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General information on the recycling of chemical power sources. Complex recycling of lead-acid batteries

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The introduction of the article gives a general view concerning the production volumes of the main chemical power sources (CPS) and, accordingly, the potential volumes of environmentally hazardous flows associated with spent systems. The analysis of the main substances contained in CPS and the environmental risks associated with them has been carried out. The need for recycling of spent systems in order to extract valuable components has been shown.

In the main part of the article, the general principles and methods of recycling waste lead-acid batteries are discussed. The recycling of lead, electrode paste, electrolyte, and polymer components of lead-acid batteries is considered. The presented literature allows evaluating the existing technologies and experimental developments in the recycling of solid lead-containing components of lead-acid batteries. It is shown that one of the most important issues in the recycling of solid lead-containing components is the development of a simple, reliable, and energetically advantageous method for paste desulfurizing.

Analysis of information on the recycling of liquid waste scrap for lead-acid batteries reveals that the optimal way is recycling into an electrolyte ready for reuse in new batteries.

The search for information on the recycling of polymeric materials of used lead-acid batteries has shown that the technology can be implemented relatively easily, however, the surface should be very thoroughly cleaned from contamination.

Keywords: chemical power source, processing waste, scrap, lithium-ion battery, lead-acid battery, nickel-cadmium battery, nickel-metal hydride battery.

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Общие сведения относительно рециклинга отработанных химических источников тока. Комплексная переработка свинцово-кислотных аккумуляторов

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Во введении статьи дано общее представление об объёмах производства основных химических источников тока (ХИТ) и соответственно потенциальных объёмах экологически опасных потоков, связанных с отработанными системами. Произведён анализ основных веществ, входящих в состав ХИТ, экологических рисков, связанных с ними, показана необходимость переработки отработанных систем с целью извлечения ценных компонентов.

В основной части статьи обсуждаются общие принципы и способы переработки отработанных свинцово-кислотных аккумуляторов. Рассмотрена переработка свинца, электродной пасты, электролита и полимерных компонентов свинцово-кислотных аккумуляторов. Представлена литература, позволяющая оценить существующие технологии и экспериментальные наработки при переработке твёрдых свинецсодержащих компонентов свинцово-кислотных аккумуляторов. Показано, что одним из важнейших вопросов переработки твёрдых свинецсодержащих компонентов является разработка простого, надёжного и энергетически выгодного способа десульфуризации пасты.

Анализ информации, посвящённой переработке жидких отходов лома свинцово-кислотных аккумуляторов выявил, что оптимальным является переработка в электролит, готовый для повторного использования в новых аккумуляторах.

Поиск информации относительно переработки полимерных материалов отработанных свинцово-кислотных аккумуляторов показал, что технология может быть реализована относительно легко, однако при этом следует очень тщательно очищать поверхность от загрязнений.

Ключевые слова: химический источник тока, переработка, отходы, лом, литий-ионный аккумулятор, свинцово-кислотный аккумулятор, никель-кадмиевый аккумулятор, никель-металлогидридный аккумулятор.

In modern times, chemical power sources (CPS) play an important role in various spheres of human life. The use of CPS in the last two decades has expanded significantly and penetrated all areas of the national economy and industry. The main advantage of CPS in comparison with other sources of electricity is their autonomy and scalability – from several mAh to tens of kWh [1, 2]. On the other hand, a large number of different systems used as CPS satisfy the different needs of consumers in terms of the required discharge voltage, operating temperature range, maximum discharge (charging) currents, possibly recharging, charge retention time, fire safety, and other characteristics. In accordance with this, at the moment, a wide range of CPS, both primary and secondary, is being produced. Different types of CPS contain metals and their compounds, caustic substances (solutions of acids and alkalis), organic components, polymers, etc. It should be noted that some of the CPS components are valuable materials. Moreover, most of these components are such that to some degree can damage the environment.

According to [3], in 2009, the top three sales leaders were lithium-ion and lead starter batteries (37 and 20%, respectively) as well as alkaline primary batteries (15%). In this case, only these three types of CPS accounted for more than 72% of sales. However, it should be borne in mind that the price of a power source is highly dependent on the specific system used in it. Therefore, it is more correct to compare the produced volumes of power sources not by sales but in accordance with energy units. Most often, the produced volumes of CPS are presented in GWh/year, which falls on this type. It is worth noting that, as a first approximation, this unit will correspond to the masses of battery production. At the same time, the differences will be associated with different voltages of the produced CPS and other parameters that affect the value of the specific energy of a specific CPS. Moreover, the volume of the spent CPS (that have lost their operational characteristics) will differ primarily depending on the type of CPS (primary or secondary) as well as on the typical number of charge-discharge cycles for a given system (secondary CPS or battery). Nevertheless, a very rough estimate of the volume of spent CPS can be made by the volumes of CPS produced in GWh.

The most common primary and secondary CPS include the following systems: lithium-ion, acid-lead, nickel-metal hydride, nickel-cadmium, zinc-manganese alkaline and zinc-manganese salt systems. It should be noted that the search for generalized data on various CPS, and even more so the comparison of data for primary and secondary CPS, is very problematic. However, separate values and dynamics of production over time for different CPS were found in the sources in GWh. For some CPS, the estimated production volumes for the previously mentioned current sources and the selected year were calculated using a linear approximation. In 2016 (Fig. *a*), the share of lithium-ion batteries accounted for 78 GWh [4, 5], lead-acid batteries – 362 GWh [6], nickel-metal hydride – 4.06 GWh, nickel-cadmium – 2.27 GWh [7]. Unfortunately, it was not possible to find the exact volume of production of primary power sources. However, regarding the environmental hazard for the given CPS, the following was noted in [8]: "... alkaline batteries (zinc-manganese with alkaline electrolyte) sold after May 13, 1996, do not contain mercury and can be disposed of in the ordinary waste. They can be identified by a green stripe, a green tree, a Mercury Free label, or an expiration date later than 1998. Older batteries may contain mercury and should therefore be taken to a collection point, recycling facility, or collected as hazardous household waste. Carbon-zinc and chloride-zinc batteries (zinc-manganese salt) are not dangerous and can be thrown into the trash ...".

Nevertheless, the recycling of these primary CPS is of interest from the point of view of the extraction of valuable components – manganese and zinc.

In turn, lithium-ion batteries contain heavy metals (HM) as well as organic solvents that can be hazardous to the environment. Taking into account that the composition of the cathode material often includes nickel, cobalt, or manganese,

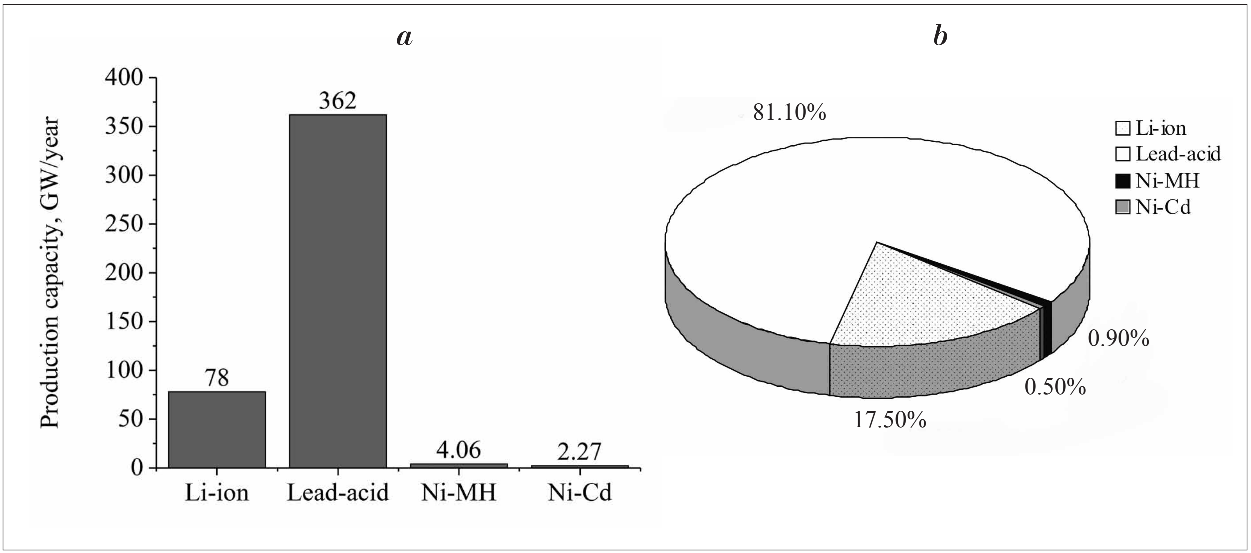

Fig. Distribution of secondary CPS by production scale in 2016:
a – in energy units (GWh/year); *b* – normalized percentage ratio between the types of systems, taking into account the average number of charge-discharge cycles

it seems interesting to recycle these CPS with the subsequent extraction of these elements. Propylene carbonate, ethylene carbonate, dimethyl carbonate in earlier versions of lithium-ion batteries as well as dimethyl sulfoxide (DMSO), sulfolane and ether-based electrolytes in later versions of these CPS [9] also have some danger to the environment. At the same time, when used as a solvent, DMSO is dangerous because it can increase the transdermal transfer of molecules dissolved in it, sharply increasing the toxicity of these substances [10, 11].

It should be noted separately that fully solid-phase lithium-ion batteries can contain elements such as zirconium, lanthanum and titanium as well as sulfur, phosphorus, silicon and germanium, which are part of a solid electrolyte. Lithium-ion batteries with polymer electrolyte most often contain polyethylene oxides, polyacrylonitrile, polyvinylidene fluoride and polymethyl methacrylate as a matrix [9]. Although the listed polymers have low toxicity [12], nevertheless, they can emit toxic substances during combustion or heating.

In addition to what has been said, it should be noted that besides the environmental aspect, there is a problem of raw lithium-containing materials for this type of CPS. Some authors argue that with an abrupt increase in the production of lithium power sources, which is observed now, in the next several decades there will be a sharp shortage of lithium-containing raw materials [13–15]. Although lithium is not a rare element on earth, its concentration is expensive. At the same time, the sources of raw materials, where this element is in a relatively concentrated form, are few and the reserves of raw materials are limited. The latter fact makes the issue of recycling spent lithium power sources, both primary and secondary, urgent in order to obtain lithium and other metals.

Lead-acid batteries are mainly used as starter batteries for starting internal combustion engines. At the same time, they find their application also as CPS in uninterruptible power supply units and some autonomous power systems. The composition of these batteries includes polymer separators and housing, electrodes made of lead-antimony alloy, or lead doped with calcium. The paste on the electrodes of spent lead-acid batteries usually consists of lead sulphate and, to a lesser extent, lead oxides. The electrolyte is a concentrated sulfuric acid with a certain content of lead ions, which is associated with a large solubility product of $PbSO_4$ since the latter is a poorly soluble compound [16, 17]. Thus, the entire structure of the battery contains lead to one degree or another. Since all compounds of lead and antimony are poisonous, the CPS of the lead-acid system must necessarily be processed with the subsequent extraction of valuable components.

Due to their high characteristics, nickel-cadmium and nickel-metal hydride batteries have found application on the railway, in mine lamps, in self-driving, electric and hybrid vehicles, and in the aerospace industry [18]. In its composition, the positive electrode of these CPS can contain elements such as nickel, cobalt, zinc, iron, graphite [19–22]. The electrolyte consists of concentrated solutions of alkalis, in particular KOH with a small amount of LiOH or NaOH [23]. Negative cadmium electrodes contain cadmium, nickel and some organic additives. In turn, the negative metal hydride electrode may contain nickel, titanium, chromium, vanadium, zirconium, chromium, manganese, cobalt, iron, aluminum, lanthanum, cerium, neodymium, praseodymium, gadolinium, and yttrium [24]. Taking into account the composition of the indicated power sources, the latter must be processed with the extraction of valuable elements, in particular nickel and cadmium.

It should be noted that the extraction and recycling of nickel are relevant since its price has approximately doubled from 7500 to 15000 USD per ton over the past four years [25]. The latter is due to the lack of this metal, which is widely used in the metallurgical industry, in the production of batteries, and as a galvanic coating [26, 27]. Cadmium, as an element of the negative electrodes of nickel-cadmium batteries, must be extracted due to the high toxicity of its compounds [28, 29].

It should be noted that if we are talking about rechargeable CPS (batteries), then qualitatively the volumes of spent power sources can be judged by the volume of output in GWh normalized relative to the average number of charge-discharge cycles that are typical for this system [30]. That is, under all the same conditions, the volumes of spent CPS will be less for those systems for which the service life (i. e. the average number of charge-discharge cycles) will be greater. For such an assessment, the data in Figure *a* have been attributed to the average number of cycles typical for this type of CPS and are presented in percentage terms in Figure *b*.

Analysis of the data in the Figure gives the following picture: the largest number of spent batteries belongs to the CPS of lead-acid and lithium-ion systems. These two systems alone account for 98.6%. In this case, the first to be processed and disposed of should be CPS of these two types.

Recycling of lead acid batteries

A large review article [31] contains background information on various aspects of the use of lead in the world: lead consumption, use of primary and secondary (after recycling) lead, etc. The presented review contains detailed information on each of the options for recycling lead from spent batteries including technological schemes, description of reactions and other reference information.

According to a review article [16], the authors classify lead-acid battery waste into liquid and solid. Liquid ones include electrolyte, in turn, solid ones include electrode grids, paste, elements for supplying current to electrodes, terminals and bridges. Besides, solid waste includes plastics such as housings and separators.

In [32], the authors provided specific data on the percentage of a scrap of spent lead-acid batteries consisting of electrolyte (11–30%), polymer materials (22–30%), lead alloy mesh (24–30%) and $PbSO_4$ paste (30–40%). The source stated that about 80–85% of secondary lead was derived from lead sulfate.

In the context of the article [16], the authors considered only the recycling of elements containing lead. Within the framework of the review, two industrial recycling methods were distinguished: hydro-electrometallurgical and pyrometallurgical ones. A characteristic of new experimental methods was also given. They were the combined (hydrometallurgical and pyrometallurgical) method, the “atomic economic method” for direct recovery of PbO from lead paste, the method of calcination with citric acid, the method of direct membrane electrolysis, the method of electrokinetic separation as well as the method of hydrometallurgical desulfurization and vacuum thermal reduction.

In their article, the authors provided an overview and comparison of the methods, the stage of implementation (laboratory, pilot, industrial) as well as a general description of the processes in the ongoing methods. There was also some information on the analysis of the methods’ effectiveness and their environmental safety.

Separately, it was noted that the recycling of liquid waste (electrolyte) was not difficult and could consist either in neutralizing the acid or in reusing the acid after its concentration.

In contrast to work [16], the authors in [33] noted that neutralization of the spent electrolyte (H_2SO_4) was not the best solution for recycling liquid waste. On the one hand, this was due to the high cost of the process. On the other hand, gypsum contaminated with some HM was formed in the process. According to the authors, a logical solution is such a method that would allow the reuse of acid in new batteries. As an example, the authors cited the technology of the American factory of lead-acid batteries, which consisted in carrying out an ion-exchange process in solution with simultaneous electrochemical treatment to reduce ferric iron. This technology made it possible to use the treated electrolyte according to the described technology in new lead-acid batteries.

In the article [34] devoted to low-temperature hydro-electrometallurgical recycling of lead-acid batteries, the subtleties of the processes of this method were analyzed and compared. It also compared pyrometallurgical and hydro-electrometallurgical process flowsheets as well as new trends in technology. The conclusion was that countries with low to medium income levels needed better control of lead levels in air at workplaces. The authors of the study consider the issue of developing new cost-effective and energy-efficient ways of recycling scrap lead-acid batteries to be no less important.

An attempt was made in [35] to improve the process of lead leaching after the desulfurization stage in the hydro-electrometallurgical method. The authors cited the data that the highest efficiency of the leaching process was implemented in the company Aquametals (USA). According to the technological process, leaching occurred in a solution containing methanesulfonic acid and EDTA, which made it possible to increase the solubility of lead salts from 25 g/L (HCl-based solution) to 75 g/L due to the formation of complex compounds of lead. This made it possible to increase the leaching efficiency. In this work, another solution was proposed to increase the solubility of lead salts based on ionic liquid Ethaline 200 and ethylene glycol. According to the researchers, such a solution may increase the efficiency of the lead recycling process in the future.

In a series of works [31, 36–38], the authors proposed a method in which lead was reduced from a powder containing $PbSO_4$ with the addition of Na_2CO_3, Fe_3O_4, coal powder and other components. Carbon powder was used as a reducing agent in the process. As a result of carrying out the process at a relatively low temperature (850 ˚C), sulfur dioxide did not evolve (this is usually observed with such a treatment). This effect was achieved by adding Na_2CO_3 and Fe_3O_4 to $PbSO_4$.

In [39], it was proposed to use tartaric acid and sodium tartrate for desulfurization and leaching instead of citric acid. The authors showed that using the method, it is possible to obtain an ultrafine PbO powder after calcination. The authors attributed to the advantages of the method a lower consumption of agents for desulfurization and leaching as well as a lower amount of vapor and CO_2 during calcination.

A solution of acetic acid and sodium citrate with H_2O_2 and other additives with pH = 6.6 was proposed in [40] for leaching and desulfurization. The proposed method made it possible not to use melting and an electrochemical stage, while the desulfurization efficiency was 99.9%. In addition, the authors noted that large crystals of lead citrate were formed as a result of the reaction, which made it possible to effectively filter them from the mother liquor.

A research group in [41] proposed a method for recycling the paste of spent lead-acid batteries after desulfurization with the addition of a lead-antimony alloy with the reduction and distillation of lead under vacuum. The method made it possible to achieve 99.29% lead reduction from the paste and simultaneously reduce the Sb content in the alloy to 0.98%. In the process, antimony reduced lead, while being oxidized to Sb_2O_3. At the same time, the authors highlighted the following advantages of the method: a reduction in the number of operations required for the recycling, a significantly lower temperature to save energy (810 °C, 50 min), and no metal losses during oxidation.The recycling of lead-acid batteries paste into nanosized lead sulfide was proposed in [42]. According to the method, PbO_2 should first be calcined to obtain a more reactive PbO powder. Then, PbO was reacted with $KHSO_4$ to obtain $PbSO_4$. In the last stage, a mechanochemical reaction of $PbSO_4$ with Na_2S was carried out to obtain PbS. The resulting lead sulfide can be used in biochemical research, the production of infrared tubes, ceramics and semiconductor materials.

An Italian research group proposed a method for recycling waste electrode paste from lead-acid batteries into β-PbO which could be directly used for the production of new batteries. The authors showed that the method has less power consumption and a limited impact on the environment. According to the description, the recycling process consisted of the following stages: desulfurization of the paste in an aqueous solution of carbonate; calcining the desulfurized lead paste at a temperature of about 600 °C to obtain PbO of low purity and subsequent grinding; leaching of PbO with an aqueous solution of acetic acid followed by filtration; precipitation of lead hydroxide with alkali followed by filtration of the precipitate; drying and thermal firing to remove residual carbonate.

A Russian group of researchers proposed to use lead-containing waste batteries as a thermostabilizing and hardness-improving component in composite materials based on polyvinyl chloride [44].

As mentioned earlier, lead-acid batteries contain structural elements made of polymer materials. In this case, a wide range of polymers is used as materials: polypropylene, polyethylene, polyvinyl chloride, acrylonitrile-butadiene-styrene plastic (ABS), bakelite, fibers of various compositions [16]. It should be noted that polymer components can degrade and produce an additional flow of microplastics and nanoplastics, the waste of which becomes a global environmental problem [45, 46]. In this part of the article, there are several works related to the recycling of polymer materials of lead-acid batteries.

One of the most common plastics in lead-acid battery constructions is polypropylene [47]. According to the source, polypropylene can change its physicochemical properties during production, processing and operation in the device. In addition, the polymer may contain impurities such as polyvinyl chloride (separator material), metal oxides and salts, residues of sulfuric acid diffused into it, adhesives, which can also affect its properties. Therefore, the tasks facing the technologists are to minimize changes in the physicochemical parameters of polypropylene and thoroughly purify it from extraneous substances.

As an example of the recycling of polymer waste of lead-acid spent batteries, the authors of [48, 49] presented a simplified recycling scheme with the extraction and separation of plastics. This scheme included the following stages: crushing of scrap, selection of paste and small waste, re-crushing, separation by density on the first hydraulic separator of pure metal (grate Pb) and lighter materials, separation by density on the second hydraulic separator, where polymer materials polyethylene, bakelite, ebonite as well as lighter polypropylene were separated. The specified scheme could be used, among other things, for new batteries that did not contain bakelite and ebonite.

According to [49], recycled polypropylene was remelted, extruded into pellets and added to a new raw material for further production. Nevertheless, as shown in the article, after all operations, including thorough flushing, secondary polypropylene contained particles of PbO, $PbSO_4$, talc, $CaCO_3$, TiO_2, iron oxides as well as halogen compounds and, in particular, bromine. The authors associated the presence of HM compounds with the fact that particles were attracted to the polymer by electrostatic forces and this did not allow a high-quality washing process. At the same time, the authors noted that such plastic could pollute the environment, especially when burnt, and with repeated recycling, the plastic can become non-recyclable.

In addition to the above, the author [50] gave a scheme for the recycling of polypropylene based on production in France. It should be noted that according to this scheme, in addition to the schemes in [48, 49], after washing and drying, there is a stage for determining the addition of the necessary additives. A stage of homogenization follows granulation.

Conclusion

Analysis of the production scale of the main primary and secondary CPS has revealed that the leaders among the systems produced are lead-acid batteries with a share of 81.1%. Lithium-ion rechargeable CPS, in turn, are the second, with a share of 17.5%, and the production volumes of these power sources are growing rapidly. Considering that together both systems make up 98.6% of the volume of all produced secondary CPS, research in the field of these batteries recycling should be carried out first.

The analysis of literary sources regarding the recycling of spent lead-acid batteries has shown the presence of a large number of works in the field of electrode paste recycling. Although there are many ways to recycle electrode paste, the search for new options is constantly being carried out since the existing methods are energy intensive and have drawbacks.

As a result of the search, information has also been found on the recycling of electrolyte and basic polymer materials used in these CPS. The researchers have shown in the works that the most optimal variant of electrolyte recycling should allow its reuse.

When recycling polymeric materials, special attention should be paid to thorough rinsing of their surfaces and removal of HM compounds from the near-surface layers.

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