PHYSICAL PROCESSING OF USED BATTERIES CONTAINING Zn AND Mn COMPONENTS

Drd. Ing. **Simona Saceanu**, Prof.univ. dr.ing. **Augustin Semenescu**, Drd. Ing. **Adrian Armangic**, Drd. Ing. **Ionuţ Cristea**, Drd. Ing. **Adrian Bibiş**, Universitatea POLITEHNICA Bucuresti

E-mail: sim@upb.ro

Abstract. *The paper presents the steps and parameters of technological process of physical processing of the used batteries components, containing Zn and Mn. By the resulting products of the mechanical processing one can obtain electrolytic Zn and electrolytic MnO2 using electrolysis of aqueous solutions from reductive acid leaching with H2SO4 and H2O2, of the pastes obtained. The resulting products may be sold or reused in the process of obtaining batteries.*

Key-words: ***batteries, recycling,*** *MnO_2*

1. INTRODUCTION

"Portable" electricity has now become a part of everyday life. Batteries feed many of the devices that function on electricity, such as telephones, computers, radios, tape recorders, and even electric cars. But after being consumed and discarded, they represent a danger to the environment.

Batteries are classified broadly into: disposable batteries and batteries that can be recharged several times, the latter usually have a larger utility. Worldwide, hundreds of millions of large batteries and small batteries containing billions of tons of toxic and hazardous metals are produced and used every year. Until recently, most of them were simply discarded. Even today, in many places only those containing valuable materials, such as nickel and cadmium are recycled.

In accordance with EU standards, new legislation the producers of batteries and accumulators, other than those for motor vehicles, are required to establish and organize a proper collection of the used ones and hand the collected quantities to the businesses performing their recovery or elimination. Used batteries are major sources of environmental pollution and they can affect human health through dangerous substances they contain: mercury, cadmium and lead.

- **Quantitatively**: batteries / portable battery on the market are constantly expanding. Today, the European Union considers it necessary to treat 250-425 tonnes of waste batteries and accumulators per year per million population, ie an average of 410 g / capita / year. The gap between countries is very important: 250-425 g / capita / year depends on the country. One ton of batteries or accumulators is, on average 20,000 to 22,000 units. Therefore the existing capacity for the treatment would be increased by a factor of 3 in the future.

Worldwide, only 8% of the "batteries" are actually rechargeable batteries, 90% of household batteries are disposable, and 2% are small batteries, button cells (like those in watches),.as we can see in Figure 1.

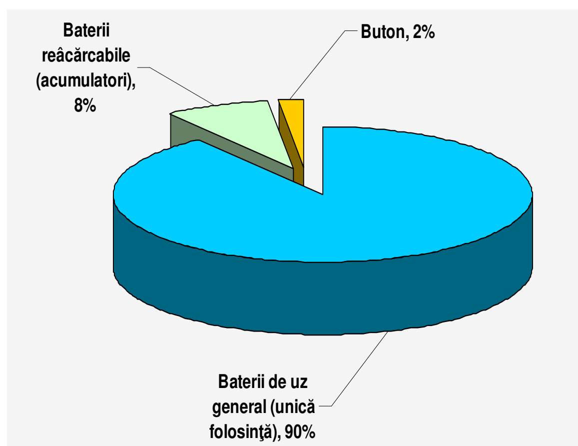

Figura 1.1 *Distribuţia bateriilor pe piaţă, pe categorii*

According to a survey conducted by "Sunlight Romania", on the domestic market are annually sold-out 40 million portable batteries which, after use, although considered hazardous waste mixed with domestic waste or incinerated.

In Europe 27,000 tons of used batteries are recycled, while on the Community market are annually in sales over 200,000 tons of portable batteries.

Average collection rate in European countries is 13% and half of this number is made only five countries, including Belgium who annually collect and recycle over 50% batteries. Poland has not yet reached only 1% of the target of proposed collection.

According to H.G. No. 1132/2008, of all batteries sold in Romania, 25% should be collected for recycling by 2012 and 45% by 2016. So, in less than a year, we must ensure that at least one of the four batteries sold-out is in the recycling process.

- **Qualitative aspect**: the complexity of the sorting system and the subsequent chemical treatment can be assessed by the number and the amount of heavy metals contained in these different types of wasted batteries and accumulators, shown in Table 2.2. Disposable batteries are 90% of household batteries market (84% of which ZnC alkaline) 8% battery button and 2%.cell batteries

- **The purity aspect:** a method of treating waste batteries and accumulators is technically and economically feasible only if the resulting products can be recycled as primary, returning to original manufacturing process. The value of these recovered products is directly related to the degree of their purity.

Various processes for wasted batteries and accumulators have been developed. Technologies are either pyrometallurgical (smelting reducing) or hydrometallurgical (leaching-electrolysis). However, in both technologies, the minimum purity of recycled products can be achieved only in the absence of foreign elements, or in the minimum quantity thereof (cross-contamination). For example, pyro and hydro processes developed for recycling NiMH batteries can tolerate only 1% of the basic elements contained by alkaline or carbon zinc batteries. In another case, thermal processes used for alkaline zinc-carbon batteries can tolerate only less than 1% of the basic elements contained nickel metal hydride batteries.

The treatment of wasted batteries and accumulators used by the public involves the problem that is difficult or impossible to predict a selective collection based on their chemical composition. A method of sorting these collected batteries or accumulators, becomes a vital necessity for the subsequent treatment processes.

This method should allow sorting of waste batteries and accumulators in a fast, safe and economical way, whatever their condition and structure.

Mixing waste batteries with different chemical compositions can be a costly mistake, compromising a whole lot of batteries for recycling.
Batteries with different chemical compositions have different ways of recycling and each type of wasted batteries have to be sorted, in order to avoid cross-contamination.

2. Equipment, mode, experimental data

In order to be processed through hydrometallurgical processes portable batteries containing Zn and Mn, require a pretreatment prior to the following cleaning. Pretreatment process represents a physical process of separation of the wasted batteries components The physical separation of the components of batteries consisting of:

- Cutting-crushing
- magnetic separation
- dimensional separation (sieving)
- ECS separation (with eddy currents)
- grinding powder fraction.

The cut-shredding resulting material is varied in shape and nonhomogeneous due to the fact that it is produced in an automatic grinding machine and contains parts of all battery components. More specifically they may contain: cathode paste (MnO2 - C - KOH alkaline or MnO2 - C - Battery ZnCl2/NH4Cl Zn-C), anode paste (Zn - ZnO - KOH), cardboard, plastic, metallic coat made of steel ,the last ones being worthless and are not desired for the recycling process.

In the cutting-crushing mechanical process, alkaline and zinc-carbon AAA and AA wasted batteries were used. Battery pieces of 10 mm dimensions were crushed in a crusher disc, the grinding being accomplished between the two discs mounted on a horizontal shaft.

In order to achieve useful streams for recycling, the crushed batteries have to have similar chemical and physical composition and the resulting crushing material must to be separated in fractions form.

After batteries crushing, ín order to separate solids crushed into granules fraction having about the same size, screen sorting was done (screening). After sieving, the material was subjected to magnetic separation and as a result one obtain the distribution of the shredded material upon nature: magnetic and non-magnetic.

In figure 1. and Table 1.The results the of grain size analysis magnetic separation for batteries Zn / C are presented.

Figure 1. *The results the of grain size analysis magnetic separation for batteries Zn / C (quality)*

Table 1. The results the of grain size analysis magnetic separation for batteries Zn / C (quantity)

Granulaţie [mm]	Componentă magnetică			Componentă nemagnetică			**TOTAL**
	greutate [g]	% gr.	% total	greutate [g]	% gr.	% total	%
Refuz sită 5 mm	96	94,77	20,02	53,4	14,12	11,14	**31,16**
Refuz sită 3,15 mm	4	3,95	0,83	33	8,73	6,88	**7,71**
Refuz sită 1,25 mm	0,6	0,59	0,13	63,4	16,76	13,22	**13,35**
Refuz sită 1 mm	0,25	0,25	0,05	25,3	6,69	5,28	**5,33**
Refuz sită 0,71 mm	0,45	0,44	0,09	24,5	6,48	5,11	**5,2**
< 0,71	0	0	0	178,6	47,22	37,25	**37,25**
Total	**101,3**	**100**	**21,12**	**378,2**	**100**	**78,88**	**100**
Total comp.	**479,5**						

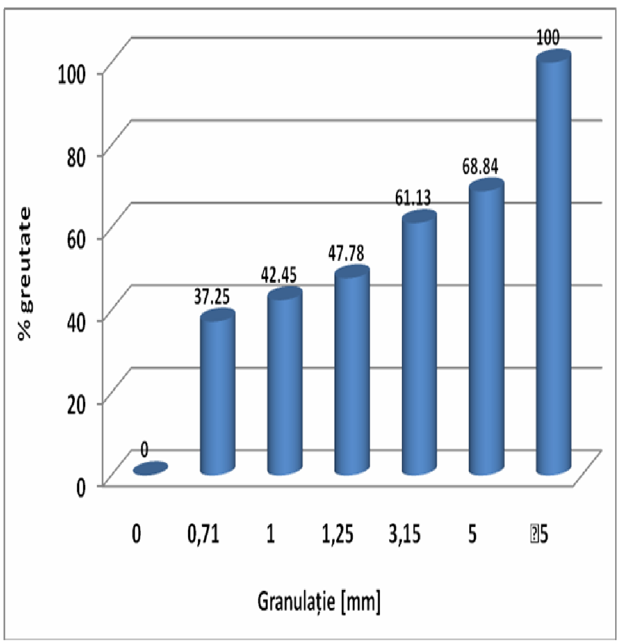

Figure 2 *Diagrama cumulativă pentru distribuţia granulometrică a bateriilor Zn-C sfărâmate*

In Figure 3. and Table 2. the results of particle size analysis and magnetic separation for alkaline batteries are presented.

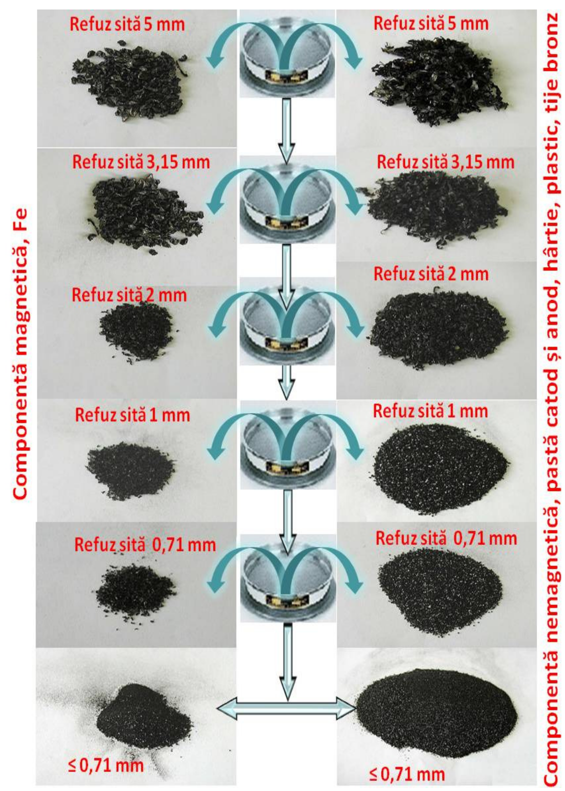

Figure 3. *Rezultatele analizei granulometrice şi separării magnetice pentru bateriile alcaline sfărâmate*

Table 2. Rezultatele analizei granulometrice şi separării magnetice pentru bateriile alcaline sfărâmate

Granulaţie [mm]	Componentă magnetică			Componentă nemagnetică			TOTAL
	greutate [g]	% gr.	% total	greutate [g]	% gr.	% total	%
Refuz sită 5 mm	54,3	70,16	16,36	12,7	4,99	3,83	**20,19**
Refuz sită 3,15 mm	15,3	19,77	4,61	10,1	3,97	3,04	**7,65**
Refuz sită 1,25 mm	3,4	4,39	1,02	37,5	14,74	11,3	**12,32**
Refuz sită 1 mm	1,6	2,07	0,48	64,3	25,27	19,38	**19,86**
Refuz sită 0,71 mm	0,7	0,9	0,21	14,5	5,7	4,37	**4,58**
< 0,71	2,1	2,71	0,63	115,36	45,34	34,76	**35,39**
Total	**77,4**	**100**	**23,31**	**254,46**	**100**	**76,68**	**100**
Total comp.	**331,86**						

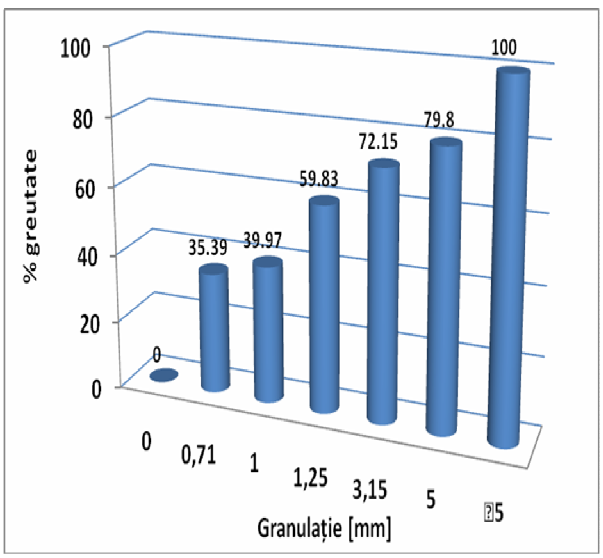

Figure 4. *Diagrama cumulativă pentru distribuţia granulometrică a bateriilor alcaline sfărâmate*

Based on size distribution analysis one note that the resulting material from used batteries crushing-grinding, a small-grained magnetic fraction exists: 0.71 mm at Zn-C batteries and even less than 0.71 mm for alkaline batteries. By magnetic separation almost of the iron was removed making the separation easier in any subsequent chemical processes.

Upon this analysis one could establish a physical separation process flow of batteries containing Zn and Mn components.
Process diagram for physical separation of used batteries containing Zn and Mn components is shown in Figure 5.

Through hydrometallurgical processes batteries having the same composition (Zn, Mn) are not recycled as a whole, but separate on components: the electrodes, the electrolyte, separators and the iron or zinc frame. Recycling is different for each component. Metal and paste electrodes are the most recycled, metal casings are more recycled than the plastic ones. Electrolytes can be reused as agent but in most cases, they are used for other purposes.

To separate on components (individual fractions) in order to valorize the contained materials, batteries having the same chemical composition are dismantled by cutting-crushing. After crashing, the material passes through a vibration feeder that feeds a conveyor belt. The conveyor has the role to standardize and homogenize the material flow for magnetic separation. Magnetic separator conveyor is transverse or longitudinal positioned over the conveyor belt, ensuring the separation of coarse ferrous material. After magnetic separation, the material divides into two streams:

- magnetic material
- non-magnetic material.

Magnetic material (iron) goes to the production of steel for new batteries and other industrial applications. Non-magnetic material is subjected to particle size separation through a sieve of 1.25 mm and hence two fractions:

- fraction> 1.25 mm
- fraction ≤ 1.25 mm.

Fraction> 1.25 mm ferrous metal separator goes to ECS. This is a device for separating the flow of material into two or more fractions, whose operation is based on eddy currents (Foucault), generated by a rotating magnetic field. Induced currents in ferrous metals creates a rejection force able to remove ferrous material from the inert materials flow.

The non-ferrous fraction (zinc shell, brass rods and so on) is recovered by various recyclers, and the inert fraction (carbon rods, pulp and / or cardboard, paper and plastic) is exploited for the production of fuel from waste.

The ≤ 1.25 mm fraction, representing the pasty battery electrodes, (contains the most valuable materials) go to chemical treatment through hydro and electro-metallurgical processes for the extraction of zinc and manganese.

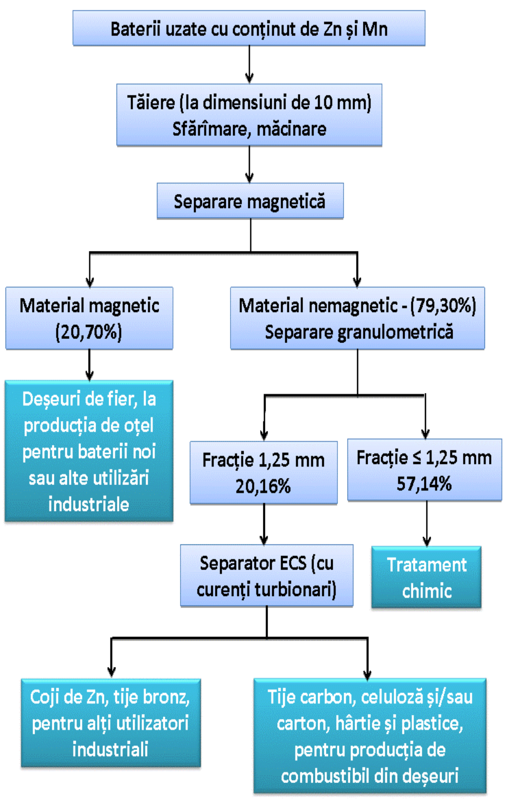

Figure 5.*Diagrama procesului pentru separare fizică a componentelor bateriilor uzate cu conţinut de Zn şi Mn*

3. CONCLUSION

The size analysis revealed the existence of magnetic fractions with d ≤ 0.71 mm in the material resulting from crushing-grinding Zn- C batteries and in batteries Alkaline this size is more fine. By magnetic separation fraction containing Fe is removed almost completely, facilitating subsequent chemical processes.

Separation of non-magnetic material is subjected to volume separation through a sieve of 1.25 mm. Fraction> 1.25 mm is sent to ECS-ferrous materials separator.

Fraction containing nonferrous (Zn shells, Bz rods, etc) is separate valorise. C inert fraction, cellulose, plastic are used for the production of fuel from waste. The ≤ 1.25 mm fraction representing electrodes pastes is sent to chemical treatment processes though hydro and electrometallurgical processes for recovering electrolyte Zn MnO_2 , which can return in obtaining batteries process.

REFERENCES

[1] *** http://www.mmediu.ro/legislatie/gestiune_deseuri.htm
[2] *** snrb.ro (Sistemul National de Reciclare a Bateriilor)
[3] *** MINISTERUL ECONOMIEI ŞI FINANŢELOR, Direcţia Reciclarea Materialelor
[4] *** http://www.anpm.ro
[5] *** www.epbaeurope.net (European Portable Battery Association)
[6] M. Anton, A. Manciulea, P. Ilea, *Comparative study of solubilization for recycling metals from spent batteries*, Studia UBB Chemia LVI (4) (2011) p. 223–233.
[7] ***Metode si tehnologii de gestionare a deseurilor, Institutul Nationalde Cercetare Dezvoltare pentru Protectia Mediului – ICIM Bucuresti, Ministerul Mediului si Gospodaririi Apelor
[8] M. Anton, A.Manciulea, P. Ilea, *The study of zinc solubilisation process from the active mass of Zn/ZnCl2/MnO2 used batteries,* Conferinţa

[9] I. D. Michelis, F. Ferella, E. Karakaya, F. Beolchini, F. Vegliò, *Recovery of zinc and manganese from alkaline and zinc-carbon spent batteries*, Journal of Power Sources 172 (2) (2007) p. 975-983.
[10] A. Manciulea, M. Anton, R. Racz, P. Ilea., *Zn recovery from spent batteries II. Zinc electrowinning process from Zn anode scraps of spent Zn-ZnCl2-MnO2 batteries,* 17th Romanian International

Conference on Chemistry and Chemical Engineering, 7-10 September 2011, Sinaia, Romania

[11] Traian Buzatu , Gabriela Popescu, Ionela Birloaga, Simona Saceanu - *Study concerning the recovery of zinc and manganese from spent batteries by hydrometallurgical processes*, Waste Management journal homepage: www.elsevier.com/locate/wasman,Volume 33, Issue 3, March 2013, Pages 699–705 b

[12] Bernardes, A.M. et al., 2004. *Recycling of batteries: a review of current processes and technologies. Journal of Powder Sources* 130, 291–298.

[13] DeMichelis, I. et al., 2007. *Recovery of zinc and manganese from alkaline and zinc–carbon spent batteries*. Journal of Powder Sources 172, 975–979.

[14] El-Nadi et al., 2007. *Leaching and separation of zinc from the black paste of spent MnO2–Zn dry cell batteries*. Journal of Hazardous Materials 143, 328–334.

15.Ferella, F. et al., 2010. *Extraction of zinc and manganese from alkaline and zinccarbon spent batteries by citric–sulphuric acid solution*, Inter. urces 152, 295–302.

Journal of Chemical Engineering 13 (article ID 659434).

[16] Nougueira, C.A., Margarido, F., TMS, 2012. *Battery recycling by hydrometallurgy: evaluation of simultaneous treatment of several cell systems*. Energy Technology, 227–234.

[17] Provazi, K. et al., 2011. *Metal separation from mixed types of batteries using selective precipitation and liquid–liquid extraction techniques*. Waste Management 31, 59–64.

[18] Sayilgan, E. et al., 2009. *Reductive leaching of manganese and zinc from spent alkaline and zinc–carbon batteries in acidic media*. Hydrometallurgy 97, 73–79.

[19] Sayilgan, E. et al., 2010. *Acidic leaching and precipitation of zinc and manganese from spent battery powders using various reluctants*. Journal of Hazardous Materials 173, 137–143.

[20] Veloso, L.R.S. et al., 2005. *Development of a hydrometallurgical route for the recovery of zinc and manganese from spent alkaline batteries*. Journal of Power So