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Recycling zinc batteries: an economical challenge in consumer waste management

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Abstract

The zinc battery has become the most popular source of portable electrical energy. Worldwide, more than 300 000 tons of batteries are sold yearly. As the battery weight becomes less and less important for a given delivered power, battery weight averages between 10 g per unit for AAA models and 140 g for D-size batteries. It is reckoned that 25 000 units are present per ton and a number as big as 7.5 billion cells are sold yearly to consumers: more than one cell per inhabitant of the world. It is a human challenge to achieve the recycling of consumer-type batteries. Individuals should cooperate in such a program in order to ensure its success. For spent consumer batteries, collection rates as high as 60% have been reported in countries like Austria, Denmark and Switzerland. Such performances will be achieved with difficulty in other bigger countries. Is it necessary or useful to recycle zinc batteries? In order to answer this fundamental question, various elements will be considered in this paper, such as the energetic balance of the chemically active part of the battery, the value and the supply of the materials and finally the important steps and alternative routes to the recycling of zinc batteries.

Keywords: Recycling; Zinc batteries; Switzerland; Economical aspects

1. High added value consumer product

Flashlight batteries can be purchased at a value of less than one dollar per unit. Small AA cells used in walkman and CD lecturer are sold by pack of four units at a price of two to four dollars. Due to the fact that they are sold in small quantities, these batteries appears to be inexpensive. When lithium cells and rechargeable batteries are purchased at a much higher price, the consumer realizes that a battery is an expensive item of the electronic component market. Fig. 1 indicates the market price of various engineered products. When the price of zinc batteries is reported at the level of a unit weight of 1 kg of commercial product, it can be classified as a high added value product. This becomes even more obvious when one compares the value of zinc batteries with some other materials made of zinc or for which zinc is a major component together with another material: zinc ingots, laminated zinc products, zinc galvanized steel structures, zinc pigments for paints, etc.

In Fig. 2, the various steps from the manufacture of zinc into a battery are presented as a function of their added value and their transformation steps into a consumer product. The manufacturing of a battery is the result of an impressive assembly process which brings elements like carbon, manganese dioxide, ammonium chloride, potassium hydroxide and zinc (the chemically active parts of the cell) together with brass, lead, steel, nickel plated steel parts, synthesis separators and plastic labels (the inactive parts of the cell).

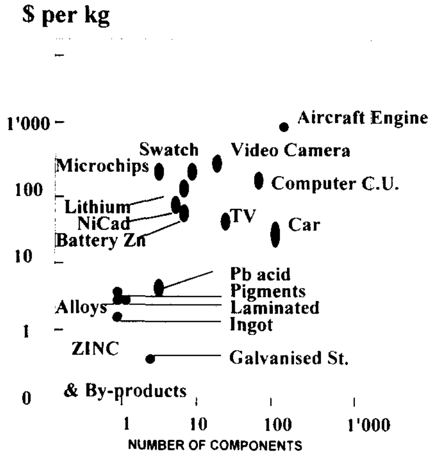

Fig. 1. The value added to engineered materials and zinc-based products.

In these conditions one would expect that a 100% of the active materials would be used in the final application. This is not the case as only 30% of the zinc is used for its electrical power capacity while the remaining portion is left in the cell. Indeed, an AA alkaline cell will practically deliver 1.4 Wh

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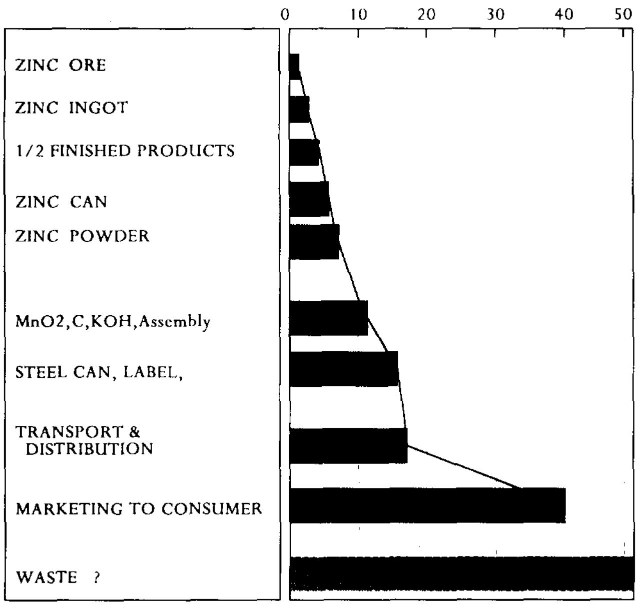

Fig. 2. Added value to zinc batteries during their manufacture in \$/kg.

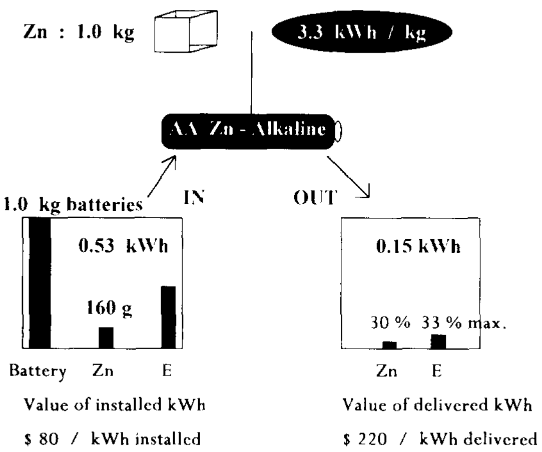

Fig. 3. Material and energy balance in zinc cells.

of electric energy while the amount of zinc stored physically in the battery has an energetic content equivalent to 10.0 Wh. The analysis of the energetic efficiency of the battery's use is presented in Fig. 3. It leads to the following conclusions:

- The price per kWh of delivered energy is much greater than the equivalent energy from a distribution network (mains power supply): \$0.10–0.20 per kWh from the distribution network versus \$220.00 per kWh from batteries
- On the materials balance side, one has to realize that only 25 to 35 wt.% of the zinc in a battery is used for the production of electric energy
- Considering the amount of energy in the battery associated with an energetic metal like zinc and the energy recovered by using the battery, it can be concluded that only 25% at the maximum of this energy is recovered. The electrolytic production of zinc requires 3.3 kWh per kg of metal

Other components of the battery like manganese dioxide, iron and various chemicals are energetic materials: energy has to be spent for their manufacture which should not be lost.

2. Zinc as a resource

Zinc is present in a limited amount on the earth. Data provided by a study of the US Bureau of Mines has revealed that the world resources of zinc, at the current technical level achieved for mining, are in the range of 20 to 40 years [1]. Those can be estimated to double with more advanced mining processes. Another factor to be accounted for is the fact that more than 50% of the world zinc consumption is realized by seven of the more industrialised countries [2].

3. Entering the recycling route

The volume of zinc used in batteries is very low compared with the other uses of this metal. From the 6×10^6 tons of zinc used annually in the world, the consumption of the metal for batteries accounts only for less than 1%. If one considers that 300 000 tons of batteries are on the market, the volume of zinc consumed in these batteries is of the order of 16% per unit or a total of 48 000 tons of metal (not taking into account the zinc chloride used in saline zinc–carbon cells).

This quantity represents an equivalent of 0.8% of the world production. It explains probably why the zinc industry is adopting a conservative attitude towards the recycling of zinc batteries. As shown in the Fig. 4, more advanced attitudes have been adopted in the recycling of lead batteries and nickel–cadmium batteries. The use of metals like lead and cadmium in batteries represents more than 80% of the application of these metals.

A battery is a composite consumer good which includes synthetics and plastics, iron and carbon, manganese dioxide and chemicals entering the electrolyte composition. When zinc batteries are collected, they are always accompanied by

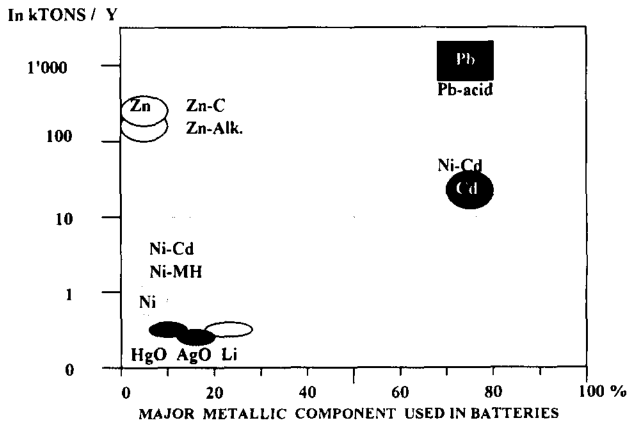

Fig. 4. Percentage of major metallic components used in batteries as a percentage of annual world production of the metal: (□) low recycling rate, and (■) high recycling rate.

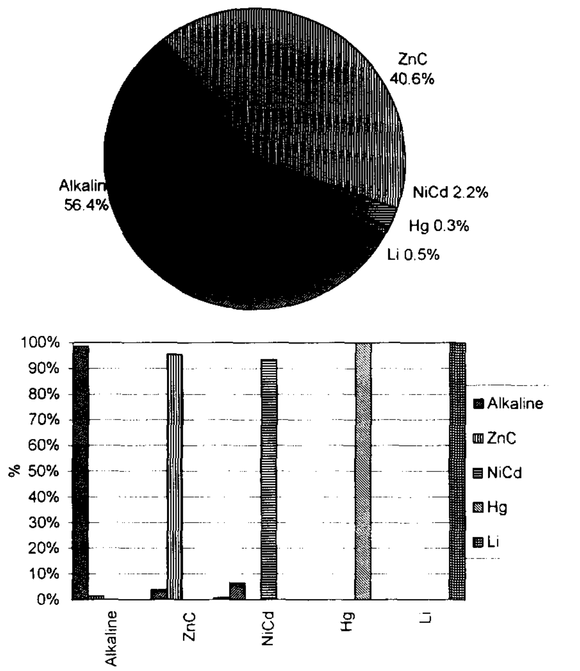

Fig. 5. Statistics of automatic sorting out of spent batteries: (a) initial composition, and (b) result of sorting out according to chemical nature.

a lot of other types of batteries like buttons cells, nickel–cadmium and lithium batteries. Very soon, collection will include nickel–metal hydride batteries. Finally, zinc batteries are not uniform in composition. Zinc batteries manufactured in the Far East still contain mercury. Saline batteries are manufactured with ammonium chloride and zinc chloride in the electrolyte while alkaline batteries have an electrolyte based on potassium hydroxide.

The recycling industry of zinc batteries is facing the problem of a primary selection before any recycling step. Indeed, no production engineer operating a metallurgical plant likes to have irregular feedstocks due a continuous variation in the composition of the inlet stream. The sorting out of spent zinc consumer batteries can be achieved automatically by a process which combines the mechanical sorting out and the identification of batteries according to their chemical properties [3]. The advantage to sort out the various spent batteries, is to give to the process engineer of a recycling plant a tool for selecting the composition of the process inlet stream. No doubt, this will influence the optimization of the process parameters and the quality of the final products. The importance of sorting out spent batteries on a large scale was recognized by the European Portable Battery Association which is facing the contamination of zinc batteries by mercury- and cadmium-containing elements when battery recycling is considered on a large scale [4].

For example, when large quantities of nickel–cadmium batteries are collected, there is an obvious economical incentive to sort them out from other types of spent batteries. In the future, the presence of a wider range of chemical elements on the battery market (like nickel–metal hydride and larger quantities of lithium cells) will also require an efficient process for the selective removal of these batteries from the large volume of zinc-based batteries. For municipalities, the sorting out of batteries can solve several critical problems like the removal of mercury- and cadmium-containing materials from municipal waste treatment and/or from controlled dumping sites. Using a sorting out process of spent batteries favours the following steps in the recycling scheme:

- selective recycling routes for secondary metals
- efficient recycling rates
- higher purity of recovered metals
- removal of undesirable products
- safer storage conditions of hazardous waste
- higher recycling ratios for materials like mercury, lead and cadmium

Results obtained on the efficiency of the separation of spent batteries are presented in Fig. 5.

4. Various methods to manage spent batteries

Several routes exist for the handling and treatment of spent batteries: from dumping to recycling, all of them, are characterized by the price to pay for the final handling of a spent consumer product. Fig. 6 summarises these various options.

4.1. Incineration

The incineration problem of spent batteries in a municipal waste incinerator (MWI) resides in the consequence of the incineration. The study of the outlet flow of metals from the

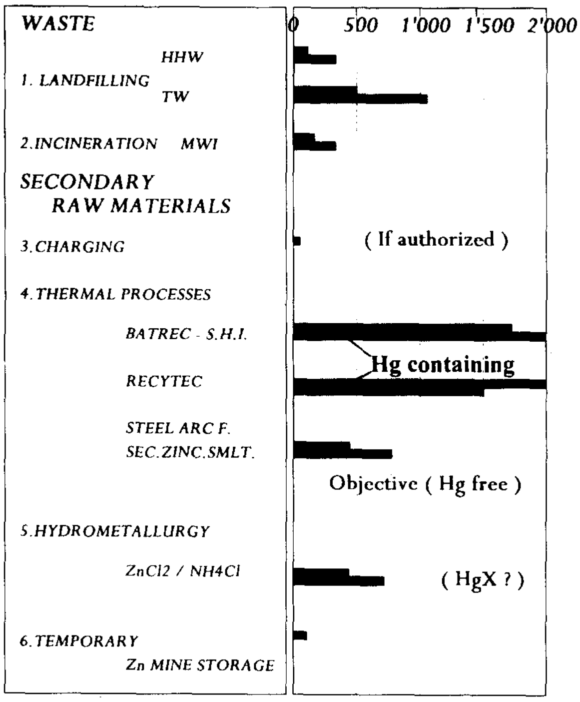

Fig. 6. Various options for the management of spent zinc batteries; cost in CHF/ton of batteries. HHW = household waste. TW = toxic waste. MWI = municipal waste incinerator.

MWI demonstrates that zinc metal will end in slag and in fly ashes. Slag can be re-used in concrete materials for road construction application. Consequently, the major problem in incinerators is the management of fly ash and sludge produced during the neutralization of outlet gases. One needs to take into account that a majority of the processed zinc will leave the incinerator in the acid fumes. They will be collected by electrofilters and by the neutralization steps. The composition of fly ash reveals that the major metallic constituent is zinc and the second major metal is lead [5].

It costs CHF 300 per ton to incinerate municipal waste in Geneva. The equipment of electrofilters and of the neutralization towers has required a budget of CHF 30 to 40 million. The incineration of 250 000 tons per year of municipal waste produces 5000 tons of fly ash that will be neutralized and stabilized at a value of CHF 1000 per ton of dry material. This requires an annual budget of CHF 5 000 000 in order to manage the waste, which requires an increase in the municipal waste management of CHF 20 per ton.

4.2. Landfilling

Spent batteries can be considered for landfilling as household waste or as toxic waste material in a controlled landfill site. In Europe it costs CHF 150 to 300 for landfilling household waste. If one ton of zinc batteries (mercury free) is deposited in a normal landfill then the value added corresponds to an average added value equivalent to these prices. In Switzerland the Federal law on environmental protection does not allow such a practise, but it is accepted in several other European countries. In the second case, if considered as toxic waste, the stabilization of the batteries in concrete would allow them to be considered for dumping in controlled sites. This operation would require an added value of CHF 1000 per ton of batteries. The disadvantage of this option is that the valuable fraction of a high added value consumer product is definitively lost.

4.3. Charging

The recharge of certain types of zinc batteries (mainly the alkaline type) has been known for many years. This possibility was recently offered to the public by the commercialization of several appliances. One must immediately confirm that the battery industry is not supporting the use of such equipment. The explosion hazard exists even if its occurrence has not been observed recently. It is obvious that the recharge of these batteries at the level of a minimum of ten cycles would rationalize the overall value added ratio. Two reasons prompt this remark:

(i) the energy needed to recharge 1 kg of an AA cell would account for 0.15 kWh. This represents an amount of CHF 0.03 per kg of battery, and

(ii) on the energetic balance aspect, any discharge/charge cycle, even with a minimum efficiency of 33% represents a net saving versus any other recycling option.

4.4. Pyrometallurgical and thermal treatment

Recycling of spent batteries by processes like the SUMITOMO-BATREC process, has now reached the industrial-scale level. With a recycling capacity of 160 tons per month, the yearly targeted volume has been reached.

It is now possible to apply realistic numbers on the process economics. We will take two figures as probably an optimization of the process is feasible by further improving and scaling-up the technology.

With a value of CHF 4800 per ton of recycled batteries, this process is obviously the most expensive from the point-of-view of value added to the base metal. It is feasible to consider a low-cost option for the treatment of mercury-free materials which would bring the price down to the value of CHF 1700 per ton.

When the RECYTEC process is considered the current option, which consists in a demercurisation step associated with the separation of the ferro-magnetic fraction, leads to price reductions for the treatment of spent batteries. A powder containing the chemicals from the batteries is concentrated and delivered to the secondary zinc smelters.

Other pyrometallurgical routes have been considered like the treatment of mercury-free alkaline batteries in the secondary steel arc furnace or in secondary zinc smelters [4]. When treated in the steel arc furnace, the zinc present in batteries will be evacuated with the flue dust and will need to be further processed in a secondary zinc processing plant.

In secondary zinc smelters, one would process the majority of unreacted zinc left in batteries without difficulty. It is not obvious if the zinc chloride content would be recovered as metal or evacuated in the flue dust as a volatile element and further collected in filters. Values for such treatments may rank between $300 per ton and $700 per ton. This turns out to be one of the cheapest routes to zinc battery recycling. Obviously, this requires mercury to be absent from the zinc batteries. Otherwise, emission control installations would require higher capital investment to comply with the legislation for mercury vapour release in the atmosphere.

4.5. Hydrometallurgy

Because Leclanché and saline batteries still represent 50% of the zinc battery market, it is useful to consider the recycling of leaches of non-alkaline zinc batteries. It would be composed mainly of zinc chloride and ammonium chloride, if both types of cell are collected (Leclanché and saline). While steel, paper, carbon and synthetic fractions would be separated by simple physical means, the soluble fraction could be re-introduced in the existing hydrometallurgical process used today on a large scale for the production of ammonium chloride and zinc chloride. Such a process, which involves the production of chemicals instead of metals, would also be one of the cheapest routes to zinc battery recycling and most probably will cost between $300 to 500 per ton.

4.6. Mine landfilling

In countries where there is no existing financial scheme to process zinc batteries, it appears that the sorting out of the batteries from municipal waste collection and the selective collection of batteries (organised on a voluntary or legal basis) would help to find a temporary solution in the selective landfilling in controlled sites. The best option being an old mine or an area where zinc waste has been concentrated by the non-ferrous metallurgical industry. It is, in a short term point of view, the best economical option until a global economical solution will be in practice. The costs of this temporary solution would only be related to the transportation fee, if no other constraint governs the long-term storage.

5. Conclusions

Batteries have to be considered as an engineered product with a high added value. When evaluated on a price per unit weight basis, their current market prices can be compared with some other manufactured products like watches or automobiles.

On a short-term basis, one has to consider that nickel–cadmium and mercury cells are on the market. Before processing zinc batteries for recycling it is advisable to sort out these batteries, in order to send each type of battery to a selective recycling route. Zinc batteries with a minimum mercury content will still be treated as mercury-bearing waste and have to be handled by processes which are taking this technical reality into account like the BATREC and the RECYTEC processes.

On a medium-term basis, if landfilling has to be considered, it should be made after sorting out the batteries, in order to store uniform lots of spent batteries (mainly alkaline and saline batteries) and in order to send the recycleable materials like the mercury cells and the nickel–cadmium batteries to their existing recycling facilities.

On a long-term basis, due to the decrease in mercury content of batteries, the major issue will be to separate the rechargeable from the non-rechargeable zinc batteries. Those will be treated following two major criteria: large volumes and economical efficiency. The steel industry and the secondary zinc industries will be ready to accept this source of secondary zinc.

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