PROSPECTS OF MATERIAL RECOVERY FROM SPENT AND REJECTED LECLANCHE-TYPE DRY CELLS

G. Subramanian and Navin Chandra

Central Electrochemical Research Institute, Karaikudi-623 006

Leclanche-type dry cells are the most widely used batteries in situations requiring small quantities of power for the mobile appliances (eg. transistor radios, flash lights etc.). Billions of dry cells are produced and used in the world every year. As these are primary batteries, the spent batteries are discarded.

The licenced capacity for production of these cells in India is 1500 millions, but about 900 million units are actually being produced. In a typical 'D' type cell, about 20 g of zinc, 15 g of MnO_2 and small quantities of other chemicals such as NH_4Cl, acetylene black etc. are used. Thus, the amount of materials used in preparation of these cells and discarded after the cells are spent is a staggering figure. To add to this figure, a large number of cells get rejected during manufacture. In spite of a large amount of values involved, at present there is no collection and reprocessing facility anywhere for recovery of materials from rejected and spent cells in an organised manner.

Reports on Attempts for Value Recovery

There are some scattered reports in literature describing research attempts for the recovery of materials from these cells. For example, attempts have been made to recover zinc from rejected cells in USA by melting the zinc cans after removing other materials. The reason given for non-commercialization of the process is that mercury vapours are ejected in the process of melting which cause atmospheric pollution [1]. Two Japanese patents [2,3] describe the procedure of obtaining Mn_2O_3 and $ZnCl_2$ from spent cells while a U.S. patent [4] describes the procedure for simultaneous recovery of zinc and MnO_2 by electrolysis. A review on recovery of zinc from used dry cells is also available [5].

Environmental Aspect of Dumping of Spent and Reject Dry Cells

A study conducted for National Electrical Manufacturers Association (USA) revealed that the cost of collection of spent dry cells and recovery of metals therefrom was not economically feasible and the presence of dry cells in the municipal wastes does not pose any threat to the environmental pollution. [1]. In this regard, it is, however, to be noted that in the municipal wastes, dry cells are dumped along with other refuse containing various organic and inorganic wastes. The possibility of formation of organo-mercury complexes (eg. methyl-mercury, ethyl – mercury etc.) in isolated cases cannot be ruled out. The problem can assume alarming proportions if organic wastes and rejected cells from industries in a large number are dumped together.

Economic Aspects of Recovery of Values from Reject and Spent Dry Cells

The economic feasibility of a process depends on the local factors in a country; due to high labour costs, the recovery of values from spent and reject cells in USA is not attractive but in Indian context, where the labour is cheap ($ 4.03 minimum wage per hour in USA compared with less than Rs.2.00 per hour in India), the recovery process is economically viable. Further, since zinc is mainly imported in India, its recycling will help in saving foreign exhange.

Thus, in view of economic attractiveness and environmental protection, recycling of materials from rejected as well as spent dry cell deserves serious consideration in our country.

Materials Used in the Production of Dry-cells

The materials used in the preparation of dry cells are listed below:

1) Zinc can
2) $MnO_2 + NH_4Cl + ZnCl_2$ mixture
3) Graphite rod
4) Brass cap on graphite rod
5) Steel or other casing used in the case of leak-proof batteries

Zinc: Zinc is the most value-fetching material in the recycling of dry cell materials. A typical D-type cell uses 20 gms of zinc metal. The freshly discharged dry cells may contain 40 to 50% of this amount in metallic form but with passage of time more of the materials is lost due to corrosion. The zinc can be recovered from dry cells either by pyrometallurgical or electrochemical process.

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Pyrometallurgical Process for the Recovery of Zinc: The process [4] for recovery of zinc from assembly line rejects consits of breaking of the cell mechanicallay and screening. The chemicals, carbon etc. pass through the screen and the retained material is melted in the furnace. The floating materials are removed and the molten zinc is drained off.

Pollution of the atmosphere by mercury vapours arising out of the light amalgamation of the zinc anode is reported to be the reason for not commercializing the above process.

The mercury pollution during melting can be overcome by slightly modifying the process and melting under isolated atmosphere and condensation of Hg vapours by coolling the emanating gases.

After breaking the cans, the zinc rich portion can be separated and washed with diluted HCl and screened. The retained portion, after magnetic separation of iron pieces present (if any), can be melted in a closed vessel fitted with an outlet to remove emanating gases. Mercury vapours in the emanating gases can be condensed by cooling. The molten zinc can be tapped from the vessel.

Electrochemical Process for Simultaneous Recovery of Zinc and MnO_2 : A process reported for simultaneous recovery of zinc and MnO_2 from spent and rejected dry-cells consists of crushing and wet sieving followed by magnetic separation of iron from the retained material. the iron-free retained material is then dissolved in acid and filtered. The filtrate is converted to sulphate and electrolysed to obtain zinc and MnO_2 on cathode and anode respectively.

In one of the Indian industries, it is reported that the quality testing is carried out before sealing. In the case of rejected cells, the contents are manually removed and the zinc can are reused after washing with HCl.

MnO_2 : MnO_2 can be recycled from both spent as well as rejected cells by electrolysis process described earlier under zinc recovery.

Alternatively, it can be precipitated as Mn_2O_3 following the procedure described in Japanese patents.

Manganese as Micronutrient for Plants: Yet another attractive alternative is to use the manganese as micronutrient for plants. For this purpose, the following procedure can be adopted. After breaking the spent/rejected cells and removing zinc-rich portions, the remainder can be crushed and iron particles removed by magnetic separation. The iron-free portion is dissovled in H_2SO_4 and filtered. The filtrate contains sulphates of zinc and manganese. Both these materials are good for plants and hence can be crystallised and sold with fertilisers after powdering and mixing with appropriate diluents.

The Unbroken Graphite Rods: Recovered from rejected cells can be reused after suitable washing. The graphite rods from spent cells, however, need very thorough cleaning and pretreatment, the cost of which may not justify recycling process.

The Brass Cap: Fitted on graphite rods can be picked manually after breaking the spent/rejected cells and melted to obtain brass.

Steel casing used in the case of Leak-Free Batteries: These can be separated by magnetic field after breaking the spent/rejected dry cells. The iron pieces can be charged in the steel making furnances. The amount recovered may not, however, be appreciable.

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