Technical sciences
BULLETIN OF POLTAVA STATE AGRARIAN ACADEMY
ISSN: 2415-3354 (Print)
2415-3362 (Online)
https://journals.pdaa.edu.ua/visnyk

original article | [621.35+66.02]502/504 | **doi: 10.31210/visnyk2020.03.32**

SAFE RECYCLING OF SPENT MANGANESE DIOXIDE-ZINC VOLTAIC CELLS

V. P. Dmitrikov[1]* ORCID 0000-0001-5016-6891
O. O. Gorb[1] ORCID 0000-0002-3141-8114
S. I. Boiko[1] ORCID 0000-0001-6871-7671
V. N. Yermakov[2] ORCID 0000-0003-4548-235X

[1] Poltava State Agrarian Academy, 1/3, Skovorody str., Poltava, 36003, Ukraine
[2] State Ecological Academy of Postgraduate Education and Management, 35-2, Metropolit Vasyl Lypkivskyi str., Kyiv, 03035, Ukraine
**Corresponding author*
E-mail: vpdmitrikov@gmail.com

How to Cite | *Dmitrikov, V. P., Gorb, O. O., Boiko, S. I., & Yermakov, V. N. (2020). Safe recycling of spent manganese dioxide-zinc voltaic cells. Bulletin of Poltava State Agrarian Academy, (3), 280–286. doi: 10.31210/visnyk2020.03.32*

Ecological aspects, connected with run-down manganese dioxide-zinc voltaic cells and their impact on the environment, are considered. General scheme of methodological approach to recycling galvanic cells scraps is proposed, including the using of information technologies with the substantiation of choosing the recycling method and analytical techniques, converting process, selecting the utilization method of the components and their subsequent selling. Non-waste scheme of technological recycling manganese dioxide-zinc voltaic cells' scraps has been developed, which successively includes their hydro-mechanical and hydro-chemical recycling following the principles of saving resources and energy. During stage-by-stage recycling of manganese dioxide-zinc voltaic cells' scraps, well-known technological methods and available hardware are applied, which are used in chemical technology and operating on the basis of hydro-mechanical and hydro-chemical processes. At all stages of recycling scraps of manganese dioxide-zinc voltaic elements, techno-chemical control is conducted together with processing the obtained data using software. As a result of recycling manganese dioxide-zinc voltaic cells' scraps according to the proposed technological scheme, graphite, ammonium chlorine zincate, zinc complex, and manganese dioxide are obtained. Safe utilization of manganese dioxide-zinc voltaic elements' scraps according to the developed hardware and technological scheme assumes the returning of metallic and soft parts to production and consumption spheres. The proposed scheme is non-waste, environmentally safe, following ecological standards for the natural environment of the region. The scheme's development is an important stage for industrial object design.

Key words: *accumulator scraps, hardware and technological scheme, safe disposal, hydro-mechanical processes, hydro-chemical processes, manganese dioxide-zinc voltaic cells, products of recycling.*

БЕЗПЕЧНА УТИЛІЗАЦІЯ ВІДПРАЦЬОВАНИХ МАРГАНЕЦЬ-ЦИНКОВИХ ГАЛЬВАНІЧНИХ ЕЛЕМЕНТІВ

***В. П. Дмитриков*[1]*, О. О. Горб*[1]*, С. І. Бойко*[1]*, В. М. Єрмаков*[2]**

[1] Полтавська державна аграрна академія, м. Полтава, Україна
[2] Державна екологічна академія післядипломної освіти та управління, м. Київ, Україна

Розглянуто екологічні аспекти, пов'язані з відпрацьованими марганець-цинковими гальванічними елементами, їхнім впливом на навколишнє природне середовище. Запропоновано загальну схему методологічного підходу до переробки брухту гальванічних елементів, що включає використання інформаційних технологій з обґрунтуванням вибору методу переробки і методик аналізів, процесу переробки, вибору методу утилізації компонентів і подальшої їхньої реалізації. Розроблено безвідходну схему технологічної переробки брухту марганцево-цинкових гальванічних елементів, яка послідовно включає їх гідромеханічну і гідрохімічну переробку з дотриманням принципів економії ресурсів і енергії. У процесі постадійної переробки брухту марганцево-цинкових гальванічних елементів застосовують відомі технологічні прийоми і доступне апаратне оформлення, що використовується в хімічній технології і працює на основі гідромеханічних і гідрохімічних процесів. На всіх стадіях переробки брухту марганцево-цинкових гальванічних елементів використовують технохімічний контроль з обробкою отриманих даних за допомогою програмного забезпечення. В результаті переробки брухту марганцево-цинкових гальванічних елементів за запропонованою технологічною схемою отримують графіт, хлорцінкат амонію, комплекс цинку, діоксид марганцю. Безпечна утилізація брухту марганець-цинкових гальванічних елементів за розробленою апаратно-технологічною схемою припускає повернення до сфери виробництва і споживання металевих і неметалевих компонентів. Пропонована схема є безвідходної, екологічно безпечною, з дотриманням екологічних норм для навколишнього природного середовища регіону, її розробка є важливим етапом для проєктування промислового об'єкта.

Ключові слова: *акумуляторний лом, апаратно-технологічна схема, безпечна утилізація, гідромеханічні процеси, гідрохімічні процеси, марганець-цинкові гальванічні елементи, продукти переробки.*

БЕЗОПАСНАЯ УТИЛИЗАЦИЯ ОТРАБОТАННЫХ МАРГАНЕЦ-ЦИНКОВЫХ ГАЛЬВАНИЧЕСКИХ ЭЛЕМЕНТОВ

***В. П. Дмитриков*[1]*, О. А. Горб*[1]*, С. И. Бойко*[1]*, В. Н. Ермаков*[2]**

[1] Полтавская государственная аграрная академия, г. Полтава, Украина
[2] Государственная экологическая академия последипломного образования и управления, г. Киев, Украина

Рассмотрены экологические аспекты, связанные с отработанными марганец-цинковыми гальваническими элементами, их влиянием на окружающую природную среду. Предложена общая схема методологического подхода к переработке лома гальванических элементов, включающая использование информационных технологий с обоснованием выбора метода переработки и методик анализов, процесса переработки, выбора метода утилизации компонентов и последующей их реализации. Разработана безотходная схема технологической переработки лома марганцево-цинковых гальванических элементов, которая последовательно включает их гидромеханическую и гидрохимическую переработку с соблюдением принципов экономии ресурсов и энергии. В процессе постадийной переработки лома марганцево-цинковых гальванических элементов применяют известные технологические приемы и доступное аппаратное оформление, используемое в химической технологии и работающее на основе гидромеханических и гидрохимических процессов. На всех стадиях переработки лома марганцево-цинковых гальванических элементов используют технохимический контроль с обработкой полученных данных при помощи программного обеспечения. В результате переработки лома марганцево-цинковых гальванических элементов по предложенной технологической схеме получают графит, хлорцинкат аммония, комплекс цинка, диоксид марганца. Безопасная утилизация лома марганец-цинковых гальванических элементов по разработанной аппаратно-технологической схеме предполагает возвращение в сферу производства и потребления металлических и неметаллических ком-

понентов. Предлагаемая схема является безотходной, экологически безопасной, с соблюдением экологических норм для окружающей природной среды региона, ее разработка является важным этапом для проектирования промышленного объекта.

Ключевые слова: *аккумуляторный лом, аппаратно-технологическая схема, безопасная утилизация, гидромеханические процессы, гидрохимические процессы, марганец-цинковые гальванические элементы, продукты переработки*

Introduction

Global systems of manufacturing and consuming technical products significantly affect the natural environment and public health. The development of electronic and computer equipment, mobile devices and vehicles is accompanied by a huge number of run-down one-use and reusable electrochemical cells, mostly batteries and compact accumulators' scraps (BAS), which are not used subsequently.

Under the absence of separate collection, BAS get into the environment in different ways, they are found in solid municipal wastes, unauthorized landfills, and confiscated products [1, 7]. The concentration of BAS components in soils and wastewaters of industrial, and in some cases, non-industrial regions often exceeds ecological standards and requirements, posing a threat to public health [3, 5]. At the same time, such pollutions are anthropogenic deposits, the development of which using modern approaches is promising from both economic and environmental points of view [21].

There are many ways of using products and wastes of BAS recycling to improve crop germination and growth, increase yields, as well as improve their resistance to diseases. Under ecological expediency of using the products of full or partial BAS recycling, the cost of such fertilizers is relatively small [22, 23]. In industrially developed countries, BAS burning and burying are prohibited; they must be recycled. Many patented ways of BAS recycling are industrially implemented, which makes it possible to do without the development of natural raw materials due to BAS utilization [6, 12]. The European Battery Recycling Association (EBRA), Nokia, Samsung, Apple, Motorola, Siemens, Philips, LG companies and others are actively working in this direction.

The set of methods used for BAS recycling is quite wide and includes mechanical (primary recycling), metallurgical, electrochemical and reagent methods, as well as the methods of biotechnological separation and / or disposal [8-11, 14, 15, 20]. In developed countries, BAS, recycled products, and in some cases waste, are market products, to which it is expedient to apply laws of marketing. When choosing and / or creating technological scheme for effective BAS recycling, both traditional approaches and innovations are applied, using typical processes and hardware in the technological scheme [16].

The analysis of literature sources shows an increased interest in complex recycling of used manganese dioxide-zinc voltaic cells (MDZVC), which, as it is known, cannot be recovered [4, 13, 17]. The components of MDZVC are steel, metallic zinc, manganese oxides, potassium hydroxide, zinc chloride, and zinc oxide.

Despite a small weight, the total amount of spent MDZVC makes many thousands of tons, which is a real threat to the natural environment. Based on this, the development of hardware-technological scheme for recycling MDZVC scraps is an urgent and specific task.

At present, MDZVC scraps are considered to be secondary raw materials, which it is expedient to include in new life cycle of technical products, using modern methods of recycling, or apply for other purposes [18, 19].

The aim and *task* of the research are to develop hardware-technological scheme for safe utilization of manganese dioxide-zinc voltaic cells' scraps.

Materials and methods

The development of the most acceptable hardware and technological scheme for safe disposal of electrochemical cells' scraps is an important stage in designing industrial facility: the final practical result of the project as a whole is determined by completeness and rationality of such scheme [2].

In any case, while substantiating the choice of BAS recycling method, IT are used taking into account market indicators of selling recycled products and mathematical and physical modeling of technological processes, especially their weak points.

Results of research and their discussion

The general scheme of ecological and economic approach to BAS recycling is presented in Fig. 1.

It is also expedient to use such approach for recycling used MDZVC.

In the process of developing hardware and technological scheme for recycling MDZVC scraps, the results of previous studies published earlier were used [3].

The sequence of work on MDZVC scraps utilization by stages and operations is shown and described below.

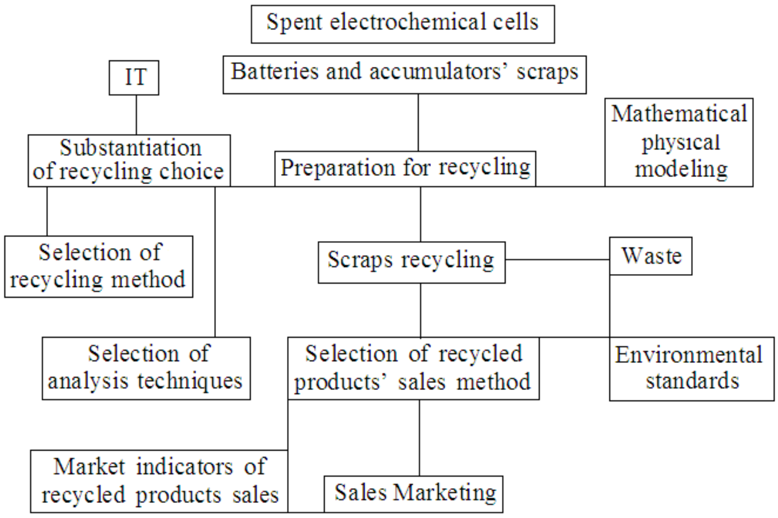

Fig. 1. Scheme of ecological and economic approach to BAS recycling

Auxiliary work (preparation of desalinated water, alkali solutions, delivery of raw materials, storage of products, etc.) are singled out in independent stages, as well as means of the processes' control and management, and they are not shown on the given conventional hardware and technological scheme of MDZVC scraps recycling.

At the stage of preparation for recycling, the spent MDZVC are sorted and separated from paper, plastic, and other undesirable components in the technological process of recycling. The sorting according to certain criteria and parameters is quite time consuming and is connected with involvement of manual labor. In some cases, soft parts after pressing are disposed by methods used for solid waste.

MDZVC scraps are recycled first by hydro-mechanical method of separating steel component and graphite, then by hydro-chemical method, separating other components. After pre-sorting, MDZVC are sent for recycling (Fig. 2), the first stage of which is their breaking to obtain fine dispersion.

Next, the MDZVC from hopper 1 enters crusher 2, where they are broken up, then powder-like substance is dispersed on screen drum 3 (if necessary, classifier is used).

Conveyor 4 consists of 2 parts that operate in different directions. The material, which has not passed screen drum 3, is directed to outlet hopper 1 by elevator 5 for repeated crushing. The sieved material is treated with magnetic separator 6, which selects steel components of MDZVC (product D), and the non-magnetic substance, after taking away plastic and paper waste, is taken to flotation unit 7.

Powdered material is subjected to pneumatic-mechanical flotation in aqueous medium on flotation installations of various types, while choosing which the effect of salt medium on flotation process is taken into account. Graphite separation from salt-water heterogeneous system takes place, which is further used for hydro-chemical recycling. After flotation, graphite is pre-centrifuged it is taken into dryer 8, obtaining dry substance A.

After flotation, the so-called "tails" are sent to decanter 9, in which they are divided into filtrate and sediment.

The filtrate gets into evaporator 10 and dryer 11, and ammonium chloride zincate (product B) is taken to the warehouse. The sediment from decanter 9 by screw conveyor 12 is fed into reactor 13, equipped with mechanical mixer, and alkali (KOH) in stoichiometric amount from measuring vessel 14 enters reactor 13. Sediment incomplete dissolution takes place in reactor 13, and under the action of alkali on zinc, hydrogen is released, which gets into gas collector 16 through hydro-lock 15.

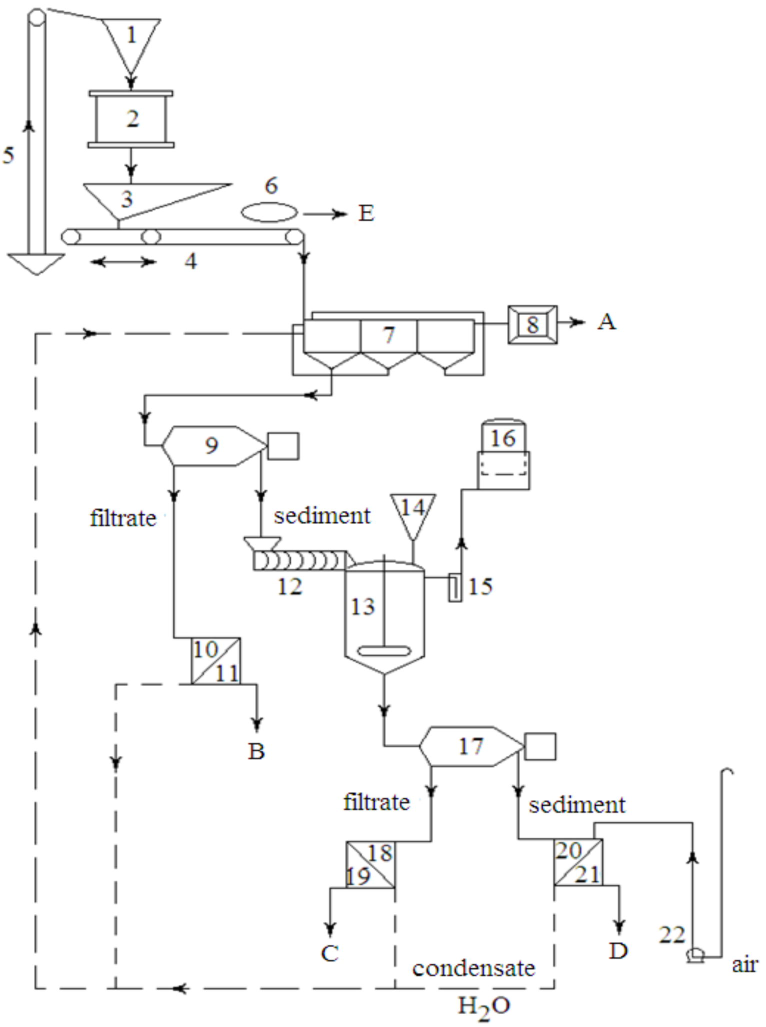

Fig. 2. Hardware-technological scheme of recycling spent MDZVC:
1-hopper, 2-crusher, 3-screen drum, 4-conveyor, 5-noria, 6-magnetic separator, 7-flotation unit, 8, 11, 19, 20-dryers, 9, 17-decanters, 10, 18- boil-off devices, 12-screw conveyor, 13-reactor, 14-measuring vessel, 15-hydro-lock, 16-gas collector, 21-furnace, 22-blower

The setting of manganese compounds and solution of zinc complex from reactor 13 is fed into decanter 17, where sediment detachment from the solution occurs. The filtrate enters boil-off device 18, the wet product – in dryer 19 and then is taken to the warehouse (product B).

The setting of manganese compounds gets into dryer 20, through which air is blown from blower 22. Complete oxidation of manganese hydroxide form in manganese dioxide (product D) occurs, which is taken to warehouse after additional heat treatment in furnace 21.

Thus, as a result of recycling spent MDZVC according to the given hardware-technological scheme, technical products are obtained: A - graphite, B - ammonium chlorine zincate, C – zinc complex, D – manganese dioxide, E – steel constituent element.

The developed hardware-technological scheme of MDZVC scraps recycling, supplemented by innovative methods of recycling similar technical products, is recommended by the authors for industrial use.

Conclusions

Ecological aspects of scraps recycling of electrochemical cells, applying recycling principles for safe disposal of their metallic and non-metallic parts were considered. The technological scheme of safe utilization of manganese dioxide-zinc voltaic cell scraps has been proposed, which under innovative approach enables to include their separate components in a new life cycle of technical production; at the same time, it is energy-saving, resource-saving, and non-waste. Graphite is used to obtain other voltaic cells, graphite lubricants, electrodes, and contacts. Potassium zincate is used for electrochemical zinc extraction, and alkaline solution is reused in the technological scheme. It is expedient to use ammonium chlorine zincate for crop growth and development, and manganese dioxide – as a component of batch mixture at ferromanganese production as a depolarizing element in dry cells, a component of mineral pigments. The creation and correction of the hardware-technological scheme of recycling MDZVC scraps taking into account the principles of safe utilization are possible also by means of CADE, Concept Draw Pro, Diagram Designer, and other computer programs.

References

1. Vinogradov, S. S. (2002). *Ekologicheski bezopasnoye gal'vanicheskoye proizvodstvo*. Moskva: Globus [In Russian].

2. Dmitrikov, V., Dudnikov, I., & Musienko, K. (2019). Recycling of waste lead-tin batteries. Report 2. Hardware-technological scheme. *Transactions of Kremenchuk Mykhailo Ostrohradskyi National University*, 6, 49–53. doi: 10.30929/1995-0519.2019.6.49-53

3. Protsenko, A. V., Dmitrikov, V. P., Gun'ko, S. A., & Yegun'ko, V. V. (2011). O soblyudenii ekologicheskikh standartov pri utilizatsii shlamov otrabotannykh marganets-tsinkovykh gal'vanicheskikh elementov. *Zbirnyk Naukovykh Prats Natsionalnoho Hirnychoho Universytetu*, 2 (36), 218–223 [In Ukrainian].

4. Sverdel, Ye. S, Mikhaylichenko, A. I., & Yagodin, G. A. (2007). Kompleksnaya pererabotka sukhikh gal'vanicheskikh elementov. *Uspekhi v Khimii i Khimicheskoy Tekhnologii*, 9 (77), 13–16 [In Russian].

5. Tarasova, V.V., Malinovskiy A.S., & Ribak, M.F. (2007) *Yekologíchna standartizatsíya í normuvannya antropogennogo navantazhennya na prirodne seredovishche*. Kiev: Tsentr uchbovoí líteraturi [In Ukrainian].

6. Yavors'kiy, V. T., Zozulya, G. Í., & Buklív, R. L. (2014) Utilízatsíya tsínnikh komponentív íz vídprats'ovanikh malikh dzherel yelektrichnogo strumu. *Visnyk Natsionalnoho Universytetu «Lvivska Politekhnika», Khimiia, Tekhnolohiia Rechovyn Ta Yikh Zastosuvannia*, 787, 117–121 [In Ukrainian].

7. Anastas, P., & Eghbali, N. (2010). Green Chemistry: Principles and Practice. *Chem. Soc. Rev*., 39 (1), 301–312. doi: 10.1039/b918763b.

8. Belardi, G., Medici, F., & Piga, L. (2014). Influence of gaseous atmosphere during a thermal process for recovery of manganese and zinc from spent batteries. *Journal of Power Sources*, 248, 1290–1298. doi: 10.1016/j.jpowsour.2013.10.064.

9. Cui, J., & Forssberg, E. (2003). Mechanical recycling of waste electric and electronic equipment: a review. *Journal of Hazardous Materials*, 99 (3), 243–263. doi: 10.1016/s0304-3894(03)00061-x.

10. Ebin, B., Petranikova, M., Steenari, B.-M., & Ekberg, C. (2016). Effects of gas flow rate on zinc recovery rate and particle properties by pyrolysis of alkaline and zinc-carbon battery waste. *Journal of Analytical and Applied Pyrolysis*, 121, 333–341. doi: 10.1016/j.jaap.2016.08.014.

11. Espinosa, D. C. R., Bernardes, A. M., & Tenório, J. A. S. (2004). An overview on the current processes for the recycling of batteries. *Journal of Power Sources*, 135 (1-2), 311–319. doi: 10.1016/j.jpowsour.2004.03.083.

12. "Waste Electrical and Electronic Equipment (WEEE) - Eurostat," (2019). *Eurostat, statistics-explained*. Retrived from: https://ec.europa.eu/eurostat/statistics-explained/index.php/Waste_statistics_-_electrical_and_electronic_equipment.

13. Ferella, F., De Michelis, I., & Vegliò, F. (2008). Process for the recycling of alkaline and zinc–carbon spent batteries. *Journal of Power Sources*, 183 (2), 805–811. doi: 10.1016/j.jpowsour.2008.05.043.

14. Haghighi, H. K., Moradkhani, D., & Salarirad, M. M. (2015). Separation of zinc from manganese, magnesium, calcium and cadmium using batch countercurrent extraction simulation followed by scrubbing and stripping. *Hydrometallurgy*, 154, 9–16. doi: 10.1016/j.hydromet.2015.03.007.

15. Ilyas, S., & Lee, J. (2014). Biometallurgical Recovery of Metals from Waste Electrical and Electronic Equipment: a Review. *ChemBioEng Reviews*, 1 (4), 148–169. doi: 10.1002/cben.201400001.

16. Kaya, M. (2016). Recovery of metals and nonmetals from electronic waste by physical and chemical recycling processes. *Waste Management*, 57, 64–90. doi: 10.1016/j.wasman.2016.08.004.

17. Oliveira, C. R. de, Bernardes, A. M., & Gerbase, A. E. (2012). Collection and recycling of electronic scrap: A worldwide overview and comparison with the Brazilian situation. *Waste Management*, 32 (8), 1592–1610. doi: 10.1016/j.wasman.2012.04.003.

18. Yeşiltepe, S., Buğdaycı, M., Yücel, O., & Şeşen, M. (2019). Recycling of Alkaline Batteries via a Carbothermal Reduction Process. *Batteries*, 5 (1), 35. doi: 10.3390/batteries5010035.

19. Tuncuk, A., Stazi, V., Akcil, A., Yazici, E. Y., & Deveci, H. (2012). Aqueous metal recovery

techniques from e-scrap: Hydrometallurgy in recycling. *Minerals Engineering*, 25 (1), 28–37. doi: 10.1016/j.mineng.2011.09.019.

20. Chen, W.-S., Liao, C.-T., & Lin, K.-Y. (2017). Recovery Zinc and Manganese from Spent Battery Powder by Hydrometallurgical Route. *Energy Procedia*, 107, 167–174. doi: 10.1016/j.egypro.2016.12.162.

21. Zhang, L., & Xu, Z. (2016). A review of current progress of recycling technologies for metals from waste electrical and electronic equipment. *Journal of Cleaner Production*, 127, 19–36. doi: 10.1016/j.jclepro.2016.04.004

22. Joensuu, M., Rahunen, J., & Rautio, L. (2019). *Patent № WO 2019/150005 A1*. Patent and Trademark Offic.

23. Guy, A. J. (2020). *Patent № US 2020/0115294 A1*. Patent and Trademark Offic.

Стаття надійшла до редакції 29.07.2020 р.

Бібліографічний опис для цитування:

Дмитриков В. П., Горб О. О., Бойко С. І., Єрмаков В. М. Безпечна утилізація відпрацьованих марганець-цинкових гальванічних елементів. *Вісник ПДАА*. 2020. № 3. С. 280–286.