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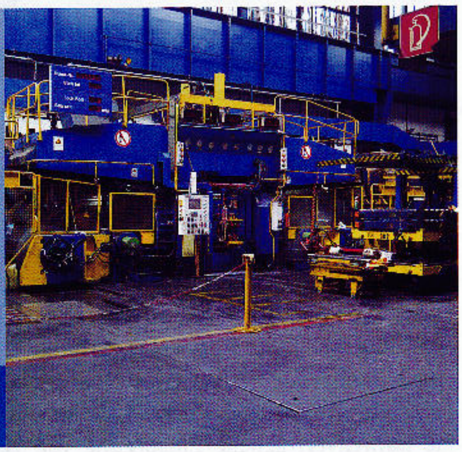

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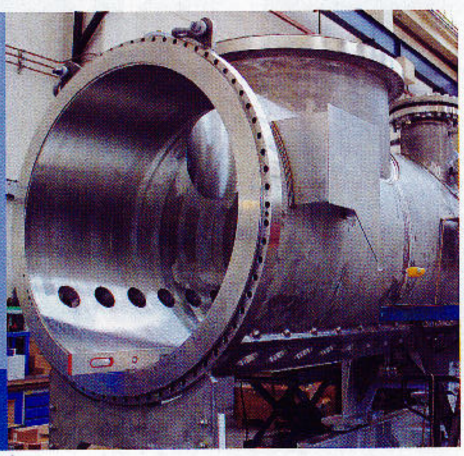

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Recycling of used portable Zn batteries: Optimization of mechanical pre-treatment of Zn-C and alkaline batteries and characterization of obtained active mass

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Used portable zinc batteries are becoming, due to its zinc content, one of the possible secondary raw materials for zinc production. Active mass of these batteries, which represents a mix of cathode, anode material and electrolyte, contains on average about 20 % Zn. The aim of this work was to liberate and obtain the active mass in required quality and quantity by mechanical pretreatment of zinc batteries. Four processes of possible mechanical pre-treatment were proposed in this work. From the tested processes, a process consisting of crushing with double rotor crusher and subsequent milling using friction mill can be considered as the most effective mechanical pretreatment process for obtaining active mass from Zn batteries. The largest amount of active mass was obtained through this process, where zinc content, depending on the type of Zn batteries, was in range 18 – 22 %. It results from chemical analysis (AAS) as well as XRD phase analysis, that composition of active mass from Zn-C batteries and alkaline batteries are very similar, what makes possible to process them together in order to recover zinc.

Actual industrial society significantly influences a growth of electric and electronic equipment production, which is associated with increase in demand for portable batteries and accumulators, which are necessary for their functionality. Portable batteries and accumulators have become an inseparable part of everyday life. Batteries and accumulators, after the end of their lifetime, became an environmental problem mainly due to heavy metals (mercury, lead, zinc, cadmium, manganese, nickel, cobalt, etc.). Directive of the European Parliament and of the Council 2008/98/EC prescribes the waste management hierarchy:

a) prevention of waste,
b) reuse,
c) recycling,
d) energy recovery,
e) disposal.

This order must be respected also in case of used portable batteries and accumulators. According to the European Directive 2006/66/EC, which set targets for collection and recycling in order to minimize the negative impact of used portable batteries and accumulators on the environment, the percentage of collection of used portable batteries and accumulators must reach 45 % by September 2016. The Directive also specifies that at least 50 wt. %. of used portable batteries and accumulators must be recycled [1].

According to the chemical composition portable batteries and accumulators can be divided into zinc, nickel, lithium, etc., depending on the primary metal present in the batteries and accumulators. The highest representation on the European market, till 90 %, belongs to zinc-based used portable batteries specifically zinc-carbon, alkaline batteries and button cells zinc-air. Those batteries contain interesting amount of zinc and manganese, therefore their recycling is very important. In recent years, there is an enormous increase in demand for zinc, what confirms topicality of this issue. Published research activities were focused on development environmentally as well as economically suitable recycling processes for processing used portable batteries. This, regarding the content of valuable compounds, brings positive economic benefits also for investors in the field of recycling.

Portable Zn batteries contain metals in significant high concentrations. Zinc content in primary zinc ore is less than 10 %, while zinc content in zinc-carbon and alkaline batteries is about 15 – 20 %. This confirms

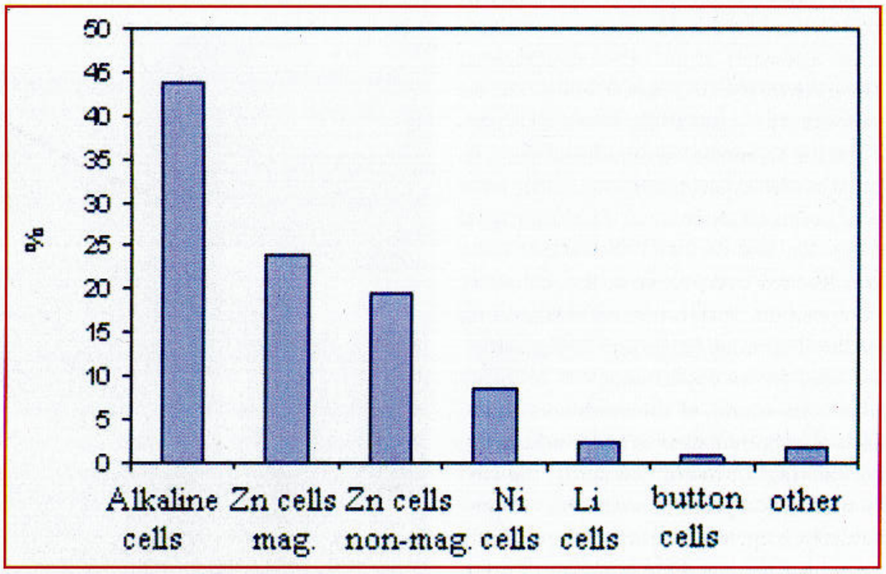

Fig. 1: Statistics of different types of used portable batteries and accumulators collected on TUKE, Slovakia

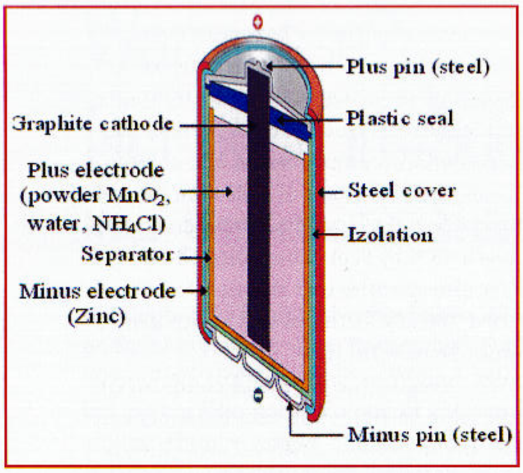

Fig. 2: A section of a zinc-carbon battery [3]

advisability of recycling Zn batteries in order to recover zinc.

Recycling of used portable zinc-carbon and alkaline batteries can be performed by following methods: physical, pyrometallurgical, hydrometallurgical methods or their combination. Hydrometallurgy brings few advantages comparing to pyrometallurgy:

- lower initial capital costs,
- lower energy consumption,
- simple pipe transportation of liquid commodities,
- possibility of leaching agents regeneration,
- production high purity metals,
- zero emission production ant etc.[2].

In already published results, authors are focused mainly on design of suitable conditions at hydrometallurgical processing of Zn batteries in order to achieve the highest possible zinc extraction into a leaching solution. For successful recycling, Zn batteries must undergo mechanical pretreatment in order to liberate and separate the active mass (powder) from other components (steel cover, plastics, paper), which can be processed in a special way. The active mass contains an increased amount of zinc. In most of the experiments, the active mass was obtained by manual dismantling of a few Zn batteries and that active mass was leached irrespective of its qualitative composition. Such a manual dismantling of small amount (or group) of Zn batteries used for an experiment can seriously affect the results of the study due to the lack of representative samples advancing to leaching. In hydrometallurgy, the step of mechanical pretreatment is very important as, except to the nature of the leaching reagent, final zinc extraction into a solution depends on quality of the active mass and also on its sufficient amount.

In this work, zinc-carbon and alkaline batteries were processed by four proposed processes of mechanical pretreatment and obtained active mass was advanced to element and phase analysis. The aim was to perform mechanical pretreatment of Zn batteries using available equipment in order to obtain representative fraction of active mass.

Experimental

Material

Since 2009, collection of used portable batteries and accumulators is realized on Technical University of Košice. This collection was introduced by Centre of Waste Processing (CENSO), which is part of the Department of Non-ferrous Metals and Waste Treatment, Faculty of Metallurgy, Technical University of Košice, Slovak Republic. Since the introduction of this collection almost 1050 kg of used portable batteries and accumulators were collected. As it is shown in Fig.1, till 86 % of collected amount is represented by used portable batteries based on zinc (zinc-carbon magnetic, zinc-carbon non-magnetic and alkaline batteries). From each type of zinc batteries, amount of 40 kg was weighted. From this amount representative sample for mechanical pretreatment experiments was obtained by using quartation.

Zinc-carbon batteries

A zinc-carbon cell consists of zinc anode (with a thickness from 0.3 to 0.5 mm) a cathode consisting of a mixture of MnO_2 (60 %), NH_4Cl (10-20 %) and carbon powder. Carbon is mixed with manganese dioxide (MnO_2) for better conductivity and maintaining moisture. In a standard Zn-C battery a solution of ammonium chloride (NH_4Cl), or zinc chloride ($ZnCl_2$) dissolved in water, is used as an electrolyte. A stick from carbon powder is placed in the center of a cell and acts as a collector of electrons. A separator made of special paper is inserted between anode and cathode, allowing ionic conductivity in an electrolyte. Surface of cylindrical batteries is very often covered by steel cover (Zn-C magnetic batteries) or by stiff paper in conjunction with a plastic film (Zn-C non-magnetic batteries) [4, 5].

Fig. 3. shows a Zn-C battery after manual dismantling.

Content of components [%]	steel	paper	graphite rod	plastic	active mass	other
Zn-C battery	22	13	7	2	55	1

Tab. 1: Material composition of a Zn-C battery

Material composition of dismantled battery is listed in Tab.1, which shows that active mass comprises more than 50 % of the weight of the battery.

Alkaline batteries

Fig. 4. shows a vertical section of an alkaline battery.

In this type of battery an anode is made of high purity zinc powder (99,85 – 99,00 %),

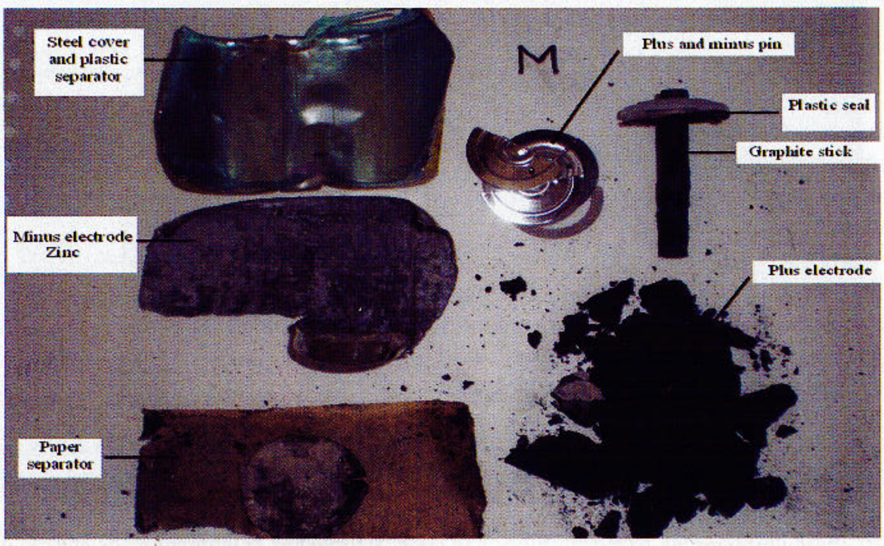

Fig. 3: Zn-C battery after manual dismantling

Content of c omponents [%]	steel	paper	brass rod	active mass	other
Alkaline battery	30	10	6	53	1

Tab. 2: Material composition of an alkaline battery

Elements	Alkaline	Alkaline	Alkaline	Alkaline	Zn-C	Alkaline	Mixture (Zn-C + alkal.)
	Content [%]						
Zn	21	12-21	19,56	17,05	28,30	13,59	15,46
Mn	45	26-33	31,10	36,53	26,30	27,65	33,59
K	4,70	5,5-7,3	7,25	4,53	0	5,1	3,26
Fe	0,36	0,17	0,17	0,07	3,40	0,1	0,5
Pb	0,03	0,005	0,005	0	0	0	0
	[8]	[6]	[9]	[10]	[11]	[12]	[7]

Tab. 3: The chemical composition of active mass

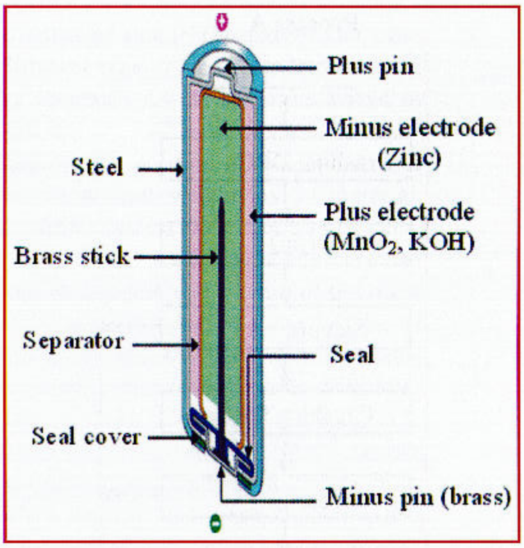

Fig. 4: A section of an alkaline battery [3]

with a particle size from 75 to 750 µm. A cathode is composed of a compact mixture of MnO_2 (85 %), graphite (10 %) and KOH (5 %). An electrolyte consists of highly concentrated KOH, which contains about 6 % of ZnO in order to avoid anodic corrosion and release of hydrogen. A membrane from synthetic fibers, e.g. PVC, separates an anode from a cathode. Positive pole of an alkaline battery is a steel container; negative pole is a separator tube, which is usually made of paper. A brass stick, where negative pole is fixed, acts as an electron collector for the electrode [4,5].

Fig. 5 shows an alkaline battery after manual dismantling.

Material composition of dismantled alkaline battery is listed in Tab. 2, the active mass also in this case represents more than 50 % of the weight of the battery.

Active mass of Zn batteries

The active mass from zinc batteries represents a mixture of anode, cathode material and electrolyte. This active mass is generated during mechanical pretreatment of batteries (crushing and milling) before their further processing. After the crushing and milling of batteries, remaining parts of steel cover, plastics and paper separator are separated obtaining a product in the form of fine-grained active mass (black powder, which represents up to 57 % of total weight of batteries) [6].

Chemical compositions of the active mass from alkaline and zinc-carbon batteries according to other authors are listed in Tab. 3.

As it results from Tab. 3, content of zinc in the active mass of the batteries is in the range of 12 – 28 %, while content of zinc in primary ores is below 10 %. From this point of view, used portable zinc batteries are becoming important secondary raw material for zinc production. Content of manganese, which accounts for approximately 26 – 45 % of the total weight of active mass, is also not negligible.

Mechanical treatment tests

Four experimental processes of mechanical pretreatment were designed. All four processes were tested for each group of Zn batteries (Zn-C magnetic, Zn-C non-magnetic, alkaline batteries).

For all experiments a common procedure was applied, as follows:

1. preparation of the sample
2. crushing – double rotor crusher,
3. drying – 12 hod., 60 °C,
4. sieving – 2 sieves (8 mm, 1.25 mm),
5. removal fraction < 1.25 mm (active mass)

After these steps, the procedures in each experiment were different. In the individual experiments either hammer crusher (ŠK 600, 7.5 kW) or friction mill was used. Also an effect of double crushing in double rotor crusher (DR 120/360, 9.2 kW) on quality of released active mass was examined. Each crushing (or milling) step was followed by sieving, where the finest fraction (-1.25 +0 mm) e.g. active mass was separated. The sample of the active mass was submitted to chemical analysis (by AAS using Varian Spectrophotometer AA 20+) in order to determine the content of zinc and to XRD phase analysis (on the PANalytical X'Pert PRO MRD X-ray diffractometer using Co K_α radiation. Remaining material proceeded to ECS separator (EPA SKR-

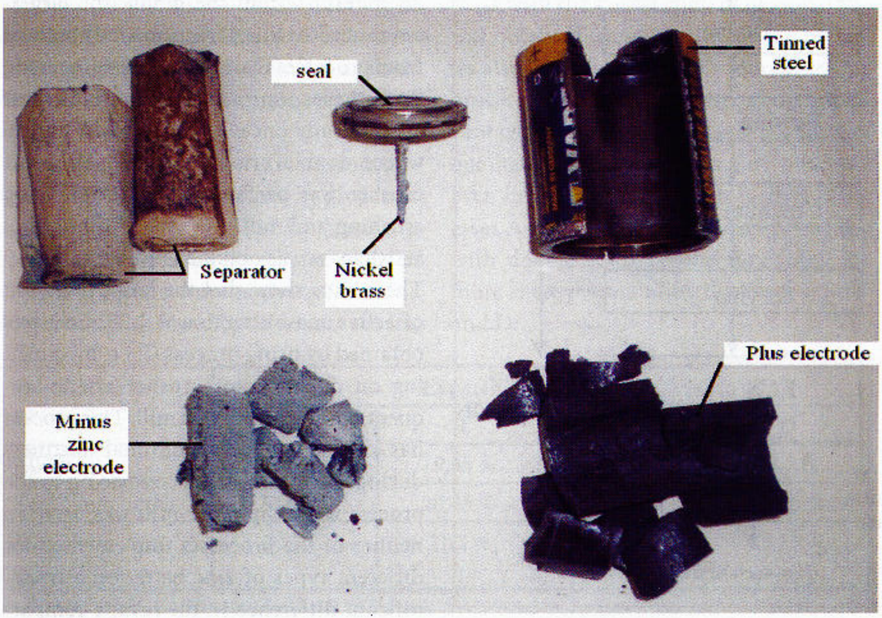

Fig. 5: Alkaline battery after manual dismantling

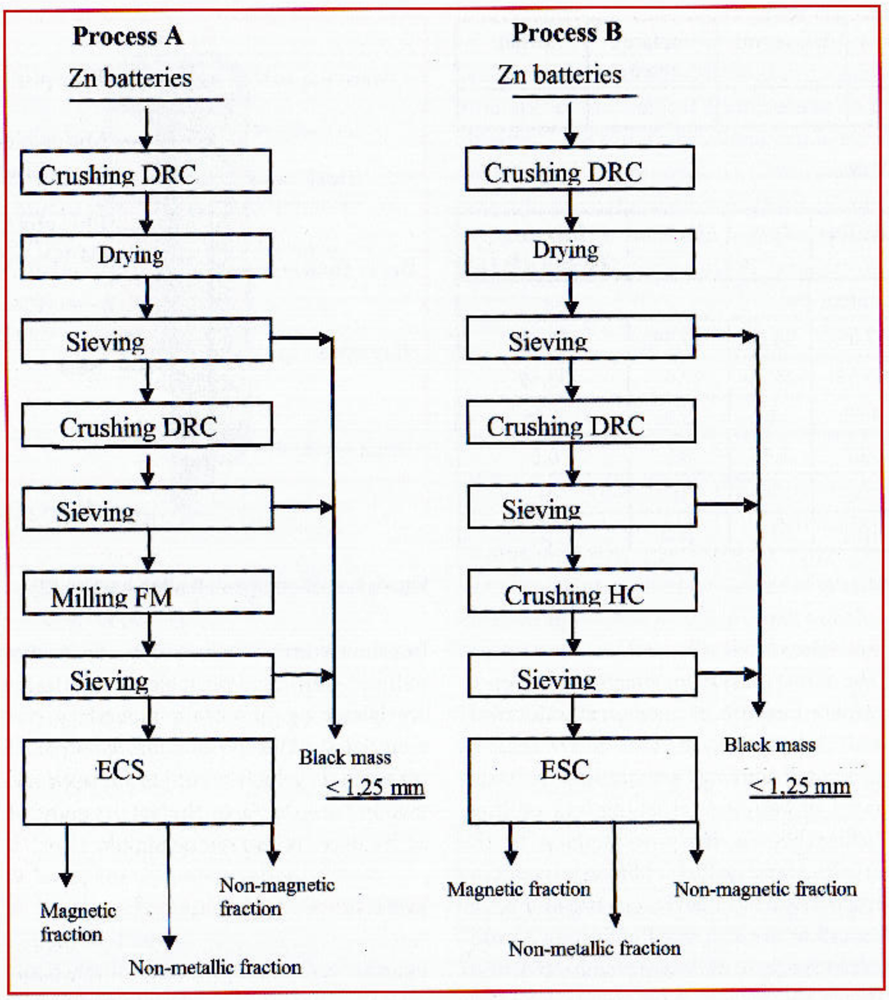

Fig. 6: The schemes of the experiments, Process A and B

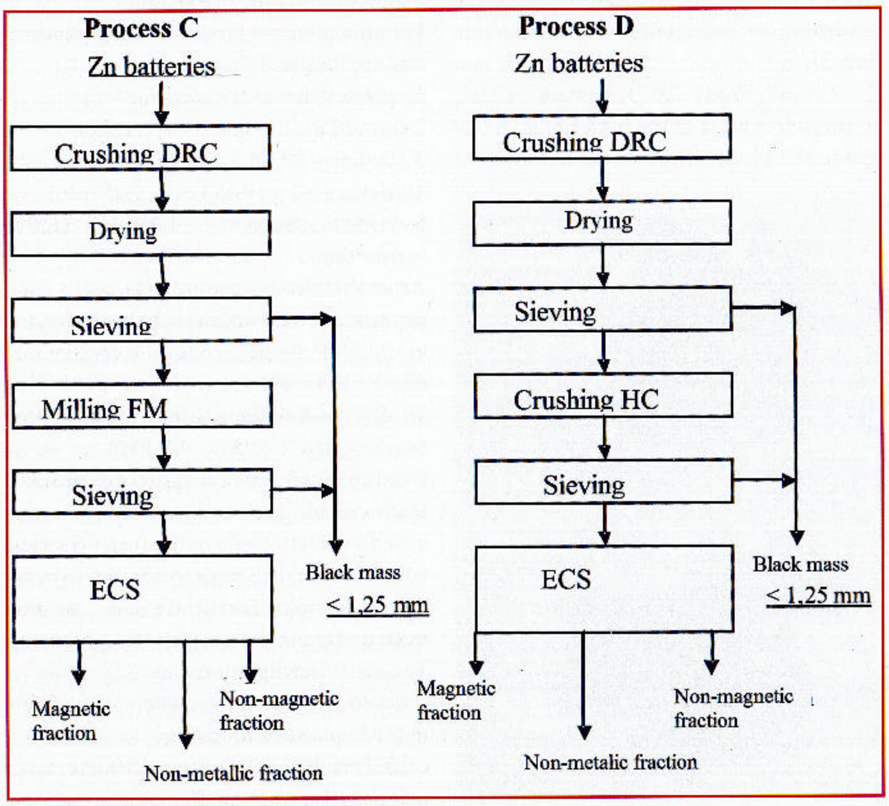

Fig. 7: The schemes of the experiments, Process C and D

240 N) where metallic magnetic, metallic non-magnetic and non-metallic fractions were separated from each other. General schemes of the processes are shown in Fig. 6 and 7.

Results

During the experiments, weight loss occurred in individual technological steps. The losses were caused by leakage of crushing facilities, adhesion of particles to the walls of equipment and containers (moisture of the material after the first crushing), loss on drying, etc.. In case of alkaline batteries, due to the moisture, the losses were relatively high (12.388 %, 18.345 %, 9.885 %). With the exception of experiments with alkaline batteries, the total material loss in eight cases did not exceed 10 % and in two cases were lower than 5 %.

The main objective of these experiments was to accumulate the largest possible amount of active mass into one fraction, concerning its character into the finest fraction, and thus separate it from other compounds. From this reason, sieving of the material was performed after each technological step. This sieving was done partly to eliminate weight losses of active mass in the following technological step and also to reduce dustiness during the experiments.

From the obtained results, it is possible to say at which of designed processes A-D, the largest amount of active mass (fractions < 1.25 mm) was separated. The results are shown in Fig. 8.

As it results from the graph, the largest amount of the finest fraction were obtained from processes C and D. In these processes, Zn batteries were crushed in double rotor crusher only once. In processes A and B, where double crushing on double rotor crusher was performed before following crushing and milling, smaller amount of active mass was obtained.

The results show that the largest amount of active mass (fraction < 1.25 mm) was obtained by using process C, i.e. by crushing on double rotor crusher and subsequent milling on friction mill. This process has also advantage of minimal dustiness during the experiments comparing to the process where hammer mill was used. In neither of the processes implemented for different types of zinc batteries, any significant difference in the results comparing to other processes, was not obtained.

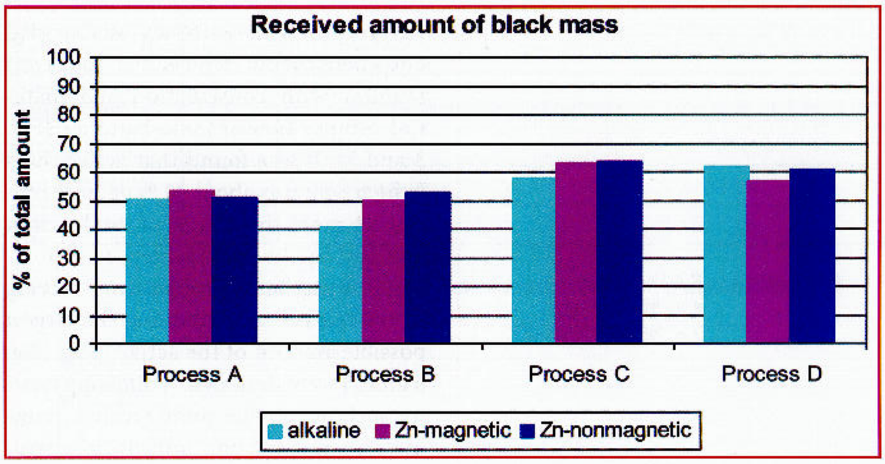

Fig. 8: The percentage of the fraction <1.25 mm with respect to the total weight of the sample in individual technological processes

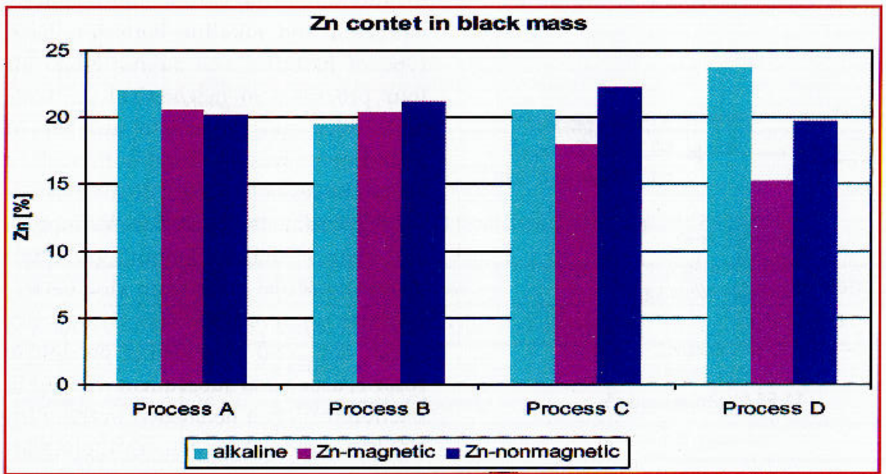

Fig. 9: Content of zinc in active mass of Zn batteries from all four processes

Therefore, it is not possible to take definitive conclusion which of the processes is the most suitable one for obtaining the largest amount of active mass from zinc batteries. From this reason, the samples of active mass from individual processes were taken and submitted to chemical analysis (by AAS) in order to determine content of zinc.

The content of zinc in active mass from different zinc batteries, obtained by processes A-D, is in the range of 15 to 23 % (shown in Fig. 9). This corresponds with the results of elemental composition of the active mass of zinc batteries stated by different authors, which are summarized in Tab. 3. The highest content of zinc, 23 %, was analyzed in the active mass from alkaline batteries obtained by the process D. The active mass with the lowest content of zinc, 15%, was obtained from Zn-C magnetic batteries also by using process D. Moreover, this process uses hammer crusher whose disadvantage is the high dustiness. Significant qualitative difference was not observed even in the active mass obtained by processes A and B, which use double crushing with double rotor crusher and thus are more energy demanding than processes C and D.

Batteries	Experimental processes			
	A	B	C	D
Alkaline	22,05 %	19,55 %	20,6 %	23,7 %
Zn-C (magnetic)	20,65 %	20,45 %	18 %	15,25 %
Zn-C (non-magnetic)	20,2 %	21,2 %	22,25 %	19,75 %

Tab. 4: Zn contet in active mass

Content of zinc in the active mass from different type of zinc batteries, obtained by processes A – D are summarized in Tab. 4.

Taking into account all conditions and results such as weight loss of material, dustiness during the experiments, energy consumption of designed processes as well as amount and quality of obtained active mass, the process C can be label as the most effective mechanical pretreatment process for zinc batteries (Fig. 10). This process consists of crushing zinc batteries using double rotor crusher and subsequent milling on friction mill. After sieving and separation of active mass (fraction < 1.25 mm), the remaining material proceeds to ECS separator where metallic magnetic, metallic non-magnetic and non-metallic fractions are separated from each other. This process results in the largest amount of active mass (which represents 57.95 % of alkaline batteries, 62.75 % of zinc-carbon magnetic batteries and 63.7 % of zinc-carbon non-magnetic batteries) containing, according to the type of batteries, 18 – 22 % of zinc.

The phase composition of the samples of active mass from different types of Zn batteries was determined by XRD phase analysis. The diffraction patterns for the samples are shown in Fig.11 to 13 and resulting phase are listed in Tab.5 to 7.

The results of XRD phase analysis confirmed the presence of phases with content of zinc, manganese, potassium, chlorine, depending on the type of analyzed active mass from Zn batteries. In case of Zn-C batteries, presence of Zn in phases $Zn(OH)_2$, $ZnMn_2O_4$ and $Zn_5(OH)_8Cl_2H_2O$ was confirmed. In the active mass from alkaline batteries zinc was present in the phase ZnO. The existence of mentioned phases in the active mass from Zn batteries was confirmed also by authors Veloso [10], Freitas [13,14] and also Ferella [15] and De Michelis [7].

Except these phases, also phases of Mn such as $MnCl_2$ and also MnO_2 were identified in the samples of active mass. The difference in phase composition can be seen only in a case of potassium (as can be seen in Tab.3). The presence of potassium was identified only in a case of active mass from alkaline batteries where KOH is used as an electrolyte. On the contrary, in active mass from Zn-C batteries, where the electrolyte is formed by NH_4Cl or $ZnCl_2$, potassium is not present.

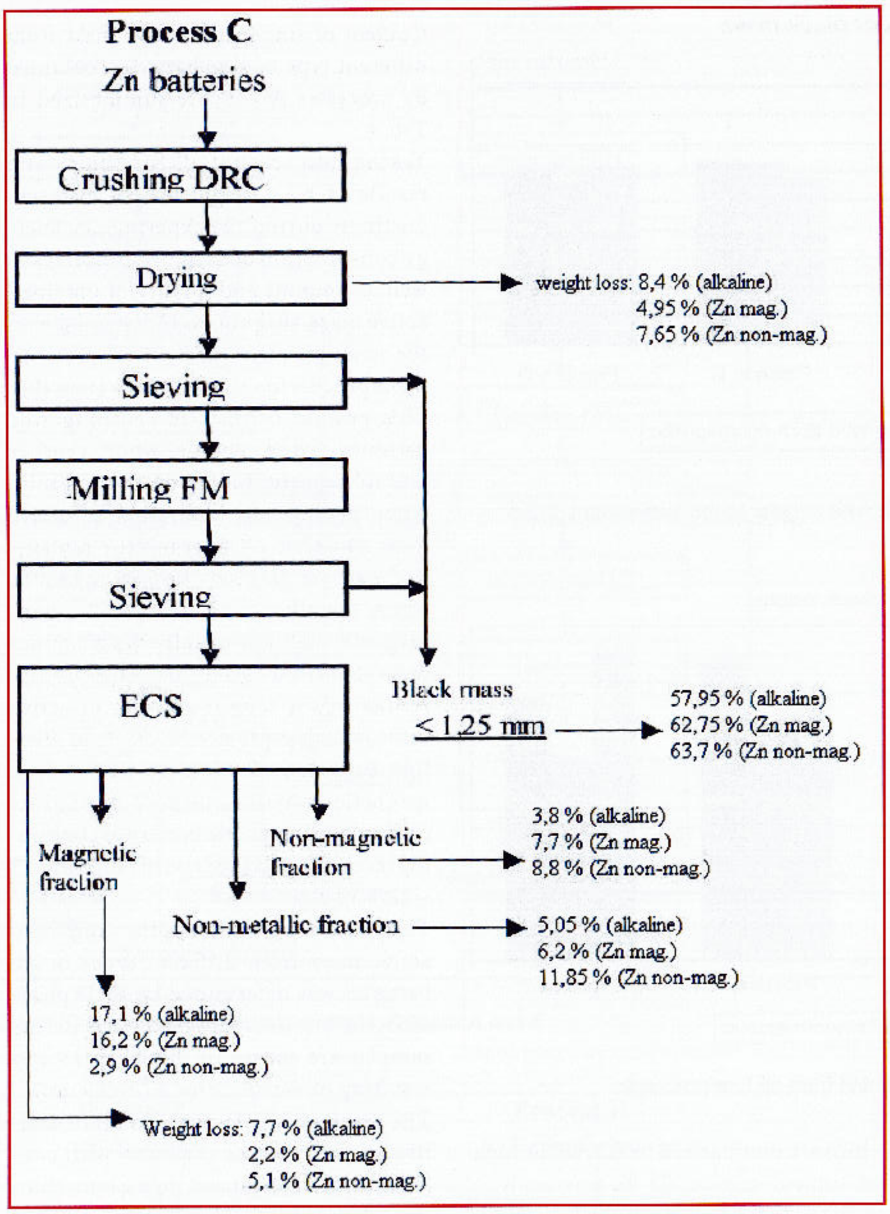

Fig.10: The most effective mechanical process

Conclusions

In order to recover zinc from used portable zinc-carbon and alkaline batteries several methods such as physical, pyrometallurgical, hydrometallurgical methods or their combination can be used. Hydrometallurgy can be described as modern, flexible processes that can be easily modified and adapted to the actual amount of input materials (in this case used portable batteries). Hydrometallurgical processing of zinc-carbon and alkaline batteries is based on leaching active mass in suitable leaching agent in order to get desired metal into the solution. This processing of batteries must be preceded by crushing, milling and separation in order to release active mass and its separation from other components (steel cover, plastics, paper), which can be processed by other way.

In the first step of experimental part of this work manual dismantling of selected types of zinc batteries was carried out where the main objective was to get familiar with construction and material composition of these batteries (Fig. 3 and 5). It was found that active mass (which contains about 20 % of zinc) represents more than 50 % of total weight of a battery. In another step, four processes of mechanical processing serving to the release and obtaining the largest possible amount of the active mass (Fig. 6 and 7) were designed. Following facility such as: double rotor crusher, hammer crusher, friction mill, ECS separator, were used for the experiments in different combinations. Input material consisted of zinc batteries (zinc-carbon magnetic and zinc-carbon non-magnetic batteries) and alkaline batteries. Each type of batteries was submitted to all four processes of mechanical pretreatment, what means that total numbers of experiments was 12. Conditions such as weight losses of batteries, dustiness during experiments, energy consumption and mainly obtained amount and quality of the active mass from zinc batteries were observed. Process C (Fig. 10), which consisted of crushing on double rotor crusher and subsequent milling in friction mill, can be labeled as the most effective process of mechanical pretreatment of zinc batteries. After sieving and separation of the active mass (fraction < 1.25 mm), the remaining material was advanced to ECS separation, where metallic magnetic, metallic non-magnetic and non-metallic fractions were separated from each other. By this process the largest amount of active mass (57.95 wt.% of input alkaline batteries, 62.75 wt.% of input Zn-C magnetic batteries and 63.7 wt.% of input Zn-C non-magnetic batteries) was obtained. Content of zinc in

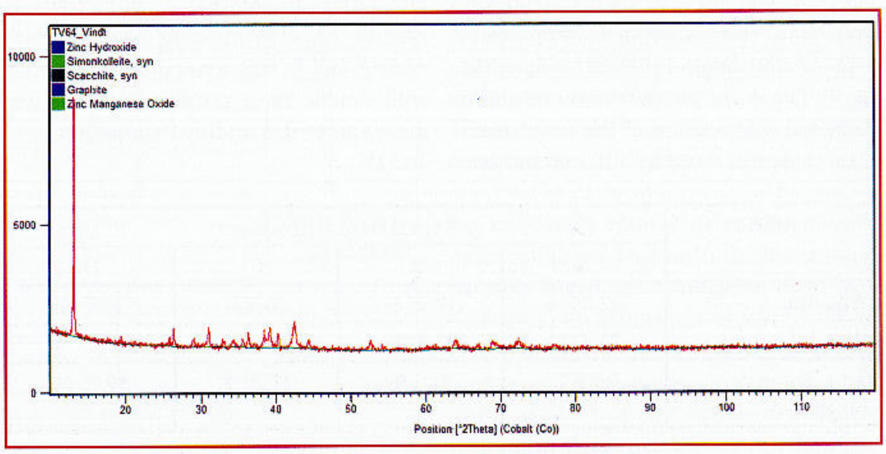

Fig.11: Diffraction pattern of the active mass from Zn-C magnetic batteries

Ref. Code	Score	Compound Name	Chemical Formula
00-048-1066	35	Zinc Hydroxide	$Zn(OH)_2$
01-076-0922	34	Zinc Hydroxide Chloride Hydrate	$Zn_5(OH)_8Cl_2H_2O$
01-075-2078	27	Graphite	C
01-077-0470	16	Zinc Manganese Oxide	$ZnMn_2O_4$
00-022-0720	8	Manganese Chloride	$Mn Cl_2$

Tab. 5: The results of XRD phase analysis of active mass from Zn-C magnetic batteries

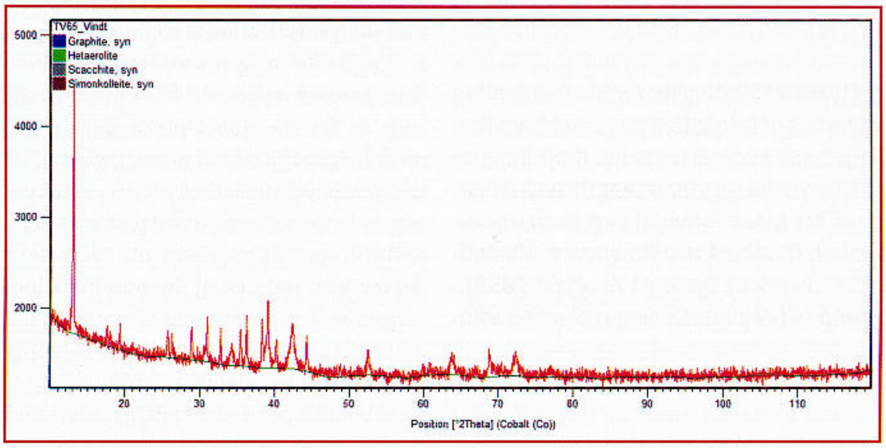

Fig. 12: Diffraction pattern of the active mass from Zn-C non-magnetic batteries

Ref. Code	Score	Compound Name	Chemical Formula
01-076-0922	76	Zinc Hydroxide Chloride Hydrate	$Zn_5(OH)_8Cl_2H_2O$
01-075-2078	45	Graphite	C
00-022-0720	20	Manganese Chloride	$Mn Cl_2$
01-077-0470	17	Zinc Manganese Oxide	$ZnMn_2O_4$

Tab. 6: The results of XRD phase analysis of active mass from Zn-C non-magnetic batteries

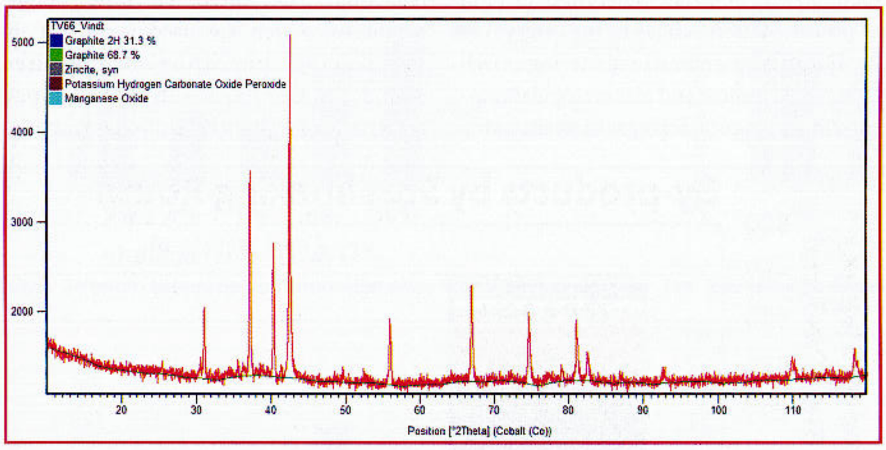

Fig. 13: Diffraction pattern of the active mass from alkaline batteries

Ref. Code	Score	Compound Name	Chemical Formula
01-079-0205	64	Zinc Oxide	ZnO
96-901-2706	22	Graphite	C6.00
03-065-1298	8	Manganese Oxide	MnO_2
96-101-1061	15	Graphite 2H	C4.00
01-088-1458	5	Potassium Hydrogen Carbonate Oxide Peroxide	$K(H(O_2)CO_2)(H_2O_2)$

Tab. 7: The results of XRD phase analysis of active mass from alkaline batteries

this active mass was in range 18 – 22 % (Fig. 9). XRD phase analysis confirmed presence of zinc in the active mass in the following phases: $Zn(OH)_2$, $ZnMn_2O_4$ and $Zn_5(OH)_8Cl_2H_2O$ (Fig. 11, 12 and 13). It results from chemical analysis (AAS) XRD analysis that compositions of active mass from Zn-C and alkaline batteries are very similar, what makes possible their common processing in order to recover zinc.

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