Environmental and Health Challenges in Battery Recycling in Bulgaria

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Abstract — **The purpose of this report is to investigate and compare the environmental and health risks of the selection of chemistry for electrical energy storage in Bulgaria at the end-of-life stage of the batteries and the inevitable decommissioning that must be followed by safe transportation and recycling.**

According to National Plan for Recovery and Sustainability of the Republic of Bulgaria, version 1.5 of 06.04.2022 [1], is expected to be generated large quantities of hazardous waste from electric batteries in the not too distant future. The choice of battery chemistry is determinant for the recycling procedures of these wastes.

Two battery chemistries considered most promising for stationary electrical energy storage – Lead Acid (LA) and Lithium–ion-Iron (Ferrous) -Phosphate (LFP). Lead-acid chemistry is well developed in the western world, including Bulgaria, and would be a logical choice, but is many times less efficient than lithium chemistry, which can only be imported from the major producers in the East.

The recycling of the waste from the two chemistries is fundamentally different - the lead chemistry can be recycled in Bulgaria in compliance with environmental and health standards or in neighboring European countries, while the lithium is likely to be recycled where it is produced (if there will obtain technological breakthrough) - in a country in the Far East with the corresponding transport and processing costs to be budgeted in the financial assessment of the projects.

Unless a technological breakthrough occurs, there remains disposal of LFPs batteries with a high risk of large-scale explosions and fires at disposal sites with the risk of harm to people and severe environmental consequences.

Keywords—energy storage, battery recycling, environmental impact, health risks.

I. INTRODUCTION

According to the "National Plan for Recovery and Sustainability of the Republic of Bulgaria" [1] published on 06.04.2022, it is envisaged to create a national infrastructure for storage of electricity from renewable energy sources (RES) named RESTORE [1].

The RESTORE project is of planned total charging energy capacity of 6 GWh by 2026 [1]. The energy storage facilities will be distributed close to renewable generation capacities [1]. The envisaged funds for the construction of a national infrastructure of electricity storage facilities, RES and batteries, amount to BGN of more than 2 billion [1].

In view of EU practice, if for a Bulgaria with a population of about 7 million, the target is to install electrical energy storage (EES) facilities in the order of 6 GWh by 2026 [1], then by the crudest calculations for EU, if normalized most approximately on the basis of a population of about 550 million should be not less than 400 GWh.

And that's just for energy storage. If the needs of the automotive industry are added in, with projections of exponential growth in the number of new electric vehicles (EV) and hybrid vehicles produced per year, mobile phones, handheld devices and other small autonomous devices, the hunger for batteries is expected to become starving.

And where there is hunger, prices take off, speculation can be expected, and not retail speculation, it is geopolitical speculation. If you add the energy war between the West (Europe and America) and the East (Russia + China + India + the whole Asian region), the forecast becomes really unreliable. All authoritative predictions made by the end of 2020 evaporate. Unpredictability sets in.

Given that in 2020 China is the producer of about 76%, and in 2025 is expected to produce 73% of the lithium chemistry [7] on which everyone in the world is relying on, it is to be expected that they are betting on a 'lame horse'.

In my estimation, lithium chemistry prices will rise despite authoritative forecasts of a significant decline by 2026-2030. Energy prices have taken off, and they are dragging all other prices down with them. Optimistic forecasts of a systematic reduction in Chinese lithium chemistry prices in the coming years are uncertain due to the changed conjuncture. Europe is inevitably dependent on China for lithium chemistry for at least the next 10 years.

And perhaps, against this background, it is right for Europe to think deeply about whether its energy storage targets for the next 10 years are realistic. Does it have the manufacturing potential or even the financial to provide the physical quantities of batteries needed for energy storage.

In my opinion, Europe has overestimated itself as a global player in the lithium battery market. Europe does not produce and will not be able to produce enough lithium batteries any time soon and will be dependent on China, as will America.

On the other hand, lead-acid chemistry is well developed as a technology in both Europe and America, and the natural resources to produce lead-acid batteries are available in their territories. Another issue is that currently these 'dirty' industries are also largely outsourced far to the east, but they could be returned relatively fast.

There is a potential opportunity to use second-hand batteries from electric cars that are cobalt chemistry. Cobalt-containing batteries are considered unacceptable for energy storage for environmental and humane reasons. They are therefore ignored in this study.

Finally, from an environmental point of view which is the subject of this paper, lead-acid batteries are almost entirely (99%) recyclable as a material, which cannot be said of lithium.

II. QUANTITIES OF BATTERIES REQUIRED FOR ENERGY STORAGE IN BULGARIA

A. *Battery Chemistries in Scope*

This paper focuses on the most widely used rechargeable lead-acid and lithium-ion chemistries, particularly VRLA and LFP listed in Table 1.

TABLE I. CHEMISTRIES CONSIDERED

Abbreviation	Explanation
LFP	lithium iron phosphate
VRLA/ LA	valve regulated lead acid/ lead acid

B. *Roughest Estimate by Volume of Batteries*

An elementary approach was chosen to obtain an idea of the approximate volume of batteries initially required for electrical energy storage (EES) from the two chemistries in Bulgaria. Based on the assumed total capacity and energy density, the total battery volume can be calculated.

According to [5], an increase in the energy density of the two chemistries is not expected until 2030, Figure 1.

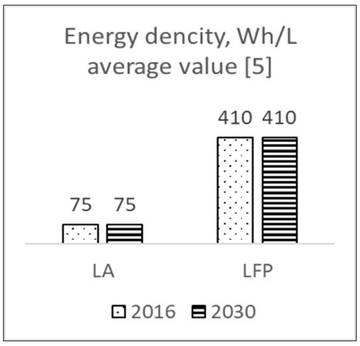

Figure 1

Then, the total volume of initially required LA batteries can be calculated by (1).

$$V_{LA} = \frac{C_{total}}{ED_{LA}} = \frac{6.10^9}{75.10^3} = 80\,000 m^3,$$

where:

V_{LA} is total volume of LA batteries needed, m^3;

$C_{total} = 6.10^9$ is the total installed capacity, Wh;

ED_{LA} is the volumetric energy density of LA batteries, Wh/Litter.

The same calculation was done for LFP batteries (2).

$$V_{LFP} = \frac{C_{total}}{ED_{LFP}} = \frac{6.10^9}{410.10^3} = 14\,634 m^3.$$

If all the batteries for the EEC are stacked a cube with side 43m for the LA and 24m for the LFP chemistry will be obtained, Figure 2.

Assuming a service life of 10 years for the EES facilities, and one duty cycle per day, accounting for the cycle life of the two chemistries Figure 3, one can calculate the total volume of batteries required for the entire service life of the facilities (3) and (4). The pessimistic case of Figure 3 is assumed for the calculations.

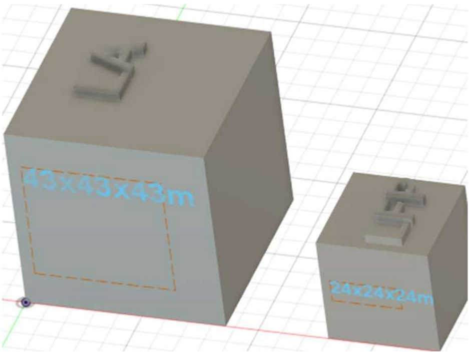

Figure 2

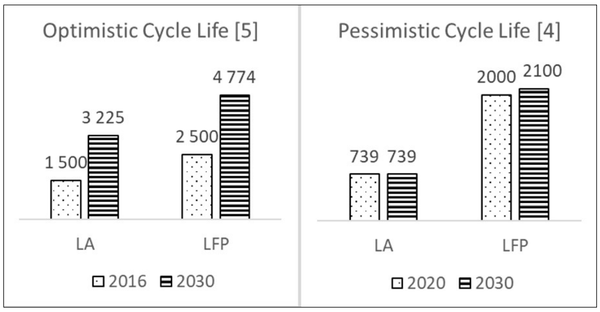

Figure 3

Simple calculations show that for the entire lifetime of the facilities of 10 years, the quantity of LA batteries is 5 times the original quantity and 2 times for LFP (3) and (4).

$$Total._{LA} = \frac{Y_{SL}.365}{CL_{LA}} = \frac{10.365}{739} = 4{,}94,$$

$$Total_{LFP} = \frac{Y_{SL}.365}{CL_{LFP}} = \frac{10.365}{2000} = 1{,}83,$$

where:

$Total._{LA}$ is the multiplicity of LA batteries required for the entire service life of the EES facilities, and $Total._{LFP}$.for LFP batteries;

CL_{LA} is the predicted cycle life of the LA chemistry, and CL_{LFP} of the LFP;

Y_{SL} is service life of the facilities.

If one calculates the total amount of batteries that will go out of service at the end of the service life of the equipment, one obtains (5) and (6).

$$Vtotal_{LA} = 5.V_{LA} = 400\,000 m^3;$$

$$Vtotal_{LFP} = 2.V_{LFP} = 29\,268 m^3.$$

It can be argued that the waste generated by LA batteries is about 14 times larger in volume than LFP. The huge volume of hazardous waste from LA batteries would have a terrible environmental impact when disposed of, but this is unacceptable. Lead chemistry is recyclable and the question is what energy costs and therefore GHG emissions would their recycling generate. The quantities of batteries to be recycled can be expected to be around 40 000 m^3/year.

Lithium chemistry is non-recyclable in Bulgaria and, under this option, would have to be sourced from foreign contractors at the appropriate cost or landfilled.

C. Roughest Estimate by Weight of Batteries

Analogous to the previous point B, the total weight of batteries required for the initial construction and for 10 years operational life of the RES was calculated. The reference values of the specific energy for the calculations are adopted according to Figure 4 [2], [3], [6].

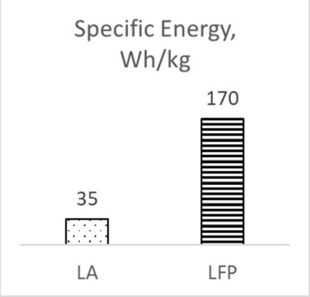

Figure 4

The total weight of initially required LA batteries can be calculated by (7).

$$G_{LA} = \frac{C_{total}}{ED_{LA}} = \frac{6.10^9}{35.10^3} = 171\ 429\ tones,$$

where:

G_{LA} is total weight of LA batteries needed, tones;

$C_{total} = 6.10^9$ is the total installed capacity, Wh;

ED_{LA} is the specific energy of LA batteries, Wh/kg.

The same calculation was done for LFP batteries (2).

$$G_{LFP} = \frac{C_{total}}{ED_{LFP}} = \frac{6.10^9}{170.10^3} = 35\ 294\ tones.$$

For a 10-year service life, the quantities increase - for LA by a factor of 5 and for LFP by a factor of 2:

$$Gtotal_{LA} = 5.G_{LA} = 857\ 145\ tones;$$

$$Gtotal_{LFP} = 2.G_{LFP} = 70\ 588\ tones.$$

Waste generated by LA batteries is about 12 times larger in weight than LFP.

III. MATERIAL COMPOSITION

A. Lead Acid Batteries Materials

Lead acid batteries are monometallic. All active materials, plate grids, straps, and connectors are made mostly of lead and lead oxide. Hence, recycling of lead from batteries is an easy process. Many countries have national lead pools (comprising production of primary lead and recycling of secondary lead) [3].

Components and relative weight of materials of lead-acid batteries are shown in Table 2 [3].

TABLE II. COMPONENTS AND RELATIVE WEIGHT OF MATERIALS OF LA BATTERIES

Component	**Material**	**Weight, %**
Container and Lid	Plastic	7
Separator	Plastic/Absorption Glass Mat	1
Top Lead	Lead/Lead Alloy	9
Grid Lead	Lead/Lead Alloy	14
Active materials	Lead/Lead Oxide/$PbSO_4$	34
Electrolyte	H_2SO_4 Solution + Additives	32

It should be noted that the total of the percentages is 97, not 100.

If the ratios from Table 2 are related to the total amount of lead batteries to be recycled within 10 years, the absolute quantities of materials to be recycled per year are shown in Figure 5.

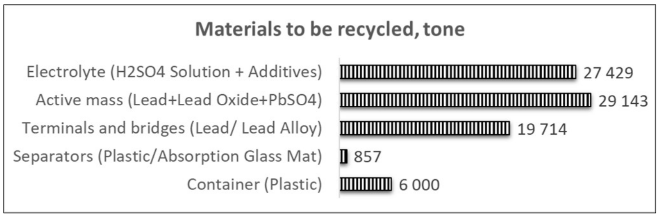

Figure 5

All the materials in Figure 5 are recyclable for reuse, including for the production of new batteries except AGM. It is about 1% inert and after washing and pressing can be safely landfilled or used as raw material.

B. Lithium Iron Phosphate (LFP) Cell Materials

An example composition and weight fraction of materials in the components of LFP cell is shown in Table 3, [9].

TABLE III. COMPONENTS AND RELATIVE WEIGHT OF MATERIALS OF LFP CELL

Component	**Material**	**Weight, %**
Housing	Steel or Al	20-25
Cathode (+)	$FePO_4$	25-35
Anode (-)	Graphite	14-19
Electrolyte	Organics* + Li Salts	10-15
Cathode current collector foil	Aluminum	5-7
Anode current collector foil	Copper	5-9
Separator	PP, PE	1-4
Others (additives)	Carbon black, silicon, etc.	-

*The organics in the electrolyte are volatile and toxic/irritating, explosive and likely to self-ignite (explode) on contact with air at room temperature. Vapors of the organic can cause skin and eye damage and poisoning if inhaled [9]. The presence of metallic lithium in the cell can also cause an explosion when unsealed or in contact with water, although normally no metallic lithium should be present in LFP cells.

It is clear from the above that the recycling of lithium cells, including LFP, is not a simple job and requires the construction of specialized installations, which do not exist in Bulgaria. Long-term storage (landfilling) is also risky - explosive and fire hazardous [12], and there is a risk of toxic electrolyte leakage into the environment.

Choosing LFP chemistry for energy storage would generate about 70 588 tons of hazardous waste within 10 years in two tranches.

The recyclable materials in the LFP cell are aluminum and copper, which are about 35% of its weight. Iron phosphate, and carbon are not directly recyclable, and processing them to iron and phosphorus is not economically viable. Expensive metals such as cobalt, nickel, manganese and titanium are not present in this chemistry to pay for processing.

LFP poses a challenge for battery recycling as it is difficult to make a profit recovering iron and phosphorous. Without valuable metals such as nickel and cobalt, the value that can be recovered from LFP batteries drops considerably from conventional recycling methods and its economic viability is a concern. LFP appears to require direct recycling to be profitable or will require regulatory intervention, frameworks or alternative business models [8].

To date, technology for full-scale industrial direct recycling of LFP batteries has not been found in the literature. And the application of the developed pyrometallurgical and hydrometallurgical technologies does not bring revenue from the final product, i.e. recycling of LFW batteries is not economically viable and therefore not feasible. The only options are disposal on special sites, which poses a risk of explosions and fires on the site, or incineration in plasma/electrode furnaces (pyrometallurgical) with subsequent disposal of the slag and appropriate flue gas cleaning.

Therefore, the techno-economic assessment of energy storage facilities with LFP batteries should take into account the costs of battery disposal and safe transport of the batteries to the processing facilities and then of the slag to landfill. In Bulgaria there are no plants for safe plasma incineration of hazardous waste, i.e. the batteries have to be shipped abroad.

But, the issue of recycling LFP batteries is being actively worked on [9]. Interesting and promising results for direct/material recycling of LFP cathodes at laboratory scale are presented in [10]. Assuming that the first batch of waste LFP batteries from energy storage plants in Bulgaria will appear in about 10yrs, one would hope that by then there would be industrial-scale plants to directly recycle the LFC chemistry at a profit, and the choice of this chemistry was promising.

IV. Environmental and Health Challenges in Battery Recycling

A. Lead Acid Batteries Recycling

The main pathways of exposure to lead from recycling used lead-acid batteries arise from environmental emissions. These occur at various stages in the recycling process, as described below. Lead particles and fumes emitted into the air can be inhaled and are also deposited onto soil, water bodies and other surfaces, including in gardens and homes. Waste materials from lead processing can, if not treated and correctly disposed of, contaminate land and water bodies. Used acid with high concentrations of lead is often dumped on land or released into waterways. Lead can enter the food chain through crops growing on contaminated land, from direct deposition onto crops, through food animals foraging in contaminated areas and consuming lead particles, and from fish and shellfish living in lead-contaminated water [11].

The potential health and environmental risks of recycling lead-acid batteries during the process are shown in Table 4 [11].

As can be seen from Table 4, the recycling of LA batteries can cause long-term complex environmental contamination and lead accumulation in the body tissues and blood of people directly or indirectly exposed. Lead is toxic to humans and animals but tends to accumulate in plants, hence in herbivores and ultimately in predators and humans. The higher up the food chain a creature is, the higher the levels of accumulated lead.

TABLE IV. The Potential Health and Environmental Risks

St.	Process	Health and Environmental Risks
1	Collection & transport	Lead and acid contamination of soil and water. Skin and eye injuries from damaged batteries
2	Draining electrolyte	Lead and acid contamination of soil and water. Skin and eye injuries from damaged batteries
3	Breaking up batteries	Generation of plastic waste and separation of parts containing lead.
3.1	Plastic burnt or dumped	Toxic smoke including sulfur dioxide, dioxins, dibenzofurans. Lead–contaminated waste.
3.2	Lead-containing components broken up	Lead fragments and lead oxide dust dispersed into air and settle on soil, other surfaces and workers' hair & clothes. Surrounding environment contaminated with lead.
4	Conveying lead components to the smelter	Such as 3.2
5	Smelting and refining	Lead fumes dispersed in air and inhaled by workers. Fumes condense as particles that settle on soil, other surfaces and workers' hair & clothes.
6	Pollution of the homes	Lead dust carried home and contaminates domestic environment and children

The main routes of exposure and absorption of lead are inhalation, ingestion and, to a much lesser extent, dermal contact. Inhalation of fumes and dust is a major route of exposure for people working with lead. Young children are particularly likely to be exposed through contaminated air-borne soil or household dust. Lead exposure may also occur from consumption of contaminated food and water [11].

The most widely used method for assessing exposure to lead is the measurement of lead in whole blood [11]. The physiological effects and diseases caused by measured blood lead on adults and children are shown in Table 5, adapted from [11] and [13].

TABLE V. Toxic Effects in Relation to Blood Lead Concentrations

Concentration	Health effect
Adults	
< 5 mg/dL	Impaired renal function, anemia
< 10 mg/dL	Hypertension, Increased cardiovascular-related mortality, spontaneous abortion, preterm birth
> 40 mg/dL	Peripheral neuropathy, neurobehavioral effects, abdominal colic
> 50 mg/dL	Decreased hemoglobin synthesis
Children	
< 5 mg/dL	Deficit hyperactivity disorder,
< 10 mg/dL	Delayed puberty
> 20 mg/dL	Anemia
> 40 mg/dL	Decreased hemoglobin synthesis
> 50 mg/dL	Severe neurological disabilities
> 60 mg/dL	Abdominal colic, features of acute poisoning but no encephalopathy
> 90 mg/dL	Encephalopathy
> 150 mg/dL	Death

Clearly, the recycling of lead-acid batteries is potentially hazardous, both for the personnel involved in the process and for those living in the area of the reprocessing plants, with children being the most vulnerable if workplace safety and environmental emissions requirements are not met.

If lead chemistry is chosen for EES, a whole new lead battery recycling industry will have to be organised in the not too distant future, with the potential to recycle around 170 000 tonnes of batteries per year. An additional logistical constraint is the logical location of EES facilities, which are scattered throughout the country. Logistics have to be organised from the points that generate batteries for recycling and the processing facilities. The question arises as to how many and where the recycling facilities should be located to minimize transportation costs and potential negative environmental and health impacts. Questions arise about the regulatory requirements for these installations and how to control and penalise them if safety and environmental impacts are ignored in favor of the 'lowest cost' criterion. Many questions arise to which there are currently no institutional answers.

B. LFP Batteries Recycling

If the LFP technology is chosen for the EES in Bulgaria, the recycling problem is currently unsolvable. In Bulgaria, it is unlikely that in the foreseeable future LFP batteries will be recycled. The hope is to achieve an economically positive technological breakthrough on an industrial scale in the coming years. The nearest recycling destination is expected to be Germany. Bulgaria is expected to organise the safe collection, storage and transportation of the batteries to the recycling point, which is no small challenge. And the quantities are not small - around 70 000 tones over 10 years. At the moment, in Bulgaria, apart from abstract intentions on paper, there is no visible action to meet the challenge of LFP batteries for EES, institutionally, logistically and financially.

V. CONCLUSIONS

A comparison is made of two battery chemistries with the potential for stationary renewable energy storage with installed capacities in the MW range and capacities in the tens and hundreds of MWh - LA and LFPs.

The undisputed in times higher efficiency of lithium chemistry for this purpose is also confirmed. However, if the recyclability of the waste from both chemistries, the health and environmental risks, including from prolonged storage of the waste, are taken into account, the obvious advantages of lithium chemistry start to fade as human health and a clean environment are a priority in modern Europe.

It is to be expected that the coming world war for lithium batteries between the two most competitive industries, the automotive and the energy storage, will be won by the automotive industry, and that the energy industry will have to use whatever batteries it can produce on its own territory and be able to recycle safely on the same territory. By now, Europe has mastered lead-acid chemistry production and recycling better.

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