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TECHNOLOGICAL PROCESS FOR SEPARATION AND RECOVERY OF METALLIC MATERIAL FROM USED HOUSEHOLD BATTERIES

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Abstract: The intense development of the recovery of non–ferrous metals from secondary resources in the second half of the twentieth century raised the issue of using new technologies, "environmentally friendly", for processing this type of raw materials, by removing as much as possible noxious processes. Used batteries are also part of this category, and currently only 3–4% of total world battery production is processed in order to recover metals. Developing countries recycle an almost insignificant percentage, and underdeveloped countries are not involved at all, batteries being disposed of with household waste. This paper presents experimental processes regarding the recovery of non–ferrous metals contained in used household batteries (alkaline and zinc–carbon) using simple but efficient processes. Following the research, a technological flow was established, being performed analyses to determine the chemical composition (XRFS) and the morphological aspect (SEM) of the obtained powdery material. The possibilities of capitalization of the materials resulting from the battery disassembly processes are also established.
Keywords: circular recycling, eco–friendly technology, non–ferrous metals, used batteries

INTRODUCTION

A huge amount of metals (Ni, Zn, Li, Co, Mn, Fe, Cr, Al, Cu and others in low concentrations) is embedded in batteries and accumulators widely used as a source of energy for any items, from remote controls and children's toys to electronics and medical devices [1]. As their number and degree of use increases then the amount of batteries required for their operation becomes higher leading to many questions about how to extract and reprocessing these secondary raw materials in an efficient and economical manner [2]. Battery recycling helps save resources by recovering valuable metals such as nickel and cobalt. In addition, the use of recycled metals from batteries requires lower energy consumption (the use of recycled nickel requires 75% less primary energy than its extraction and refining in its natural state) [3, 4, 5, 6, and 7].

There are two main types of batteries: primary batteries (disposable batteries – saline, alkaline and lithium batteries) and secondary batteries (rechargeable batteries – NiCd, NiMH and Li–ion). Globally, only 8% of "batteries" are actually rechargeable batteries (batteries), 90% are single–use household batteries, and 2% are small, button–like batteries [8].

According to recycling companies, the recycling process will only be a profitable business when a steady stream of sorted batteries is established. The process becomes profitable when the batteries contain large amounts of recoverable metal (in the case of NiMH batteries), and not when low–metal batteries are used for recycling (in the case of Li–ion batteries) [8, 9].

Of all the municipal waste generated, used batteries are the most harmful to human health and the environment. Cadmium–containing batteries still have a high market share in most countries so their storage together with household waste leads to serious long–term environmental problems, but in Europe they have been banned from sale and replaced with other types of batteries (such as NiMH, NiOOH, $LiMnO_2$, $LiSOCl_2$, $LiFeS_2$, Li–ion types, alkaline/carbon–zinc) [10]. NiMH batteries contain nickel and electrolyte, which are considered semi–toxic substances, and proper storage and recycling is recommended [11]. Lithium–containing batteries when exposed to moisture give a violent reaction, so batteries must be disposed of properly. Before recycling, lithium batteries must first be completely discharged [3, 12]. One method of processing lithium batteries is to cryogenize them with liquid nitrogen and then crushing and grinding them. In order for the lithium not to become reactive, it is dissolved in a special solution [13]. Cobalt is separated in the same way.

The process of recycling batteries begins with sorting them according to their composition (zinc–carbon, alkaline, Li–Ion, pill type, lead–acid, etc.) and charge level. Sorting is a time consuming process. For each type, a process of shredding, separation and reprocessing follows. Pyrometallurgical or hydrometallurgical processes are most often used in the technological flow. At the end of the processes, metals such as Ni, Zn, Li, Co, Mn, Fe, Cr, Al, Cu and others are extracted [5, 6, 7, 14].

Mechanical treatment of batteries consists in their crushing and milling, magnetic separation, separation by sieving and qualitative separation of particles. The common goal of all processes is to separate the component metals of the batteries in order to obtain the highest possible purity so that they can be reused in different industries. Ferrous and non–ferrous fractions re–enter the economic circuit in the steel and zinc industry, and paper and plastic are used as alternative fuel in the cement industry [15]. From one ton of alkaline batteries, 330 kg of zinc and zinc compounds and 240 kg of iron and nickel–based alloy can be recovered. These metals can be reused immediately for the manufacture of everyday and industrial objects [16].

In pyrometallurgical battery recycling processes, 6 to 10 times more energy is consumed to extract constituent metals. In order to reduce costs, some companies in the field of battery recycling do not separate the metals independently but melt them and then deliver the products obtained to the manufacturers of ferroalloys and stainless steels. Thus, these energy–intensive and sometimes polluting processes must be replaced by hydrometallurgical processes, using efficient and non–polluting solutions and especially those that can be easily recovered and reused [6] and by completing it with an electrochemical process (electrolytic deposition and refining of metals) we have the possibility to obtain metals with high purity. By using appropriate parameters (current density, intensity, electrolyte concentration and temperature) can reduce energy consumption.

Today, in the European Union, it is estimated that it is necessary to treat 250–425 tons of waste batteries and accumulators per year per million inhabitants, i.e. an average of 410 g / inhabitant / year. Most developed countries face an increasing problem, namely the recycling of used batteries through processes that must meet several key elements: ease of application, environmentally friendly and last but not least economically feasible. Any method of treating waste batteries and accumulators is technically and economically feasible only if the resulting products can be recycled as primary products, which return to the original manufacturing process. The value of these recycled products is directly related to their degree of purity [17].

There is still a big gap between the percentage of waste defined by law that needs to be collected and recycled and that which is actually recycled. Currently only 3–4% of total world battery production is processed in order to recover metals. Australia has a high degree of recycling with 80% of total used batteries, then the USA with 60% and EU with 48%. Developing countries recycle an almost insignificant percentage, and underdeveloped countries are not involved at all, batteries being disposed of with household waste [2, 14, 17].

A recent European Commission study found that more than half of the batteries used in the EU are not collected or recycled. The study concludes that the level of battery waste collection in the EU is insufficient; thus a large amount of batteries end up in municipal waste [4]. Romania still does not meet the collection targets for battery waste. Insufficient quantities of such waste, poorly developed technologies and a fluctuating market for recycled materials make these types of waste unattractive to local processors. Preserving the value of existing materials in waste, especially in waste batteries, and reintroducing them into the economic circuit, through extraction and reuse can be part of the idea of circular economy.

EXPERIMENTS

The non–rechargeable batteries (primary batteries) used in the experimental process, shown in figure 1, were of the types based on their chemistry – alkaline ($Zn/Alkaline/MnO_2$) and zinc–carbon – and were processed according to the technological flow shown in Figure 2.

Figure 1. Types of batteries by shape and size used in the experiment: AA, AAA, C, D and 9V

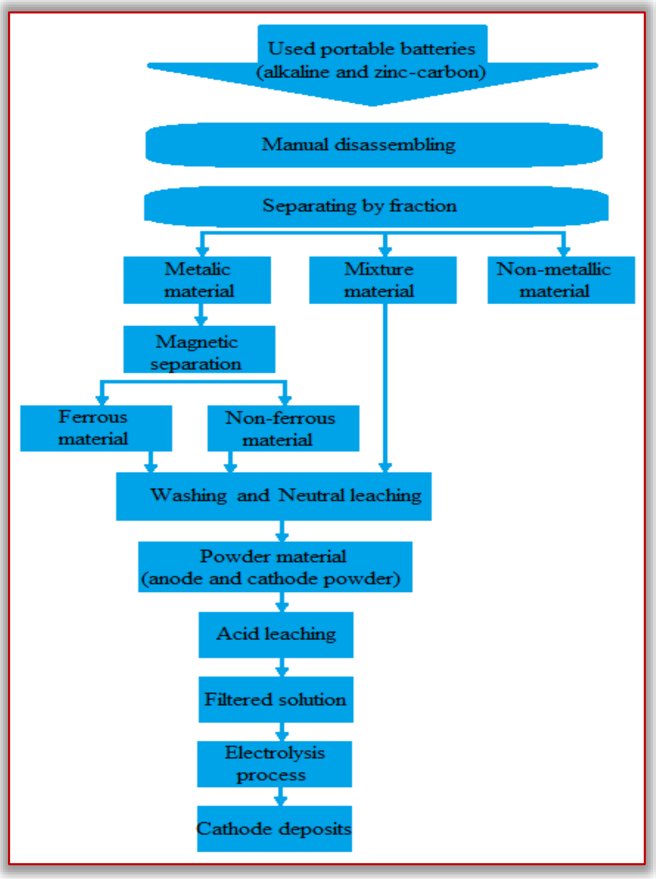


Figure 2. Technological scheme of the process

The used batteries (alkaline and zinc–carbon) were manually dismantled by cutting, the component materials being separated into different fractions and the mixture of the cathodic and the anodic materials was extracted. The obtained material was dried in a drying stove at a temperature of 110ºC for one hour, to remove moisture and perform chemical analyses to determine the constituent elements by means of X–Ray Fluorescence Spectrometer (WDXRF S8 Tiger Bruker).

Sorting materials into categories was done manually and by magnetic separation, due to the small amount of material used in experiments (the batteries weighed 382g). These were divided as follows:

- non–ferrous metal fraction (bronze or brass connectors, Zn cases);
- ferrous metal fraction (steel components – exterior case, pin connectors, negative and positive pole);
- mixture material fraction (anode and cathode powder);
- non–metallic fraction (graphite connectors, plastic polymers – insulators, separators, paper).

In a zinc–carbon dry cell, the zinc is oxidized by the chloride (Cl^-), according to the following half–reactions:

Anode:

$$Zn + 2\,Cl^- \rightarrow ZnCl_2 + 2\,e^- \qquad (1)$$

Cathode:

$$2MnO_2 + 2\,NH_4Cl + H_2O + 2\,e^- \rightarrow Mn_2O_3 + 2\,NH_4OH + 2\,Cl^- \qquad (2)$$

The overall reaction:

$$Zn + 2\,MnO_2 + 2\,NH_4Cl + H_2O \rightarrow ZnCl_2 + Mn_2O_3 + 2\,NH_4OH \qquad (3)$$

If ZnCl is substituted for NH_4Cl as the electrolyte, the anode reaction remains the same (Eq. 1) and the cathode reaction becomes:

$$2MnO_2 + ZnCl_2 + H_2O + 2\,e^- \rightarrow Mn_2O_3 + Zn(OH)_2 + 2\,Cl^- \qquad (4)$$

Result the overall reaction:

$$Zn + 2MnO_2 + H_2O \rightarrow Mn_2O_3 + Zn(OH)_2 \qquad (5)$$

In an alkaline battery, Zn represent the negative electrode and MnO_2 the positive electrode. During the discharge reactions only the Zn and MnO_2 are consumed, the alkaline electrolyte of potassium hydroxide remains because is not part of the reaction. The half–reactions are:

Anode:

$$Zn_{(s)} + 2OH^-_{(aq)} \rightarrow ZnO_{(s)} + H_2O_{(l)} + 2e^- \qquad (6)$$

Cathode:

$$2MnO_{2(s)} + H_2O_{(l)} + 2e^- \rightarrow Mn_2O_{3(s)} + 2OH^-_{(aq)} \qquad (7)$$

The overall reaction:

$$Zn_{(s)} + 2MnO_{2(s)} \rightleftharpoons ZnO_{(s)} + Mn_2O_{3(s)} \qquad (8)$$

The separated non–ferrous and ferrous fractions will be washed with water to remove the active mass, electrolyte and other components adhering to these components of the batteries, and the resulting wash water will be used in the chemical treatment step.

Neutral leaching was performed at a temperature of 60ºC for about one hour, during which time the pH of the solution was constantly measured using the HI–83141 pH Meter (Hanna Instruments) with Electrode and Temperature Probe. After a contact time of one hour the pH of the solution was 9.9, so most of the KOH was dissolved in water.

In this paper we focused on the physical–mechanical processes of processing used batteries and obtaining different types of metallic or non–metallic materials. Following, we will focus on the selective recovery of various metals through electrochemical processes, which are much more complex and require extensive research.

RESULTS AND DISCUSSION

The portable batteries are very diverse in terms of chemical composition. Depending on the size and shape we can sort them into categories and depending on the chemical composition we can determine which metals can be recovered from each category, which categories can be treated together and which separately. Household batteries – alkaline MnO_2, and saline Zn–C represent 83% of the total portable batteries collected these containing the same metals Mn and Zn, so they can be processed together, recovering and reuse the materials, instead of being incinerated in municipal waste incinerators or landfilled.

After dismantling the batteries and sorting the materials obtained into fractions, they were weighed resulting in the quantities of materials shown in Table 1.

The mixture material (Figure 3) was weighed before and after drying in the oven to determine the moisture content of the batteries. The loss of material was also established (by the difference between the total quantity and the sum of all the quantities obtained).

Figure 3. Mixture material (anode and cathode powder)

Table 1. Material compositions of the dismantled batteries

Fractions	Composition	(g)	(%)
Non–ferrous metal	Zinc	59.35	15.54
	Bronze	8.77	2.30
Ferrous metal	Steel	21.66	5.67
Mixture material	anode powder	26.29	6.88
	cathode powder	183.51	48.04
Non–metallic	graphite connectors	24.68	6.46
	plastic polymers	7.20	1.88
	paper	28.47	7.45
Moisture		20.85	5.46
Losses		1.218	0.32
Total		382	100

Ferrous metal fraction can be used in the production of ferroalloys or even in the elaboration of steel for new batteries and other industrial applications. The zinc shell, brass rods and so on, which represent the non–ferrous fraction are recovered by various recyclers for the production of the same elements or other applications and the non–metallic fraction compose of carbon rods, pulp and / or cardboard, paper and plastic can be used for the production of different types of fuel.

The material mixture fraction is used in chemical treatment processes through hydro and electrometallurgical routes for recovering electrolyte Zn and MnO_2, which can return in the battery manufacturing processes.

Regarding the recovery of other metals from the mixed fraction, the processes become more complex. So far no optimal strategy has been established and their recovery is selective and largely depends on the process used. We can only increase extraction yields or reduce pollution by using environmentally friendly and accessible substances so that these processes become economical and can be applied on a larger scale.

In the experiment, the resulting mixture powder obtained after dismantling the used batteries was subjected to the chemical composition analysis by three successive XRF analyses (X–Ray Fluorescence) (CC1, CC2 and CC3) and the average of the values (ACC) was calculated and rendered in table 2.

The obtained material will be used in experiments of solubilisation and electrolytic extraction of metals, which can be reused for battery production or in other fields.

The mixture material, separated from the batteries, was subjected to the process of washing with water to remove easily soluble components and will be used in the chemical treatment step together with the resulted material after cleaning with water the non–ferrous and ferrous fractions. The powder separated by washing the non–ferrous and ferrous fractions and filtration (Figure 4) will enter the hydrometallurgical circuit, in which the metals are selectively dissolved in aqueous sulphuric acid solution followed by a purification and cementation process, and the obtained solutions will be subjected to electrolysis processes for the selective recovery of metals.

Table 2. Chemical compositions of the powder obtained after dismantling the used batteries

No. crt.	Symbol	CC1	CC2	CC3	ACC
1	Zn	18.320	19.740	22.067	20.042
2	Mn	34.070	33.870	39.560	35.833
3	K	6.470	7.090	4.890	6.150
4	Fe	0.410	0.550	0.510	0.490
5	Pb	0.004	0.007	0.007	0.006
6	Hg	0.008	0.008	0.006	0.008
7	Cr	0.110	0.150	0.180	0.147
8	Cd	0.006	0.007	0.005	0.006
9	Na	0.150	0.180	0.120	0.150
10	Al	0.520	0.790	0.630	0.647
11	Cl	2.890	3.020	3.220	3.043
12	Ti	0.360	0.280	0.240	0.293
13	Si	0.610	0.560	0.480	0.550
14	Ni	0.019	0.018	0.013	0.017
15	Ca	0.120	0.304	0.140	0.188
16	Si	0.180	0.290	0.250	0.240
17	Cu	0.410	0.640	0.590	0.547
18	Others	35.343	32.496	27.091	31.643
Total		100	100	100	100

Figure 5. The powder separated after washing and filtration process

The water wash step (neutral leaching) was used to reduce the amount of unwanted ions in the solution and to remove potassium in order to improve the subsequent electrolysis process of the solution, by reducing the interference due to the alkali metals which have the effect of reducing the process yield. Further removal of potassium from the material mixture may also contribute to the reduction of sulphuric acid consumption in the leaching steps.

An SEM analysis of the obtained mixture material was also performed; the morphological aspect is presented in Figure 6. These particles are in fact aggregates of submicron particles.

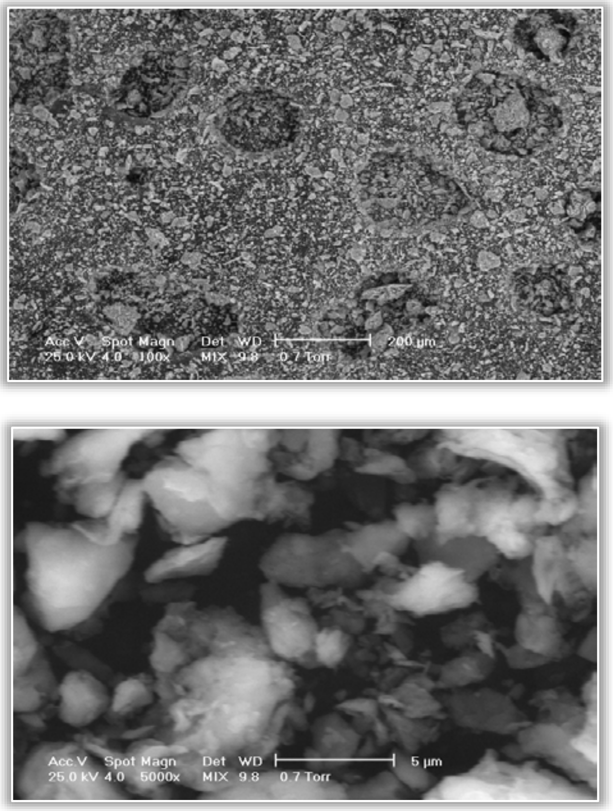
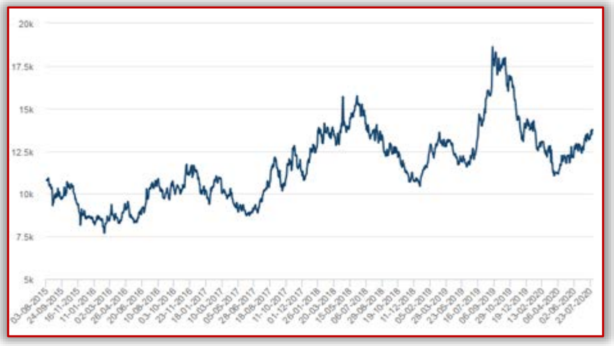
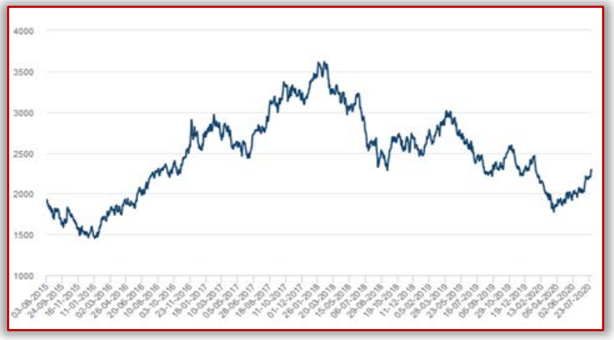


Figure 6. SEM images of alkaline and zinc–carbon battery black mass (a) ×100, (b) ×5000

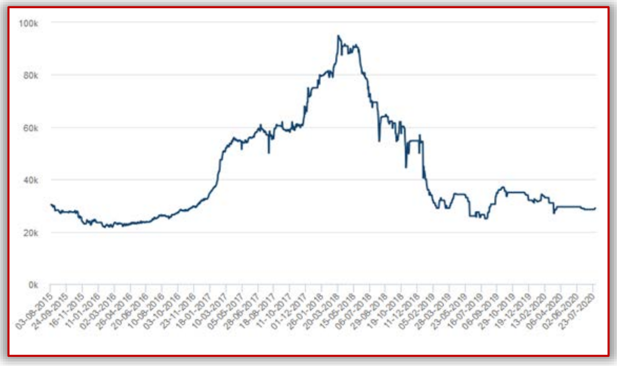
Sustainable development must focus on the implementation of economic activities that are consistent with issues related to society and the environment and this goal is the only valid option to develop activities with a positive long–term impact on human quality of life.



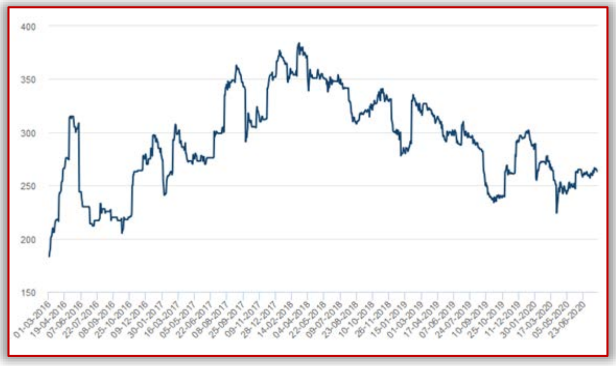
Nickel



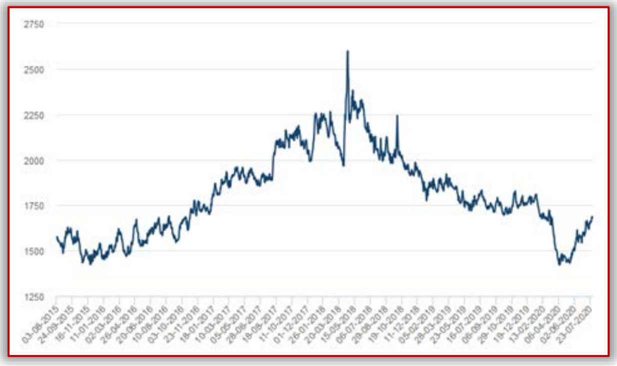
Zinc



Cobalt



Iron



Aluminium

Copper

Figure 7. Price evolution (Dollars / metric ton) in the last 5 years

Source: London Metal Exchange

As can be seen, for the metals listed on the London Metal Exchange, prices are on an upward trend. Under these conditions, their recovery represents a double benefit, both economic and environmental.

CONCLUSIONS

In this paper we focused on the physical–mechanical processes of processing used batteries – alkaline MnO_2, and saline Zn–C, which represent over 80% of the total portable batteries collected worldwide. Thus, their useful metal content is huge and their recovery and recycling is a beneficial opportunity for both the environment and the economy.

After dismantling the batteries and sorting the materials we obtain four different fractions: non–ferrous metals, ferrous metal, and a mixture material with metal content and non–metallic materials establishing the weight of each fraction (this may vary from case to case).

The resulting mixture powder obtained after dismantling the used batteries was subjected to the chemical composition analysis by three successive XRF analyses and the average of the values was calculated. The obtained mixture material together with the powder separated by washing the non–ferrous and ferrous fractions and filtration will enter to a hydro–electrometallurgical circuit for the selective recovery of metals.

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