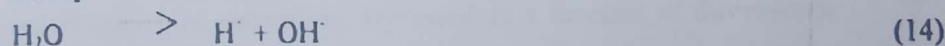
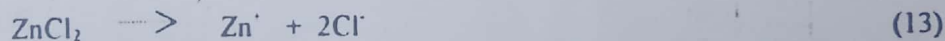
Chlorine and hydroxide ions, both migrate to the anode, that is the platinum; chlorine ion will preferentially discharge as follows:



#### Stage VI - Electrolysis

The solution coming from stage V is electrolyzed, using lead as the anode and a commercial steel net as the cathode, each having a surface area of 6cm<sup>2</sup>. The temperature is the same as in stage V, with a constant current of 300mA supplied for about 8½ hours. Almost all the zinc is being recovered and any manganese present in the solution will be deposited on the anode as an oxide. The resulting solution from the electrolysis is acidic and could, therefore, be recycled back for leaching in stage III.

Zinc-chloride and water form the electrolyte. The dissociation of the electrolyte is given as.

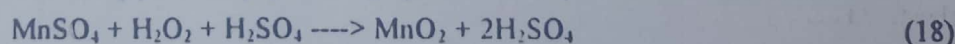


Both zinc and hydrogen ions will migrate to the anode, where zinc ion will preferentially be discharged. At the cathode are chlorine and hydroxide ions, but the hydroxide ion will discharge giving water and oxygen gas in accordance with the following equations:



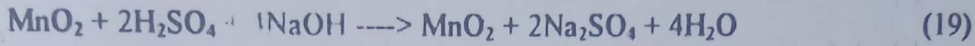
#### Stage VII - Leaching 2

The solid residue from stage III is partly solubilised, using 35% hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) at moderate heat. The leaching is then done using concentrated tetra-oxo-sulphate VI acid (H<sub>2</sub>SO<sub>4</sub>). Manganese-dioxide will completely dissolve in the solution leaving a residue containing plastics, paper and graphite. The equation of the reaction is



**Stage VIII - Alkalization**

The resulting solution is found to have a lower pH. In order to allow for easy separation of the manganese dioxide, the pH of the solution is raised, using 50% sodium hydroxide at 40°C under constant stirring. All the manganese-dioxide present in the solution is precipitated. The equation of reaction is:



The residue containing plastic, graphite and paper could be dried and burnt in a furnace, giving rise to flue gas and ash for other uses, like in the potash and shoe polish industries.

**MATERIAL BALANCE**

The main equation for the whole reaction is given in Eqn. (5), which can be used to carry out an overall material balance. A basis of 100kg/day of ground material is assumed.

The result of the material

balance is summarized in Tables 1 and 2.

**Table 1: Various reactants and their amount**

INPUT	AMOUNT (kg/day)
ZnCl <sub>2</sub> .4Zn(OH) <sub>2</sub>	43
Total	100

**Table 2: Various products and their amount**

OUTPUT	AMOUNT (kg/day)
MnO <sub>2</sub>	56.0
Total	100

**ENERGY BALANCE**

The rate of heat liberation or absorption, expressed as a function of the reaction rate and various thermal properties of the reaction system, is obtained from an energy balance. This information is then used in the design of the heat-transfer equipment for the reactor system. In other words, the specification of the duty of each equipment can only be ascertained when one has obtained the energy balance.

The total energy requirement for the process is summarized in Table 3.

**Table 3: Total energy requirement**

STAGE	QUANTITY (J/kmol)
III	488653.35
IV	19496.075
V	0.180
VI	9.180
VII & VIII	- 22776.955
<b>TOTAL Q</b>	<b>= 485381.83</b>

**EQUIPMENT COST EVALUATION**

The major components considered are: Reactor 1, Reactor 2, Alkalization Reactor, Oxidizer, Pumps, and Electrolytic tanks. Table 4 gives the summary of the cost estimates for the plant equipment.

The fixed capital cost estimate of the project is determined by using the following Lang factors [Max and Klaus, 1989]: Equipment Erection (0.40), Piping (0.70), Electrical (0.1), Building (0.15),

Instrumentation (0.20), Utility (0.50), Storage (0.15), Site Development (0.15), Auxiliary Building (0.15). With these, the total fixed cost is ₦1,040,375.88.

**Table 4: Summary of cost estimate**

EQUIPMENT NO	ITEM	COST (NAIRA )
01	Reactor 1	2,097.86
02	Reactor 2	694.85
03	Alkalization Unit	855.80
04	Oxidiser	2,430.88
05	Pumps	6,000.00
06	Electrolytic Tanks	2,380.63
<b>TOTAL</b>		<b>15,306.04</b>

The total variable cost, made up of raw material cost, maintenance and miscellaneous costs, is ₦1,767,603.67.

Other costs (sales expenses and general overheads) is taken as 10% of direct production cost, which is the sum of variable and fixed costs; and, this amounts to ₦280,797.76. Therefore,

$$\begin{aligned}\text{Total annual production cost} &= \text{variable cost} + \text{fixed cost} - \text{other costs} \\ &= \text{₦}(1,767,603.67 + 1,040,373.88 + 280,797.76) \\ &= \text{₦}3,088,775.31\end{aligned}$$

Total income realisable from the sale of zinc and manganese dioxide produced is estimated to be ₦4,739,880.00.

Annual profit is, therefore, ₦1,651,104.69.

#### BY - PRODUCT FROM THE PROCESS

The ash produced could be marketed for more income. The ash could be used in the shoe polish and potassium producing industries. From the process of leaching we have 22kg as wet residue. It could be assumed that after drying we have 21kg which was burnt in the furnace. On the whole we assumed the ash remaining to be 10kg. The selling price for 1kg of the ash can be estimated to be ₦5.00. Therefore, 10kg of the ash will sell at ₦50.00 per day giving a total of ₦15,000 yearly.

#### CONCLUSION

The dry cells industry and other chemical industries, using manganese dioxide and zinc as their raw materials can be hopeful of their availability, if recycling of spent dry cells is embarked upon. The recycling process proposed (i.e hydrometallurgy) within this work shows that zinc and manganese-dioxide can be recovered from spent carbon-zinc dry cells. It also shows that the recovery can be successfully achieved in Nigeria like other countries.

From the process, 5.38kg/day and 4.62kg/day of manganese dioxide and zinc respectively could be recovered. These represent about 91 per cent recovery of manganese dioxide and 78 per cent recovery of zinc. The huge amount of money thus spent on importation of the basic raw materials will be avoided and, probably, spent on other areas of development. The environmental hazards due to conventional disposal methods will be minimized. From the design, a total of ₦1,651,104.69 can be realised as profit from the recovered manganese dioxide and zinc.



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