TECHNICAL AND ORGANISATIONAL CONDITIONS IN THE MANAGEMENT OF RECOVERY AND RECYCLING PROCESSES OF WASTE BATTERIES AND ACCUMULATORS

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Introduction/background: Waste batteries and accumulators are hazardous waste and should not be sent to landfill sites. Their presence in the waste mixture causes the release of dangerous heavy metals into the natural environment.
Aim of the paper: The aim of the study is to review the processes currently used in the recycling of used batteries and accumulators, currently used in the world and in Poland, as well as installations and technologies, depending on the types, kinds and physicochemical properties of waste, and to draw attention to the ventures to prevent waste generation.
Materials and methods: The paper discusses the nature of waste, storage and transport conditions, organisation of collection, processes and processing technology. The article presents examples of waste management facilities dealing with recovery and recycling of batteries in Poland and Silesia. The research was based on an analysis of legal acts, statistical data, professional literature and company experiences. The second part is a case study. Selected environmental systems presented on descriptive models are based on the results of an environment (region) system analysis.
Results and conclusions: EU directives and national law force the reuse of raw materials used in their production. Therefore, one should strive to apply the most effective technologies of waste recovery and recycling. The most recommended and cost-effective is product salvage followed by material recovery, especially of scarce, rare and precious earth metals. Various processes and technologies (installations) for the recovery of raw materials from waste batteries and accumulators are used around the world. The best known are: Jogmec, Batrec, Recytec, Accurec, Everead, Inmetco, Sab-Nife, Snam-Savam, Citron, Batenus, TNO. Long battery life minimises the amount of waste, and thus reduces the burden on the environment. Therefore, in the process of producing batteries, it is important to improve the technology already at the production stage. An example is the Polish experience (Europower; Tuborg; Tuborg-Silver).

Keywords: hazardous waste, waste recovery and recycling, recycling efficiency, recycling technologies, waste battery and accumulator processing plants.

1. Introduction

Used batteries are a source of valuable raw materials. Recycling the metals they contain saves energy used to extract, process and separate metals from minerals. In addition, the use of recycling reduces the risk to the environment posed by the metals contained in waste batteries/accumulators. Collection of these wastes at landfill sites leads to decomposition and accumulation of toxic metals in landfill leachate (Grzybowska, 2009). The substances that make up batteries and accumulators become dangerous for the environment and human health after they are used up, as they contain: lead, mercury, cadmium, nickel, cobalt and their compounds and the hydroxides: potassium, sodium, lithium. The management of this waste is complex due to its basic composition, as well as the wide range of equipment used in many areas of life (Kawczyńska, 2014; Act of 27 April 2001; Act of 14 December 2012; Kłopotek, 2004; Grzesik, 2005). Recycling of batteries eliminates waste that poses a serious threat to the environment, while at the same time acquiring substances of high purity, useful for various industries.

The hazardous waste management system designed as part of the "Comprehensive hazardous waste management programme for the region of southern Poland" is based on an organised network of municipal collection points (GPZON), transhipment stations (SPON) and enterprises and recovery organisations that have their own network covering the entire country. In terms of the level of collection, recovery, recycling and disposal, as well as the number of units carrying out these processes, batteries rank third in the recycling system (Wengierek, 2017a, 2017b).

2. Nature of the waste

2.1. Battery types and substances contained therein

In accordance with the Regulation of the Minister of the Environment (Regulation of the Minister of the Environment of 27 September 2001; Regulation of the Minister of the Environment of 9 December 2014), waste batteries and accumulators were classified into group 16 (waste removed in other groups) and subgroup 16 06 (batteries and accumulators). In this subgroup, the following types of hazardous waste are listed (*):

16 06 Batteries and accumulators.

16 06 01* Lead batteries and accumulators.

16 06 02* Nickel-cadmium batteries and accumulators.

16 06 03* Batteries containing mercury.

16 06 04 Alkaline batteries (except 16 06 03).

16 06 05 Other batteries and accumulators.

16 06 06 06* Selectively collected electrolyte from batteries and accumulators.

The Act of 24 April 2009 defines a battery and accumulator as a source of electrical energy generated by the direct conversion of chemical energy, which consists of one or more:

- primary non-rechargeable battery cells,
- secondary rechargeable battery cells.

This Act defines different categories of batteries and accumulators (Act of 24 April 2009):

- industrial battery, industrial accumulator — intended exclusively for professional use — industrial use or for installation in electric vehicles,
- portable battery, portable accumulator — a battery and accumulator including button cells or sets that are tightly closed and capable of being carried in the hand and are not industrial or automotive batteries or accumulators,
- automotive battery, automotive accumulator — battery and accumulator used for starter, lighting or ignition initiation in vehicles.

The most popular cells, depending on the type of construction, are: AAA, AA, AA, R1, R14 (UM2, MN1400, HP11), R20 (MN1300, UM1) and PP3-PP9. There is also a division according to the chemical composition of the cells (Jaśnikowski, Marcinkowski, Marek, 2002).

Depending on the composition of the electrolyte and the design of the electrodes, the following battery types are distinguished:

a) Lead-acid batteries — where the electrolyte is a sulphuric acid solution, the electrode (-) is made of lead (with additives) in the form of a grid, and the electrode (+) is made of lead oxide (IV) PbO_2 immobilised on a lead frame – such batteries are used extensively in cars.

b) NiCd accumulators — also known as secondary alkaline batteries – in which the electrodes are made of nickel hydroxide and cadmium hydroxide, and the electrolyte is a semi-fluid or solid substance with a chemical composition varying according to the manufacturer but always having a strongly basic (or alkaline) reaction.

c) NiMH accumulators — an improved version of NiCd accumulators, in which one of the electrodes is made of nickel and the other of sintering rare earth elements (REE) in a hydrogen atmosphere. An electrolytic key is a spongy structure soaked in alkaline substances and a chemically complex catalyst.

d) Li-ion batteries, where one of the electrodes is made of porous carbon and the other of metal oxides, and the electrolyte is made up of chemically complex lithium salts dissolved in a mixture of organic solvents.

e) Lithium polymer batteries — a variety of Li-ion batteries in which the liquid electrolyte is replaced by a solid polymeric electrolyte made of, for example, a polyacrylonitrile-based sponge.

Depending on the charging cycle, a differentiation is made:

- Non-renewable batteries — these are batteries whose construction allows them to be discharged only once. They are made of materials used for the production of secondary batteries, but their construction and production stages are completely different. Therefore, it is not recommended to recharge the primary batteries. Batteries of this type are dominated by the following batteries:
  - Alkaline-manganese.
  - Zinc-carbon.
  - Zinc-air.
  - Lithium.
  - Silver.
  - Mercury.
- Renewable batteries work in the same way as primary batteries, but their chemical processes can be reversed by recharging. The battery is able to recover its original properties and can be used again. Typical secondary batteries are:
  - Nickel-cadmium.
  - Nickel-hydrogen.
  - Lead-acid.
  - Lithium-ion.
  - Alkaline-manganese.

Batteries and accumulators are used in means of transportation, for emergency or power supply in torches, measuring equipment, telephones, tablets, portable computers, cordless electrical appliances, household appliances, etc. Currently, 80% of the batteries used in Poland are disposable batteries. 90% of the amount of waste batteries is generated in transportation, both by business entities and individual users (www.rewolucjawsmieciach.pl/......).

One tonne of used batteries contains on average the following ingredients: 270 kg manganese dioxide, 210 kg iron, 160 kg zinc, 60 kg graphite, 35 kg ammonium chloride, 20 kg copper, 10 kg potassium hydroxide, mercury (mercury oxide) 3 kg, a few kilograms of nickel and lithium (4 kg), 0.5 kg cadmium, 0.3 kg silver (silver oxide), small amounts of cobalt (Korkozowicz, 2010).

The table below presents an example of the material balance of the recycling process of used automotive accumulators, as well as nickel-cadmium, nickel-metal hydride and lithium batteries. The data is related to 1 tonne of waste (Orzeł Biały SA).

Table 1.
Material balance of the recycling process of waste batteries/accumulators

Waste types	Income (kg)	Outcome (kg)
Used automotive batteries	1,000	
Gypsum		140
Granulate		55
PVC		35
Lead		770
TOTAL	1,000	1,000
Used nickel-cadmium batteries	1,000	
Nickel		190
Cadmium		270
Iron		310
Cobalt		10
Other elements		220
TOTAL	1,000	1,000
Used nickel-metal hydride batteries	1,000	
Nickel		420
Iron		290
Lanthanum		110
Cobalt		10
Other elements		170
TOTAL	1,000	1,000
Used lithium batteries		
Lithium		10
Iron		100
Phosphate minerals		190
Copper		110
Aluminium		240
Graphite		130
Other elements		220
TOTAL	1,000	1,000

Source: Own work based on Orzeł Biały SA.

3. Collection, transport and storage of waste batteries and accumulators

Transport of batteries from collection points to specialised processing plants should be in compliance with applicable laws and regulations. In the case of waste batteries/accumulators, collection schemes are limited and mainly operated by recovery organisations or entities that fulfil the obligations of producers of batteries or accumulators. In the Silesian Voivodeship, these are, among others, the following companies: Elektrozłom Sp. z o.o. — Ślemień, Marco Ltd. Sp. z o.o. — Katowice, Baterpol Sp. z o.o. — Katowice, Przedsiębiorstwo Techniczno-Handlowe TECHNIKA Sp. z o.o. — Gliwice, Mariola Studnic Ekoland — Chałupki, Orzeł Biały SA — Bytom, Prolimit Sp. z o.o. — Katowice, Andrzej Kochel Śląskie Centrum Utylizacji SCU — Katowice, Amper Sp. z o.o. — Tarnowskie Gory, Adam Ben EKO-RORT — Bielsko-Biała, Wektor A. Chudak Sp. j. — Katowice, Włodzimierz Błachut — FPHU BŁACHUT — Sienna (Waste Management Plan ...; Voivodeship ...).

Used portable and small-size batteries are collected in most educational institutions, local government entities and chain stores selling such products.

A separate collection scheme is proposed for waste portable batteries and accumulators, as they are small and very dispersed, as well as to fulfil the obligation to meet the required collection levels.

Used batteries/accumulators as hazardous waste require special EU-approved containers and cars for collection and transport, hence processing plants equip their suppliers with acid-proof containers. Processors also have their own trucks adapted to transport this waste, but their delivery is also handled by specialised transport companies and companies collecting and buying recyclable materials.

The storage and treatment of used batteries should be carried out in places with a hardened, impermeable, weather-resistant surface or in suitable containers resistant to the substances contained therein. On the other hand, waste lead-acid batteries should be stored on impermeable surfaces connected to a closed-circuit sewage system, directing the sewage to special tanks or to an installation processing waste batteries. Used batteries should be stored for a maximum of one year in total.

The main sources of supply of used batteries are:

- companies with their own purchasing points,
- companies specialising in the purchase of scrap from various sources and in its transport to processing plants,
- manufacturers of batteries and accumulators,
- complementary import from abroad.

The level of battery collection in selected EU countries, Poland, including the Silesian Voivodeship, is as follows. Poland is ranked 6th after Belgium, Denmark, the Netherlands, Germany, Czechia (g/person collection rate). In terms of the number of collection points, the Silesian Voivodeship is ranked 2nd (3,003 collection points) after the Masovian Voivodeship (3,305 collection points). Other voivodeships are: Greater Poland, Lower Silesia, Lesser Poland, Łódź, Pomerania and Kuyavian-Pomeranian (www.reba.com.pl).

An important part of the EU directives and the Batteries and Accumulators Act is the minimum requirements for the recycling efficiency of waste batteries and accumulators. These standards depend on the type of waste treated (Directive...; Commission Regulation...).

On 27 September 2011, the minimum recycling efficiency levels came into force by means of technologies and installations for the treatment and recycling of specific types of waste batteries/accumulators (www.mos.gov.pl; Regulation of the Minister of the Environment of 3 December 2009):

- achieving a collection rate for used portable batteries/accumulators of at least 45% of the mass of introduced portable batteries/accumulators in 2016 and subsequent years,
- maintaining the level of recycling efficiency:
  - used lead-acid batteries/accumulators of at least 65%,
  - used nickel-cadmium batteries/accumulators of at least 75%,
  - other used batteries/accumulators of at least 50%.

In 2014, Poland achieved the required recycling efficiency levels for waste batteries and accumulators set out in Directive 2006/66/WE. This is (Report...):

- 77.3% for waste lead-acid batteries/accumulators,
- 85.5% for waste nickel-cadmium batteries/accumulators,
- 56.7% for other waste batteries.

According to the report of the Chief Inspectorate of Environmental Protection [GIOŚ] on the functioning of the system of management of batteries and accumulators and waste batteries and accumulators for 2014, all collected used batteries and accumulators were subjected to treatment, including recycling (in accordance with Article 12, paragraph 1 of Directive 2006/66/WE).

The collected waste has not been exported outside the EU. In 2014, over 1,402 Mg of waste with code 16 06 01* (in 2013, this was 1,917 Mg) was imported to Poland from Germany, Slovakia and Cyprus (rzseie.gios.gov.pl/...; www.mos.gov.pl).

The recycling rate of waste batteries and accumulators in 2015 amounted to 109.68%. In the previous years, the recycling rate achieved by Poland was lower. This was 80.43% in 2014, 91.23% in 2013 and 98.59% in 2012. The plants did not process all used batteries; surpluses were accumulated in warehouses and, depending on the volume and capacity of the installation, were gradually processed in 2015 (Report...).

For waste portable batteries/accumulators, 38.35% (assuming a 40% level) was collected in 2015 (Directive ...; Report ...).

In the Silesian Voivodeship in 2014, a total of approximately 2,300 Mg of waste batteries and accumulators were produced, including 2,200 Mg of hazardous waste. However, approximately 14,700 Mg was collected, including 14,400 Mg of hazardous waste. A total of almost 76,000 Mg of waste was recovered (six recovery and recycling plants). The dominant recovery process was process R4 (Recycling and recovery of metals and metal compounds) (Voivodeship...).

Due to the progressive development of technology, more and more batteries and accumulators are being used in various areas of life. Assuming an increase of 1-1.5% in the amount of collected waste batteries and accumulators per year, for 2030, this increase in relation to the base year 2013 will amount to about 20-25%, while maintaining the percentage level of collection set for 2016 (www.mos.gov.pl/pl/......).

In the Silesian Voivodeship, the forecast of the volume of battery waste expected to be collected separately by 2030 is as follows: 2020 — 2,627 Mg/year, 2022 — 2,951 Mg/year, 2028 — 3,414 Mg/year, 2030 — 3,883 Mg/year (ietu.pl).

Such a small upward trend in the quantity of collected waste batteries will result from the improvement of their quality and the extension of their lifespan.

4. Recovery and recycling technologies of batteries and accumulators

All types of batteries/accumulators contain metals and their compounds and possible additives, e.g. graphite, polymers, etc. This makes it necessary to use different processing methods and technologies (ippc.mos.gov.pl/ippc/...).

Depending on the type of waste (cells of one type or a mixture of cells), three basic types of material recovery processes are used in the battery/accumulator recycling process (Pyssa, 2007; Kopczyk, 2005; Rogulski, 2005):

- Mechanical (separation).
  They are most often used for large batteries (industrial type) and as a preliminary operation in most of the processing technologies. They involve mechanical loosening of the structure (body) of the battery and separation of components with characteristic physical properties (density, size, magnetic properties). These activities are usually simpler and cheaper than other processes and should therefore be used to prepare the material stream for further chemical processing. Mechanical methods most often boil down to shredding and separating into individual fractions of used battery mass: ferromagnetics (steel, chromium, nickel), diamagnetics (paper, plastics, tar), paramagnetics (other impurities, non-ferrous metals, graphite) (Lower Silesia...). Technologies for recovery and disposal of batteries and accumulators were presented in detail on the example of the DKE Oława Sp. z o.o. battery recycling installation in Polkowice (Dolnośląska...; www.reba.pl).

- Thermal (pyrometallurgical).
  They are based on the recovery of materials by melting metals in special furnaces. Their advantage is the possibility to recycle various types of cells, including those containing organic electrolyte. On the other hand, the relatively low efficiency of such recycling and the possibility of creating secondary waste during the process significantly limits their use. There are industrial installations that process unsorted battery and accumulator scrap, such as CITRON (France). The technology applied there allows for the recovery of zinc, lead and cadmium after their evaporation in a rotary kiln at a temperature of 1,250°C. Other metals, such as iron, manganese, nickel, chromium, cobalt, copper and others, found in the reaction sludge, may undergo further processing. Pyrometallurgical technologies (Sab-Nife, Snam, INMETCO), based on the distillation of cadmium at 900°C are used in the processing of Ni-Cd batteries. Cadmium is recovered in the form of powder – cadmium oxide. The oxide obtained is used, among other things, for the production of accumulator masses and cadmium pigments, and any ferro-nickel-containing parts are used for the production of alloy steels. In these technologies, nickel and cadmium are not fully recovered. In addition, pyrometallurgical processes are energy-intensive and cause the emission of dust and gases into the atmosphere.
- Hydrometallurgical.
  They are based on acidic or alkaline leaching of properly prepared battery waste (after mechanical treatment processes). It is followed by a sequence of physicochemical operations that lead to the separation and concentration of valuable or burdensome components between the relevant phases, all the way to commercial products and semi-finished products for separate technological processes. The advantages of these methods are low energy inputs and the generation of small amounts of secondary waste. The overall process generally involves the following steps: dissolving the respective waste fractions, purifying and concentrating the resulting solution, separating pure chemicals. In industrial practice, the Batenus technology is most often used. This is a multi-stage hydrometallurgical process that has been in use since 1996. It allows for the recovery of more than 99.5% of components from used batteries and accumulators, and the recovered metals are directly reusable. The TNO process, which involves leaching in hydrochloric acid, is also often used, followed by cadmium extraction with tri-butyl phosphate. Finally, nickel and cadmium are recovered by electrolysis. Bertolozzi has developed a method based on selective leaching in sulphuric acid (VI) and metal recovery by ion exchange and solvent extraction of the sludge fraction of crumbled Ni-Cd batteries. The final product of this technology is nickel, cadmium and iron salts. Recovery of the useful components of Ni-MH batteries is possible thanks to a combination of two-stage leaching (HNO3, HCl), solvent extraction and precipitation techniques. As a result of these processes, 16% of used batteries and accumulators is recovered (Wengierek, 2018; Sobianowska-Turek, 2009).

4.1. Recycling of lead-acid batteries

A lead-acid battery consists of two sets of lead plates and a vessel with electrolyte. One plate set is a positive pole. These plates are coated with lead dioxide (PbO_2). In the second group of plates, which is a negative pole, the so-called spongy lead is used. Plates made in this way are placed in the electrolyte. The electrolyte in this type of batteries is a sulfuric acid solution.

In motor vehicles, lead-acid batteries are still the most frequently used source of static energy (Merkisz, 2011).

The process of recycling lead-acid batteries consists of the following stages (Bendkowski, Wengierek, 2004; Pyssa, 2006):

1. Separation of the battery into components. This technology involves dismantling the battery, then separating and filtering the components: metallic fraction, polypropylene from the battery casing, pastes (mainly lead sulphate and lead oxides), polyethylene, electrolyte.
2. Desulphurisation. As a result of this process, the sulphur content of lead paste drops from approximately 8% to maximum 1%.
3. Crystallisation of sodium sulphate. The filtered and chemically purified solution is directed to the crystallisation line. This process results in high-purity crystalline sodium sulphate.
4. Production of raw lead. The metallic fraction recovered in stage 1 and the lead paste desulphurised in stage 2 are melted down into crude lead in fully automated melting lines.
5. Production of refined lead and lead alloys. Raw lead is melted in refining boilers and subjected to refining processes, i.e. removal of foreign metal impurities.

The main product of battery recycling is refined lead of high purity and lead alloys intended mainly for battery manufacturers. Other products recovered in the process of battery scrap recycling include: polypropylene intended for manufacturers of plastic products and crystalline sodium sulphate used in the chemical, glass, paper and textile industries.

4.2. Recycling of large and small size nickel-cadmium batteries

The nickel-cadmium battery (Ni-Cd) is one of the most common types of battery, which is equipped with high quality electrodes made of basic nickel oxide and metallic cadmium. Ni-Cd batteries and accumulators can be divided into small and large size. While the former are mainly used in cordless and mobile phones, the latter, due to their large electrical capacity and durability (10-12 years), are used in mining, metallurgy, telecommunications and railways. The treatment of Ni-Cd batteries and accumulators includes recycling processes using various technologies. These include (Wolff, Ziaja, Stryjewski, 2006):

- Accurec technology.
  The first stage of processing is to remove the electrolyte and then to separate the casings, mainly made of plastics. The remaining material is vacuum distilled in a quartz tube furnace, in which a container of raw material is placed and inductively heated. The process is carried out in two stages at a pressure of about 10 mbar. First, the plastic parts are burned at a temperature that does not exceed 500ºC; the temperature is then raised to 850ºC, and cadmium is distilled. A single operation takes about 12 hours. Cadmium purity is 99.95% unless other batteries are mixed in the batch. The processing plant is located in Mülheim, Germany, with an annual capacity of 1,000 Mg.
- Everead technology.
  Another process developed for the recycling of nickel-cadmium batteries (Ni-Cd) is the Canadian Everead process. It was created for waste containing cadmium. It is a pyrometallurgical technology whose three basic operations are carried out in one furnace. The cycle begins with heating the material for about 1.5-2 hours at a temperature of 200-300ºC. Its purpose is to remove moisture. The temperature is then raised to 500-700ºC, and heating continues for another 2-2.5 hours. In this phase, organic material is fired. Ultimately, the temperature is raised to 900-1,100ºC, and cadmium is distilled. This stage lasts 2.5-3.5 hours and is carried out under inert gas conditions (argon) and after the charge surface has been covered with carbon material. Cadmium vapours are condensed in the adjacent chamber, where a temperature of 300-400ºC is maintained. The declared purity of cadmium produced in this way is 99.9998%.
- Inmetco technology.
  lnmetco is a process developed by the International Nickel Company (INCO). Originally, it was designed to process dust from electric furnaces, but it can also be used for other materials, e.g. nickel-cadmium batteries. Technological operations begin with placing dusts with carbon reducing agents in a rotary kiln, in a thin layer, and heating them up to 1,350ºC. Zinc and lead pass into the gaseous phase, while chromium and iron remain in the granular material. In the case of batteries, e.g. Ni-Cd, Ni-Fe, Ni-MH, Li-ion and Zn-Mn (excluding those containing mercury), cadmium is also transferred into the gaseous phase. The products of the process (volatile dust and firings) are processed separately. Pre-selection of batteries plays an essential role in the technology, preventing contamination of the product, removal of electrolyte and crushing of the larger ones. Currently, in the developed variant, the material from cadmium batteries, after preliminary preparation, is heated for 12-14 hours in a chamber furnace at 950ºC, in a non-oxidising atmosphere, in order to isolate cadmium. Only after this process is the material directed to the electric furnace. The purity of cadmium obtained in this way remains at a level of 99.95%.

- The Sab-Nife process.
  One of the first nickel-cadmium battery recycling processes developed in Sweden in the 1980s is Sab-Nife. At the beginning, electrolyte is removed, and the electrodes are cleaned and dried. The material (electrodes) then goes to the reactor, where three consecutive operations are performed. The first reactor is heated to 400-500ºC, and the organic matter is burned in a controlled atmosphere of a mixture of nitrogen and oxygen. This stage lasts approximately 24 hours, and the control of the process conditions (especially the oxygen potential) is related to the reduction of cadmium evaporation. Process gases are burned in a separate chamber. After the organic matter is burned (gasified), the reactor temperature is raised to approximately 900ºC, and cadmium is distilled. During this process, a reduction atmosphere (a mixture of nitrogen and hydrogen) is maintained. This stage lasts about 20 hours, and after its completion, the batch contains no more than 0.01% of cadmium. In the last part, the temperature is raised to about 1,300ºC to obtain an Fe-Ni alloy. The purity of cadmium obtained in this way is, as in the case of other processing technologies, 99.95%.
- Snam-Savam technology.
  The Snam-Savam process originates from work conducted by two companies in the 1980s: Société Nouvelle Dáffinage dês Métaux (Snam) and Société Aveyronnaise de Valorisation dês Métaux (Savam) in France. Currently, the process is used for Ni-Cd and Ni-MH batteries. First, the plastic containers are pre-treated, i.e. they are cut and separated. The recovered electrolyte is cleaned of cadmium and sold to battery manufacturers. The cathode and anode material, together with household batteries, is divided into three categories: containing cadmium, containing nickel but not cadmium, not containing any of these elements. In the cadmium material, the organic part is gasified, and the metallic cadmium is distilled. It is then melted together with components containing nickel, but without cadmium, into an Fe-Ni alloy.

4.3. Recycling of portable batteries/accumulators

In the case of recycling of portable batteries and accumulators, the recycling process is more standardised, despite the use of different treatment methods (Sobianowska-Turek, 2009).

The Ni-MH battery recycling process consists of the following steps:

- sorting,
- a discharge of residual energy from the battery,
- thermal decomposition of organic parts, mainly plastics,
- extraction metallurgy, i.e. melting and purification of metals,
- recovery of nickel and iron, for use in the production of stainless steel,
- return of metal hydride elements as slag (low value, used e.g. as road aggregate).

The recycling process of lithium, lithium-ion batteries consists of the following steps:

- sorting,
- a discharge of residual energy from the battery,
- cooling the battery to at least -160°C with liquid nitrogen,
- cutting and shredding of batteries,
- separation of shredded material (sorting),
- conversion of lithium to lithium carbonate or lithium oxide,
- neutralisation of electrolytes to the form of permanent compounds,
- recovery of cobalt from lithium-cobalt oxide ($LiCoCO_2$), if possible.

The existing recycling processes for the material recovery of lithium-ion and Ni-MH batteries and cell packs are based on a melting process in which batteries, cell packs and other output materials are loaded into a kiln without pre-treatment, which minimises the risk for operators (prevents the formation of carcinogenic hazardous substances, i.e. dioxins and furans).

Melting conditions are strictly controlled. In the process, we obtain pure slag (used in the construction industry as an aggregate for concrete). In the cobalt and nickel cleaning installation, alloys containing these two elements can be further processed to obtain pure cobalt and nickel. In a further process, the cobalt obtained is converted into final lithium-cobalt dioxide ($LiCoO_2$), which can be used in the production of new lithium-ion batteries.

The nickel-metal hydride battery recycling project was developed by Jogmec, supported by the Japanese government. It aims to increase metal recovery and to reuse and reduce the amount of hazardous waste. In addition, the company has developed a technology to increase the recovery of nickel, cobalt and cerium/rarity metal alloy (lanthanum and cerium) for reuse. Thermal recovery processes used for Ni-Cd cells are designed to recycle large industrial cells used in the railway industry, by power plants, the army and telecommunication companies, as back-up energy sources. Small Ni-Cd cells used in transmitter-receivers, portable tools and electrical devices, medical equipment and emergency lighting installations are also reprocessed.

The recovered cadmium is used to produce new Ni-Cd batteries. Nickel and iron are melted again into an alloy used for the production of stainless steel. Battery electrolyte can be used as a reagent in wastewater treatment plants (www.jogmec.go.jp).

Lithium-metal-hydride batteries provide even longer service life (much higher energy storage density). Currently, there is a lot of research going on into silicon, which is the best lithium absorbing material with the highest capacity of all known materials.

5. Recovery and recycling facilities for batteries and accumulators in Poland, including the Silesian Voivodeship

As of 31 December 2014, a total of 2,798 businesses were registered, including 2,774 businesses placing batteries or accumulators on the market (630 businesses placing only batteries and accumulators on the market and 2,144 businesses placing batteries or accumulators together with electrical and electronic equipment on the market) and 24 businesses operating waste battery or accumulator treatment plants. The number of entities introducing batteries/accumulators in the territory of the Silesian Voivodeship as of 11 October 2015 amounted to 339 (Voivodeship...).

Within the territory of Poland, there are two installations for processing waste nickel-cadmium batteries and accumulators with a capacity of over 2,000 Mg. Taking into account the mass of waste nickel-cadmium, large and small batteries and accumulators recycled in 2014 (504 Mg) and the mass of those batteries placed on the market in 2014 (939 Mg), it can be estimated that the capacity of the installations for the treatment of this waste group in Poland is sufficient.

The waste batteries and accumulators produced in the Silesian Voivodeship are estimated at about 7,000 Mg/year. These are mainly used lead-acid batteries with electrolyte produced in an amount of about 6,650 Mg/year, large-size Ni-Cd batteries – 300 Mg/year, small-size Ni-Cd batteries – 50 Mg/year and other small-size (including mercury) batteries – about 6 Mg/year. In the voivodeship, the recovery of Ni-Cd batteries is handled by MarCo Ltd. located in Rudniki near Częstochowa, which recovers iron-nickel plates, iron-cadmium plates and electrolyte. The electrolyte is neutralised, and the iron-cadmium plates are transferred for processing into cadmium oxide, which is collected by the Kadm-Oława company for the production of cadmium oxide. Nickel-iron plates are exported. An alkaline electrolyte is used to neutralise acidic solutions. The Kadm-Oława company (at "Oława" steelworks) [hutaolawa.pl] specialises in the processing of ferro-cadmium plates into cadmium oxide. It has technologies where in one cycle, cadmium oxide is directly obtained from ferro-cadmium electrodes. Oxide is used for the production of accumulator masses and cadmium pigments, and iron and nickel-containing parts are used for the production of alloy steels.

The co-owners of the company are "Oława" steelworks, MarCo Ltd. Sp. z o.o. and Permedia S.A. [listed company]. Another plant is located in Polkowice and belongs to Ecoren DKE Sp. z o.o. [Ltd.]. The company has a crusher, a mill and a magnetic separator. Waste batteries are shredded and magnetically separated. The processing generates metal-bearing fractions and waste fraction (ferromagnetic, paramagnetic, diamagnetic) (batteries.eko.org.pl/...). The installation has a capacity of 1,500 Mg of portable batteries and accumulators per year.

There are only a few recycling facilities for portable batteries and accumulators in the country. One of the largest plants of this kind is located in Stanowice. The French company Recupyl, together with Zakład Utylizacji Odpadów Sp. z o.o. in Gorzów [Waste Treatment Plant in Gorzów Ltd.], built a plant for sorting and processing used batteries with a capacity of 2,000 Mg per year. In 2010, a technological line for battery recycling was launched and is the only one in this part of Europe. Today, the plant collects batteries from Sweden, Latvia, Lithuania, Germany and Finland. The plant recovers coal, alkaline, zinc-air and lithium batteries (gorzow.gazeta.pl/...).

The processing of lead-acid batteries is carried out by only two companies located in the Silesian Voivodeship: Orzeł Biały in Bytom – capacity of 120,000 Mg of scrap metal per year, and Baterpol in Świętochłowice — capacity of 70,000 Mg per year. These companies have a waste battery collection network.

The battery recycling process is mainly aimed at recovering lead and sulphuric acid. The demand for processing of lead batteries in Poland is estimated at approximately 80,000 Mg, and the processing capacity of these two plants significantly exceeds this.

In the case of zinc batteries in Poland, there are four large processing plants with a capacity of more than 14,000 Mg (eneris.pl).

5.1. Recycling of batteries at Baterpol S.A. [listed company]

Recycling of battery scrap in the company consists of several stages (baterpol.pl; ecogroup.info; ekogroup.info; wnp.pl/...):

1. Separation of the battery into components.
   The technology is based on dismantling the battery and then separating and filtering the components. After breaking the battery, the electrolyte is filtered and recovered. The remaining solids are subjected to flotation separation. The following are formed: metallic fraction (the so-called grid, battery terminal clamps, intersectional connections in the battery), polypropylene from the casing, paste (mainly lead sulphate and lead oxides), polyethylene. All products are repeatedly washed and deacidified.
2. Desulphurisation of paste.
   The recovered lead paste and electrolyte are directed to the line in the previous stage. The sulphur content of the paste drops from approximately 8% to maximum 0.5%. Chemical reactions in this process result in a solution of sodium sulphate.
3. Crystallisation of sodium sulphate.
   The filtered and chemically purified solution is directed to the crystallisation line. This process generates high purity crystalline sodium sulphate. Stages 1, 2 and 3 of the activities are carried out using the equipment of the Italian company Engitec Technologies S.p.A. [listed company].

4. Production of raw lead.
   The metallic fraction is melted into raw lead in the furnaces of the Lead Plant in Szopienice, and the desulphurised lead paste in stage 2 is melted into raw lead in the modern, automated melting line of the French company BJ Industries, which is located in Świętochłowice.
5. Production of refined lead and lead alloys.
   Raw lead from both plants is melted in refining boilers in Szopienice and subjected to refining processes, i.e. removal of foreign metal contamination.

The products obtained from the recycling process are refined lead and lead alloys, which are collected mainly by the producers of lead batteries.

Moreover, rolled and extruded products from lead and lead alloys, crystalline sodium sulphate used in the chemical industry, mainly for detergents, as well as polypropylene, used in the manufacture of plastics, are obtained.

Technological solutions in the company close the cycle of battery recycling and allow for economic use of more than 95% of the mass of battery scrap. The plant can process over 70,000 Mg of battery scrap by recovering 17,500 Mg of metallic lead, 28,500 Mg of lead paste, 3,500 Mg of polypropylene, 700 Mg of ferrous waste and 1,400 Mg of electrolyte.

The processing of battery scrap is executed in the modern technological lines of the ENGITEC TECHNOLOGIES company utilising the so-called CX Technology.

5.2. Recycling of batteries at Orzeł Biały S.A. [listed company]

The technological process of Orzeł Biały S.A. is characterised by the so-called closed production cycle, which means that waste is processed and managed or stored inside the company. The company's technological facilities are constantly being modernised, and its refinery is one of the most modern in Europe. The company has been cooperating with the Institute of Non-Ferrous Metals in Gliwice for many years. The entire technological process consists of several stages (orzel-bialy.com.pl; orzel-bialy.com.pl/pl...; bj-industries.net/...; gravitatechnomech.com): separation of electrolyte from used batteries, crushing of battery scrap at the Battery Scrap Processing Department (so-called breaker), smelting of lead-bearing materials at the Metallurgical Department, refining of crude lead at the Refinery Department (high quality lead alloys and refined lead, so-called soft lead).

The first stage of the production cycle is the separation of individual battery fractions, which include electrolyte, plastic fraction (polypropylene), PVC, lead-bearing paste and metallic fraction. The electrolyte is processed (neutralised) into gypsum, which is then stored and sold. Polypropylene is crushed, cleaned and converted into granules, which is also stored and sold. The separated polyvinyl chloride (PVC) is transported and stored in the Bytom Municipal Enterprise [Bytomskie Przedsiębiorstwo Komunalne]. The remaining fractions, i.e. lead-bearing paste and metallic fraction, are sent to the metallurgical division, where the process of their remelting takes place. For this purpose, a BJ Industries tilt and turn furnace is used.

The result of this stage is raw lead, which is sent to the refinery and then refined. As a result of refining, refined lead and high-quality lead alloys are produced. The final product is subjected to control tests in a laboratory to confirm the correct composition of lead, i.e. 99.97% to 99.99%. If the requirements are not met, the product is re-melted and re-refined. A product with appropriate properties goes to a warehouse, where it is stored in one room with batteries intended for recycling. Ultimately, the product is sold. In addition to soft lead, the following are also final products: low-processed alloys with a low content of other metals, antimony alloys with the addition of other metals and calcium alloys.

6. Summary and conclusions

Uncontrolled disposal of waste batteries and accumulators leads to contamination of the soil and groundwater with hazardous substances. The recovery and recycling of these wastes, especially the material recovery (acquisition of secondary raw materials) allows for a reduction in the demand for and extraction of valuable natural resources. On a global scale, it contributes to saving raw materials and energy, eliminating or reducing the quantity and toxicity of solid, liquid and gaseous waste and reducing the negative impact throughout the entire life cycle of the product. Prevention of waste batteries and accumulators is mainly based on the use of long-life batteries and accumulators, including the selection of energy-efficient appliances. As a matter of fact, benefits can also be achieved by restricting the use of disposable batteries in favour of reusable batteries. An example of extended-life batteries are those of the company Emu sp. z o.o., spk from Gdańsk – Europower and Tuborg batteries by AutoPart from Mielec (http://www.emu.com.pl…; http://www.prostowniki-akumulatory.pl/…).

Conclusions of the study

1. Depending on the types of waste (single cell, mixed cell), three basic types of processes are used to recycle batteries and accumulators. These are: mechanical, pyrometallurgical and hydrometallurgical.
2. Mechanical processes are used to prepare a given material for further chemical processing (mechanical and magnetic separation). An example is the recovery of nickel-containing alloys from waste nickel-hydrogen batteries and accumulators (Jogmec – Japan) (www.jogmec.go.jp).
3. Pyrometallurgical processes are used to recover materials by melting metals in special furnaces. They also allow for the recovery of metal oxides (iron, manganese, zinc). Some examples are processes of conversion of zinc-manganese batteries (Batrec — Switzerland (www.batrec.ch), Recytec — France (www.recytec.fr)) and conversion of nickel-cadmium batteries (Accurec — Germany (https://accurec.de), Everead — USA

(www.eveready.com), Inmetco — USA (www.inmetco.com), Sab-Nife — Sweden (saftbatteries.com), Snam-Savam — Sweden, France (www.snam.com)). The advantage of these processes is the possibility to recycle various types of cells, including those containing organic electrolyte.

4. Hydrometallurgical processes are based on acidic or alkaline leaching of battery waste pre-prepared in mechanical treatment processes. Batenus and TNO technologies for the recovery of nickel and cadmium from nickel-cadmium batteries and accumulators are most frequently used in industrial practice.
5. In Poland, the basic method of recycling cells is their mechanical shredding, capturing the resulting ferromagnetic fraction used in the iron and steel industry, converting the diamagnetic fraction (paper and plastic elements) into alternative and paramagnetic fuel (non-ferrous metals and graphite) constituting waste consisting of non-ferrous metals and residues of the ferromagnetic fraction used, among others, for pencils and paints.
6. Recycling of lead-acid batteries in Poland is carried out by only two companies (Orzeł Biały, Baterpol — the Silesian Voivodeship). The recycling process carried out in these companies is mainly aimed at the recovery of lead and sulphuric acid. Despite the unfavourable situation (low lead prices, overproduction of cheap lead in China), almost 100% of waste batteries is currently processed, and the capacity of these two plants significantly exceeds the demand for processing of lead batteries in Poland.
7. Collection of small size batteries and accumulators is very poor in the country. A positive example is Nokia's operations (forty service points, including six in Silesia).
8. At present, Poland lacks an effective system for collecting and processing small nickel-cadmium batteries (no plants with appropriate processing technologies). Export could be the solution — France, Sweden, Germany.
9. In the case of large-size batteries and accumulators, the processing is started periodically, only if an order is placed, due to the withdrawal of cadmium from use (Oława steelworks). Due to the lack of sales to CdO, it is necessary to change the technology of processing cadmium plates to metallic cadmium (does not harm the environment when stored). In the disposal of batteries, the nickel plates are mainly recovered (economically viable sales). The remaining disassembly products are removed by pouring the electrolyte into the sewage system or soil, while the iron-cadmium plates are transferred to steelworks as scrap.
10. Nickel-cadmium batteries and accumulators are gradually being replaced by other types of cells, e.g. nickel-metal hydride, lithium-ion or lithium-polymer. There is a technology of freezing lithium batteries in liquid nitrogen before they are crushed. The lithium is then dissolved in a special solution. The element recovered in this way can be used repeatedly. The main source of this element is to be the recycling of lithium-ion batteries (relatively low price and small fluctuations in price changes). The most cost-effective way to recycle is to recycle nickel-metal hydride batteries.

References

1. Bendkowski, J., Wengierek, M. (2004). *Logistyka odpadów, t. II. Obiekty gospodarki odpadami*. Gliwice: Politechnika Śląska.
2. Dolnośląska Fundacja Ekorozwoju (2006). *Baterie: segregacja czy degradacja*. Wrocław.
3. Dyrektywa 2006/66/WE Parlamentu Europejskiego i Rady z dnia 6 września 2006 r. w sprawie baterii i akumulatorów oraz zużytych baterii i akumulatorów.
4. gravitatechnomech.com.
5. Grzesik, K. (2005). Uwarunkowania prawne recyklingu baterii. *Przegląd Komunalny. Recykling, vol. 1*.
6. Grzybowska, K. (2009). *Podstawy logistyki*. Warszawa: Difin.
7. http://www.batrec.ch.
8. http://www.emu.com.pl/?ochrona-srodowiska,60.
9. http://www.prostowniki-akumulatory.pl/aktualnosci/187-tuborg-silver-technologia-produkcji.
10. http://www.recytec.fr.
11. https://accurec.de.
12. Jaśnikowski, A., Marcinkowski, T., Marek, J. (2002). Odpady baterii i akumulatorów małogabarytowych. *Ekotechnika, vol. 4*.
13. Kawczyńska, K. (2014). *Bateryjne ABC*. Zakład Gospodarki Komunalnej Organizacja Odzysku Biosystem SA.
14. Kłopotek, B. (2004). Zużyte baterie i akumulatory. *Przegląd Komunalny, vol. 10*.
15. Kopczyk, M. (2005). Technologie recyklingu zużytych baterii i akumulatorów w Polsce. *Przegląd Komunalny, vol. 4*.
16. Korkozowicz, M. (2010). Co dalej z recyklingiem baterii? *Odpady i Środowisko, vol. 5*.
17. Merkisz, J. (2011). Recykling samochodowych akumulatorów kwasowo-ołowiowych – aspekt środowiskowy. *Systemy Zarządzania w Inżynierii Produkcji, vol. 1*.
18. Plan gospodarki odpadami dla województwa śląskiego na lata 2016-2022 (2015). Katowice.
19. Pyssa, J. (2006). Gospodarka odpadami przemysłowymi na przykładzie odzysku ołowiu ze zużytych akumulatorów. *Gospodarka Surowcami Mineralnymi, vol. 22, no. 2*. Kraków: IGSMiE PAN.
20. Pyssa, J. (2007). Uwarunkowania prawne, organizacyjne i techniczne postępowania z zużytymi bateriami i akumulatorami. *Problemy Ekologii, vol. 11, no. 4*. Mysłowice: GWSP.
21. Raport o funkcjonowaniu gospodarki bateriami i akumulatorami oraz zużytymi bateriami i zużytymi akumulatorami za 2015 rok (2016). Warszawa: GIOŚ.
22. Rogulski, Z. (2005). Technologie odzysku i recyklingu zużytych akumulatorów. *Przegląd Komunalny, vol. 4*.

23. Rozporządzenie Komisji Unii Europejskiej Nr 493/2012 z dnia 11 czerwca 2012 r. ustanawiające szczegółowe przepisy dotyczące obliczania wydajności recyklingu dla procesów recyklingu zużytych baterii i akumulatorów.
24. Rozporządzenie Ministra Środowiska z dnia 27 września 2001 r. w sprawie katalogu odpadów, DzU. nr 112, poz. 1206.
25. Rozporządzenie Ministra Środowiska z dnia 3 grudnia 2009 r. w sprawie rocznych poziomów zbierania zużytych baterii i akumulatorów przenośnych, DzU. nr 215, poz. 1671.
26. Rozporządzenie Ministra Środowiska z dnia 9 grudnia 2014 r. w sprawie katalogu odpadów, DzU. 2014, poz. 1923.
27. Sobianowska-Turek, A. (2009). *Odzysk cynku i manganu z baterii Zn-C i Zn-Mn*. Wrocław: Politechnika Wrocławska, Instytut Inżynierii Ochrony Środowiska.
28. Ustawa z dnia 14 grudnia 2012 r. o odpadach (DzU 2013, poz. 21), Rozporządzenia wykonawcze do ww. ustaw – Ministra Środowiska, Ministra Gospodarki.
29. Ustawa z dnia 24 kwietnia 2009 r. o bateriach i akumulatorach (DzU nr 79, poz. 666 z późn zm. 2013 r., poz. 21 oraz DzU 2015, poz. 687).
30. Ustawa z dnia 27 kwietnia 2001 r. o odpadach (DzU 2007, nr 39, poz. 251 z późn. zm).
31. Wengierek, M. (2017a). Sposoby postępowania z odpadami niebezpiecznymi w województwie śląskim. Część I – Uwarunkowania prawne i organizacyjne. *Zeszyty Naukowe, seria Organizacja i Zarządzanie, no. 103*. Gliwice: Politechnika Śląska.
32. Wengierek, M. (2017b). Sposoby postępowania z odpadami niebezpiecznymi w województwie śląskim. Część II – Uwarunkowania prawne i organizacyjne wybranych rodzajów odpadów. *Zeszyty Naukowe, seria Organizacja i Zarządzanie, no. 101*. Gliwice: Politechnika Śląska.
33. Wengierek, M. (2018). Sposoby postępowania z odpadami niebezpiecznymi w województwie śląskim. Część I – Uwarunkowania techniczne w procesach zarządzania odzyskiem i recyklingiem odpadów. *Zeszyty Naukowe, seria Organizacja i Zarządzanie, no. 121.* Gliwice: Politechnika Śląska.
34. Wolff, S., Ziaja, J., Stryjewski, J. (2006). Recykling odpadów niklowo-kadmowych. *Ekologia, vol. 4*.
35. WSO – Wojewódzki System Odpadowy (2015). Katowice.
36. www.baterie.eko.org.pl/rec3.php.
37. www.bj-industries.net/bj5.html.
38. www.ecogroup.info.
39. www.ekogroup.info.
40. www.eneris.pl.www.baterpol.pl
41. www.eveready.com.
42. www.gorzow.gazeta.pl/gorzow/1,35211,12372328,baterie_bakterie_i_gorace_smieci.html.
43. www.hutaolawa.pl.
44. www.ietu.pl.

45. www.inmetco.com.
46. www.ippc.mos.gov.pl/ippc/?id=36.
47. www.jogmec.go.jp.
48. www.mos.gov.pl.
49. www.mos.gov.pl/pl/srodowisko/odpady/odpady-pouzytkowe-zuzyte-baterie-i-akumulatory/.
50. www.orzel-bialy.com.pl.
51. www.orzel-bialy.com.pl/pl/o-spolce/zakład-produkcyjny.
52. www.reba.com.pl.
53. www.rewolucjawsmieciach.pl/baza-wiedzy/odpady/strumienie-odpadow/baterie-i-akumulatory/.
54. www.rzęsie.gios.gov.pl/szukaj_baterie.php.
55. www.saftbatteries.com.
56. www.snam.com.
57. www.wnp.pl/wiadomości/recykling-akumulatorow-wg-baterpolu,-4153.html.