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Impact of household batteries in landfills

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Abstract

Heavy metals are present at different levels and concentrations in all the household dry batteries. The related environmental hazard is well known. The heavy metals are toxic and thus liable to produce serious problems for the health of the population and for the maintenance of the biosphere. Therefore, there has been recently an increasing concern on the risk associated with uncontrolled disposal of exhausted dry batteries. In this paper, we report on the efforts in progress in Italy for collecting spent batteries, as well as the most suitable strategies which can be followed to assure their safe disposal.

Keywords: Batteries; Disposal; Household batteries; Italy

1. Introduction

Typical household portable devices, such as watches, cameras, radios, tape recorders, toys, etc., are conveniently powered by dry batteries, namely by primary cells using immobilized electrolytes [1,2]. Consequently, the world production of these batteries amounts to several billions of units per year [2]. In Italy alone, the dry battery market is estimated to be approximately 400 million units per year, with a pro-capita consumption of 0.4 kg for a total of 20 000 tons [3]. From Fig. 1, which illustrates the annual turnover of the Italian household battery market, it appears that the most used are the zinc–carbon and the alkaline manganese dry batteries, which alone contribute to more than 90% of the total national market. While these two cells are used for mass consumption, mercury and lithium cells are directed to a somewhat more specialized market which may involve sophisticated devices, such as expensive cameras, medical and military equipment. Following the general trend of industrial countries, including Italy, there is a decline of zinc–carbon in favour of alkaline manganese cells and, in specialized area, a constant increase in the innovative lithium batteries over traditional systems, such as the mercury cells (Fig. 1).

As is well known, all the common dry batteries use zinc as the negative electrode. In fact, this metal offers a series of advantages as the electrode material, which include a favourable electrochemical factor (i.e. a favourable ratio between potential and mass), a relatively low-cost and versatile processability. However, to prevent corrosion and to increase the mechanical resistance of the zinc anode, until recently, small quantities of mercury and cadmium were added to the battery system [2]. Consequently, these heavy metals – and mercury in particular – were inevitably present, even if at different levels and concentrations, in all the exhausted dry batteries.

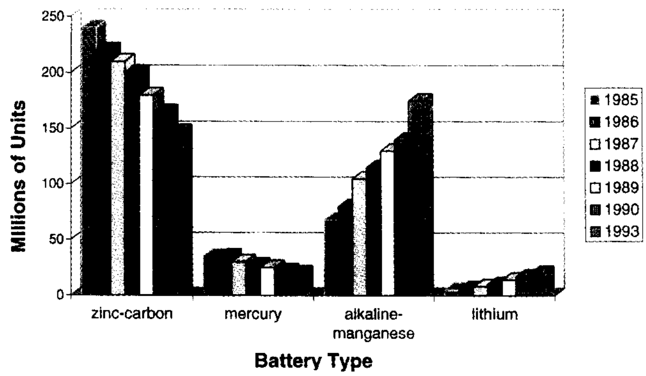

Fig. 1. Evolution of the Italian market of household dry batteries.

The related environmental hazard is well known: mercury and cadmium are very toxic metals and are liable to induce serious risk for the health of the population and the environment. Thus, in recent years, concern over the environmental risk associated with the uncontrolled disposal of exhausted batteries has consistently increased. Accordingly, in 1991 the Commission of the European Community has passed a draft imposing directions on the member Countries for issuing a legislation on the evaluation and on the disposal of batteries containing hazardous materials [4]. In synthesis, the draft imposes a reduction in the heavy metal content in dry household batteries and the promotion and commercialization of new batteries with reduced the amount of hazardous materials

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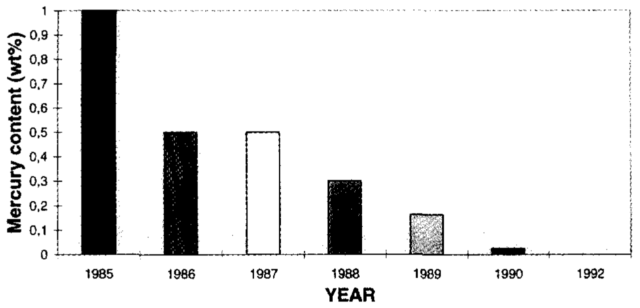

Fig. 2. Evolution of mercury content (wt.%) in alkaline-manganese household dry batteries.

and/or based on non-polluting components. In particular, the draft fixes at 0.025 wt.% the maximum mercury content allowed in commercial alkaline-manganese batteries.

The major battery producers have adapted their products to this recommendation and consistent improvements have been achieved in the recent years, to the point that the mercury and cadmium content in dry batteries sold for mass consumption has been reported to be reduced to almost 0% for both in the case of alkaline manganese (Fig. 2) and zinc–carbon (Fig. 3) cells.

This is certainly a promising result; however, the above numbers have to be taken with some care since they are deduced from average figures and without considering the contribution from batteries arriving to the European market from Countries where control in the content in heavy metals may not be a major concern and which may still represent a significant fraction of the total sale in Italy. Furthermore, although the elimination of mercury and cadmium is certainly of importance, this does not necessarily mean that the batteries are safe and suitable to be directly inserted in the solid urban waste stream. Indeed, various aspects of battery disposal are far from being solved and the procedures for approaching this important problem vary from country to country. In this work, we report on efforts presently in progress in various Italian cities for collecting and disposing exhausted batteries. Furthermore, the results of an analysis of the heavy metal content of a few different commercial battery prototypes, as well as simple methods for their inertization and recovery, are also reported and discussed.

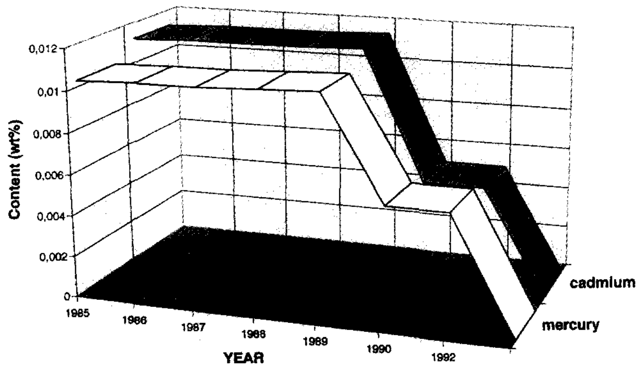

Fig. 3. Evolution of mercury and cadmium content (wt.%) in zinc–carbon household dry batteries.

2. Experimental

The determination of the total heavy metal content in seven 'spot' samples of different commercial batteries was carried out by the following procedure. The dismantled battery sample was placed in a beaker containing diluted 1:1 (v/v) HNO_3 for 24 h. The dissolution was completed with a microwave mineralizator (Model CEM MDS-81D) by exposing the sample to an acid attack program which develops in two steps, namely 10 min 20% full power followed by 10 min at 50% full power (full power corresponding to 600 W). Afterwards, the sample was concentrated to 5 ml and then filtered (using a 0.45 micrometry millipore filter on a Swinnex support) and brought to a final volume of 100 ml with distilled water.

The heavy metal content was determined using plasma emission spectrophotometry for the detection of Mn, Zn, Pb, Ni, and atomic absorption spectrophotometry (VARIAN Spectra 400) for the determination of Cd (GTA-96 graphite furnace) and of Hg (cold water technique). The releasing tests were carried out on two samples for each of the selected seven commercial battery types. Each sample was reduced to a maximum of 9.5 mm granulometry, placed in a beaker in which distilled water was poured up to 16 times the weight of the introduced solid material. The whole was stirred for 24 h keeping the $pH<5$ by continuous and programmed additions of 0.5 M acetic acid, maintaining the total amount of added acid within 4 cm^3 g^{-1} of the battery material. The heavy metal content was then determined by inductively coupled plasma (Jobin-Yvon-Type III Sequential) spectrophotometry for Mn, Zn and Ni, while Pb, Cd and Hg due to their low content were determined by atomic absorption spectrophotometry (see above).

The recovery of zinc was carried out by placing the dismantled battery sample in a beaker in which 50 cm^3 of HCl (1:9) were poured until complete solution of the metals, as chlorides, was achieved. The solution was left at rest for 24 h and then submitted to electrolysis. The latter was conducted at constant current using a steel working electrode (0.07 cm^2 surface) and a steel (or platinum) counter electrode. To prevent water splitting, the acidity was lowered by the addition of ammonium tartrate and by drop-by-drop addition of sodium hydroxide. The amount of deposited zinc was detected gravimetrically.

This treatment process was a modification of the traditional lithosynthesis inertization processes which involve mixing of the waste with a cement/silicate slurry. It was optimized by introducing a third component (a complex silicate) into the slurry.

3. Results and discussion

3.1. Collection and disposal of exhausted batteries in Italy

At the present state of knowledge, it is difficult to assume that the exhausted batteries can be directly dumped in com-

Table 1
Separated collection of exhausted batteries in some Italian cities

Cities	Inhabitants (1994) (millions)	Special containers (N°)	Amount of exhausted batteries (t/year)
Milan	1.3	501 (street) 1360 (others)	90
Padua	0.213	547 (street) 40 (others)	17
Modena	0.175	40 (street) 68 (others)	16
Bologna	0.391	2029 (total)	44
Florence	0.405	1353 (total)	39
Rome	3.5	1215 (total)	44
Naples	1.1	separated collection in program	
Palermo	1.27	400 (total)	

mon landfills without affecting the ambient conditions. A proper environmental control requires an appropriate disposal, which can only be obtained with a separate collection of exhausted batteries, followed by inertization and/or by recycling processes.

In fact, the Italian Government has listed exhausted dry batteries in the category of hazardous wastes and has imposed their collection separate from the other solid urban waste. However, although this law has been in force for several years, the results have not been very encouraging: reasonable efforts have been undertaken only in some regions of the central and the northern part of the country. Even in these cases, separate collections amount only to 20–30% of total battery consumption, as indicated by the data in Table 1 which reports the results obtained in some sample Italian cities. There are various reasons, mainly related to promotional and economical aspects, which may account for such a somewhat disappointing result. In fact, a successful treatment of the exhausted batteries requires the promotion of an adequate and persistent campaign to solicit public opinion on the opportunity of separate disposal, as well as a consistent investiment for assuring a widespread collection and an efficient disposal. Consequently, only the richest municipalities have so far had the possibility of affording an efficient and widespread battery collection policy. In fact, it is not surprising that the most successful results have been achieved in the central and northern part of Italy, namely in these regions which are traditionally the wealthest in the country. In the south, where most of the cities are still affected by serious economical and social problems, the separate collection of batteries is still an action to be started or even to be programmed.

The collection of exhausted batteries in Italian cities is generally organized by installing street or shop containers from where the disposed batteries are collected and stored. However, the collection is only one part of the procedure: disposal and, hopefully, recycling are still the most crucial and often unsolved parts of the battery waste cycle. According to the present legislation, the collected batteries should either be disposed in special 'type C' landfills or, in the case of the unavailability of the latter, they should be treated for inertization before being disposed in common 'type 2B' landfills [1]. Because of the lack of special landfills and of adequate treatment and separation plants, most of the Italian municipalities simply store the batteries, to eventually ship them abroad to those countries having landfills available for battery waste acceptance.

The Italian situation is not unique; in fact, apart from Switzerland where two plants for the treatment and recycling of batteries are presently in operation [5,6], other European countries suffer from a lack of appropriate procedures for the disposal of spent batteries. It is therefore quite surprising that relatively little attention has been devoted to the problem of the battery waste so far. Apart from a few research reports [7,8] and international conferences [9], no special and systematic work has been so far dedicated to the solution or, at least, to the identification of the difficulties which still prevent the establishment of effective procedures for recycling spent batteries.

Many questions are still to be answered. First, whether the commercial, so called 'mercury-free' or 'green' batteries can be directly disposed in common landfills with no consequent environmental risk. Second, whether simple, low-cost treatment processes can be identified and proposed for appropriate inertization of the battery waste prior to its disposal. Third, the major question whether recycling plants operating with economical benefits can be effectively realized.

With the aim of providing some contribution to the answer of these questions we have first analysed seven different types of commercial batteries to establish their residual metal content. Then, we have identified and tested an experimental process for battery treatment and metal recovery. No attempt has been made to provide an answer to the third question, since this is expected to be provided by the Conference to which this Proceeding Volume is devoted.

3.2. Analysis of spot samples of spent commercial household batteries

Seven different types of commercial dry household batteries were dismantled and analysed for their metal content. The results, obtained as the average of four different determinations for each battery type sample, provided the following indications.

(i) Mercury is absent in most of the batteries. However, in a few cases traces of the metal are still present. Therefore, the 'true' mercury-free condition is not reached by all the products examined.

(ii) Cadmium is present in traces in all samples, probably as an impurity of other metals.

[1] 2B and 2C are designations for 'second category' landfills by Italian law.

(iii) Lead is present in amounts ranging from 0.024 to 0.114 wt.%, and to even 0.26 wt.% in the case of one sample. These contents are somewhat high, and may be a matter of concern.

(iv) Obviously, zinc and manganese are at high levels. A high content of manganese may give rise to environmental risks.

3.3. Releasing tests

Further information on the disposal impact of commercial batteries has been obtained by performing a releasing test using an acetic acid solution as the extracting liquid. The aim of this test was to evaluate the impact of the eluate on waste waters. In fact, eluating with acetic acid is a procedure used to mimic the biochemical action occurring in typical urban waste landfills. Although this method is obviously recommended for evaluating the effect of wastes of organic type, it is also considered suitable to define the release of toxic metals from dismantled batteries. From the results of the test (where the concentration of the detected metals is expressed in terms of mg l^{-1}), the following may be noticed.

(i) As expected and obvious from the chemical analysis, mercury is not released by the effective mercury-free batteries; in the two other analytical methods, the mercury content is slightly higher than the limit (0.05 mg l^{-1}) fixed by present the Italian law for the acceptance of wastes in common 'type 2B' landfill [10].

(ii) The cadmium concentration is very low and within the accepted limit (0.02 mg l^{-1}) for all cases. A similar situation applies for lead, whose concentration limit is set to 0.2 mg l^{-1}.

(iii) As expected, an opposite situation occurs for the concentrations of zinc and manganese which, for all cases, are greater than the fixed limits of 0.5 and 2 mg l^{-1}, respectively.

(iv) Finally, the content of nickel is low and always within the fixed limit of 2 mg l^{-1}.

3.4. Recovery and treating processes

The data of the above described tests suggest that, although with a low level of Hg, Cd and Pb, the batteries cannot yet be accepted for direct disposal in common landfills without a pretreatment to remove the residual high Mn and Zn content. The question here is whether such pretreatment processes can be easily achieved and carried out on a large scale at low costs from the urban municipalities. In an attempt to provide some elements of evaluation, we have considered a simple treatment process which first involves the recovery of zinc by electrolysis, followed by an inertization process of the residue.

The first step involved the dissolution of the dismantled battery samples using a HCl attack. The resulting chloride solution was separated from the residue and then electrolyzed using stainless-steel as the working and the counter electrode. This first step is operationally simple and provides a straightforward and economical way of recovering zinc. The second step involved the treatment of the residue by a modification of traditional lithosynthesis inertization processes. The latter achieves the entrapment of the heavy metals in a siliceous matrix [8]. The main drawback of these processes, namely their inability of trapping Hg, was solved by introducing a complex silicate to the liquid cement slurry [11]. Our modified process leads to a final residue which was again submitted to the acetic acid releasing test in order to establish its validity. The results clearly indicated that, following the treating process, all the metal levels were indeed reduced well below the fixed limits.

4. Conclusions

The processes of battery disposal in Italy and, presumably, in most European countries, are far from being optimized. The collection of the exhausted household battery amounts to only a fraction of the total scale, and the waste procedures are not yet clear and uniformally established. The major battery producing companies have consistently reduced the mercury and cadmium content. However, tests run on commercial batteries, although far from being conclusive, considering the small number of samples examined, tend to suggest that even the so-called 'green batteries' cannot be disposed directly in common urban landfills. Pretreating processes are always necessary to reduce the Mg and Zn levels. These processes do not appear to be too complicated or too expensive. A simple example, based on Zn recovery by electrolysis followed by inertization, is proposed here as an effective action to reduce the metal levels to values well below the limits set for common 'type 2B' landfills. These results are very preliminary but they are promising in suggesting that with efforts from the battery community the problem of a safe disposal of exhausted batteries could possibly be achieved with consequent great benefit for the conservation of the environment and the health of the population.

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