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Recycling of spent battery electrolytes for construction material production

Получение строительных материалов из отработанных аккумуляторных электролитов

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Abstract. The issue of spent battery electrolytes recycling in the process of construction material production and also the negative impact of such wastes on environment are considered in this article. Modern methods of processing as spent batteries and their electrolytes are analysed. In this article proposed to recycle spent acid battery electrolyte, applying it as additional component of the mixing liquid for phosphate systems, featured by high mechanical properties, heat and acid resistance. Also authors proposy to recycle spent electrolyte as preparation liquid for mortar made of blast-furnace slag, which is used for construction material production. Values of thermodynamic functions, obtained as a result of calculations, show that hardening reaction of the phosphate system is spontaneous ($\Delta G°298$ = -423.6 kJ/mol) and exothermic ($\Delta H°298$= -719.6 kJ/mol). Hardened system represents strong artificial stone which can be used, for example, in construction of floors in workshops with aggressive media, for lining of towers, etc. Test results have shown that maximal strength value of artificial stone (17 MPa) is reached when 15 % of spent acid battery electrolyte is added into phosphate system. The method of geoecological assessment of designed technological solutions is also described.

Аннотация. В статье рассмотрена проблема утилизации отработанных аккумуляторных электролитов с точки зрения негативного воздействия на окружающую среду. Проанализированы современные способы переработки, как отработанных аккумуляторов, так и их электролитов. Авторами предложено новое технологическое решение утилизации отработанных аккумуляторных (кислотных и щелочных) электролитов. Суть решения заключается в применении отработанных аккумуляторных электролитов в качестве дополнительного компонента жидкости затворения в фосфатных системах, отличающихся высокими механическими свойствами, термо- и кислотостойкостью. Также предлагается использовать отработанный электролит в качестве жидкости затворения при получении шлакощелочных материалов. Полученные значения термодинамических функций свидетельствуют о том, что реакция твердения фосфатной системы является самопроизвольной. Результатом отвердевания фосфатной системы является прочный искусственный камень, который рекомендуется использовать для устройства полов в цехах с агрессивными средами, для футеровки башен и т.д. Результаты испытаний показали, что максимальное значение прочности искусственного камня (до 17 МПа) достигается при введении в

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фосфатную систему до 15% отработанного кислотного аккумуляторного электролита. Описан метод геоэкологической оценки разработанного технологического решения.

Introduction

Nowadays reality implies that there is no any sector of national economy, which could work without batteries, while their average lifetime is not exceeding five years [1]. Among wide range of the batteries the most environmentally dangerous are acid [2–4] (mainly automotive) and alkaline batteries [5] (e.g. Ni–Cd, Cd-Ni, Ni–Fe). For example, according to the data by author [6] in Moscow only up to 4000 tons of waste batteries are piled up annually. Each battery is container filled with an electrolyte for 11-30 % of the total [7, 8], which represents aggressive substance and it is dangerous to the environment.

During operation of acid batteries, electrolyte (most commonly it is sulphuric acid) accumulates highly toxic substances, such as lead (16.9 %), its compounds: $PbSO_4$ (19.7 %), PbO_2 (17.9 %), PbS (3.6 %) and other components: Sb (0.6 %), H_2SO_4 (18.1 %), H_2O (10.1 %), $[-CH_2-CHCl-]_n$ (3.1 %), $[-CH(CH_3)-CH_2-]_n$ (10.0 %) [9]. Lead is polytropic toxicant with negative effects on immune, nervous and cardiovascular systems due to, first of all, its denaturizing effect upon tissues and cells of the body [10]. In addition, lead has mutagenic activity. Being a heavy metal, lead has toxic impact on human health [11, 12] and it is classified by the Russian Standard GOST 12.1.007-76 “Occupational safety standards system. Noxious substances. Classification and general safety requirements” as first hazard class. On the other side lead as a waste is classified by [13] as moderately dangerous and by [14] mirror non-hazardous.

Lead processing facilities, as battery scrape consumers, apply technologies which do not involve recycling of electrolytes, and direct recycling of electrolytes is performed by special chemical plants using rather expensive technology. Furthermore, the widespread disposal way of the spent electrolyte by the unscrupulous consumers is its discharge into sewers or upon soil at unauthorized dumps. Recovery period of environmental components after such negative impacts is over 30 years after complete removal of exposure source.

Spent alkaline battery represents polymer container filled with electrolyte. Main components of this electrolyte are Ni (23.5 %) and Cd (22.7 %) compounds, which also have first hazard class. Also electrolyte of alkaline battery includes Na_2O (3.2 %), LiOH (5.5 %), H_2O (13.9 %), Fe compounds (0.2 %) and $[-CH_2-CH_2-]_n$ (31.0 %) [9, 15, 16]. Being both heavy metals, Ni and Cd can accumulate in human body, causing diseases of various kinds [10]. For example, excess of Ni causes changes in liver, kidneys, cardiovascular, nervous, and digestive systems, it damages metabolic processes, and can lead to development of asthma, atherosclerosis, anaemia, diabetes mellitus, dementia, nasopharyngeal and bronchial cancers, and other diseases. Cadmium is not less dangerous, too. When entering into human body, it can block functions of some enzymes, affect the liver, kidneys, pancreas, lead to lung cancer and bone deformities, impact central nervous system, and so on. Biological half-life of cadmium in human body lasts 20 to 30 years.

In some countries the recycling process of spent batteries includes the following steps: collecting the life-expired batteries, pouring out and neutralization of the electrolyte, the separation of the battery lead and plastic parts, recovery of lead by smelting lead scrap and the refining of lead bullion obtained. Widely used in practice methods of recycling spent batteries described in works D.C.R. Espinosa et. all [17], J. Xu et. all [18], X. Zeng et. all [19], G. Pistoia et. all [20], J. Nan et. all [21], E. Sayilgan et. all [22], T. Georgi-Maschler et. all [23], A. Zabaniotou et. all [24], N. Zhu et. all [25], A. Chagnes and B. Pospiech [26].

Meanwhile methods of recycling spent battery electrolytes may be tentatively divided into three groups:

1. Electrolyte neutralization up/down to pH value 7 followed by discharge of neutralized electrolyte without any further use of resulting products. It should be noted that neutralization is used only when a small amount of electrolyte is gained, and if it does not contain organic impurities.
2. Spent battery electrolyte application in the other manufacturing processes, for example, recycling of the acid electrolyte in production of sulphate fertilizer.
3. Regeneration of the electrolyte in order to obtain a commercial product, such as sulphuric acid – this method nowadays is one of the most common ways of using spent battery electrolytes. This method includes: thermal decomposition, extraction of organic impurities, adsorption, catalytic oxidation with hydrogen peroxide, coagulation and evaporation. Among listed above

methods the most often used is thermal decomposition (pyrogenic method), in which under the action of high temperatures (about 950-1200°C) regeneration of acid occurs.

Also, some technological approaches are known, which allow, on the one hand, to neutralize acid or alkaline electrolyte, and, on the other hand, to block the toxic substances, for example, heavy metals. In the publications [27–29] authors propose to perform neutralization of the electrolyte with converter sludge in mass ratio (0.65–0.95):1. Into the vitreous viscose mass formed, granulated blast-furnace slag is added as a binder under stirring.

In spite of considerable progress in this area the problem of spent battery electrolyte recycling still remains relevant primarily because of the high cost of the proposed methods.

In this connection the aim of this article to develop technological solution for the recycle of spent battery electrolytes. To achieve this aim the following tasks are set:

– to conduct lab tests on the application of spent battery acid electrolyte for obtaining phosphate systems;

– to conduct lab tests on the application of spent alkaline battery electrolyte as preparation liquid for mortar made of blast-furnace slag;

– to carry out comparative evaluation of the developed technological approach with already known ones.

Methods

In this paper, phosphate systems were obtained in the laboratory by mixing *FeO* powder, Cambrian clay and H_3PO_4 sand, diluted with spent battery acid electrolyte. The main chemical reaction which occurs during production of phosphate materials schematically can be described with equations (1) and (2).

$$Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O + 6H_3PO_4 \rightarrow 2Al(H_2PO_4)_3 + 2(SiO_2 \cdot 2H_2O) + H_2O \quad (1)$$

$$Al_2O_3 \cdot 4SiO_2 \cdot 2H_2O + FeO + 2\tfrac{2}{3} H_3PO_4 + 3\tfrac{1}{3} H_2O \rightarrow \rightarrow \tfrac{1}{3} Fe_3(PO_4)_2 \cdot 4H_2O + 4(SiO_2 \cdot H_2O) + 2Al(OH)_2H_2PO_4(s) \quad (2)$$

Taking into account wide range of recently known recycling and application methods of spent battery electrolyte, it is reasonable to carry out comparative evaluation of the developed technological approach with already known ones. For such evaluation, property quality (PQ) method [34] can be used, which allows carrying out comparison of different technological approaches within single scale. Following aspects of comparison recycling methods for spent battery electrolyte are selected:

- aspect of geo- and ecology protection (PQ^1);
- economical aspect (PQ^2);
- operational aspect (PQ^3).

Due to environmental hazard of spent battery electrolyte, importance of comparison aspects can be assigned as 50%, 30% and 20%, respectively.

For the aspect of geo- and ecology protection, following properties are taken into account:

- regeneration possibility (PQ^1_1);
- absence of wastes after regeneration (PQ^1_2);
- possibility to obtain new useful product (PQ^1_3).

In this case importance of the properties can be assigned as 40 %, 30 % and 30 %, respectively, depending on their effectiveness.

For the economic aspect, following properties are taken into account:

- utilization cost (PQ^2_1);
- final product cost (PQ^2_2).
- Importance of the properties 50% for each.

For the operational aspect, following properties are taken into account:

- the need for special equipment (PQ^3_1);
- processing time(PQ^3_2);
- availability of method in the Russian Federation(PQ^3_3).

Importance of the properties e assigned as 40 %, 30 % and 30 %, respectively.

In accordance with the method for determining PQ index, the best condition is assigned to value 1, the worst condition is assigned to value 0.

PQ index for each area is calculated by the formula (3):

$$PQ=0.5\cdot\left(0.4\cdot PQ_1^1+0.3\cdot PQ_2^1+0.3\cdot PQ_3^1\right)+0.3\cdot(0.5\cdot PQ_1^2+0.5\cdot PQ_2^2)+0.2\cdot(0.4\cdot PQ_1^3+0.3\cdot PQ_2^3+0.3\cdot PQ_3^3) \quad (3)$$

Results and Discussion

The term “recycling” in this article means application of spent battery electrolyte to obtaining environment-friendly product, which has useful consumer properties. As elaboration of works led by L. Svatovskaya [30-34], who had shown that phosphate systems possess unique environment protection properties due to capabilities to neutralize and block pollutions, this article proposed to recycle spent acid battery electrolyte, applying it as additional component of the mixing liquid for phosphate systems, featured by high mechanical properties, heat and acid resistance.

Phosphate hardening is based on the chemical process of interaction between oxides of d-metals and finely ground special compositions with orthophosphoric acid. Binding properties of the system “metal oxide – orthophosphoric acid” depend on ionic potential, which represents ratio of electronic charge of the ion to its effective radius. As far as ionic potential of cations in groups with homogeneous electronic structure decreases, hardening process accelerates, while increase of ionic potential causes deceleration of this process.

Synthesis of phosphate binders is based on high chemical activity of phosphate solutions towards powders of different chemical compositions. In this case phosphate compositions are considered as dispersed systems of “solid – liquid” type, where (with a certain speed) irreversible chemical reactions of acid-base interaction type take place. It is appropriate to use mineral products of complex chemical and mineralogical composition, e.g. clay, as primary solid components of these phosphate systems.

Values of thermodynamic functions, obtained as a result of calculations, show that hardening reaction of the phosphate system is spontaneous ($\Delta G°_{298}$ = -423.6 kJ/mol) and exothermic ($\Delta H°_{298}$= -719.6 kJ/mol). Considerable amount of the heat produced by reaction (1) promotes removal of excessive moisture from the system and helps crystallization of products. These factors result in formation of practically insoluble and safe for environment phosphate bonds. Thus, hardened system represents strong artificial stone which can be used, for example, in construction of floors in workshops with aggressive media, for lining of towers, etc.

Test results have shown that maximal strength value (17 MPa) is reached when 15 % of spent acid battery electrolyte is added into phosphate system. After saturation of the material with water during two days its strength practically does not change due to formation of phosphates which have low solubility, increased thermodynamic stability and tendency to easy crystallization. Analysis of the aqueous extracts from obtained artificial stones shows that these extracts do not contain contaminants.

Identifying feature of these phosphate materials is small setting time, which in most cases is a positive feature of material, allowing quick extraction of products from moulds. However, in some cases quick setting is undesired. Studies have shown that addition of spent battery electrolyte to phosphate system retard setting time up to 1.5 hour, which increases convenience of placing binder mixture.

Thus, not only a technological approach, which provides comprehensive utilization of spent acid battery electrolyte is proposed, but also a new material with high strength properties is obtained.

Authors proposed to recycle spent alkaline electrolyte as preparation liquid for mortar made of blast-furnace slag, which is used for construction material production. Materials made of blast-furnace slag are obtained by mixing finely ground, granulated blast-furnace slag and sand with an alkaline component, such as sodium silicate. Hardening of the mortar made of blast-furnace slag and alkaline component is based on the following chemical reaction (4):

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$$2.5(C_2AS)(s)+0.5(Na_2O \cdot H_2O)(s)+12.5SiO_2 \cdot H_2O(s)+Na_2SiO_3(s) \rightarrow$$
$$\rightarrow 2.5[Na_2O \cdot Al_2O_3 \cdot 4SiO_2 \cdot 2H_2O](s)+ C_5S_6H_{5,5}(s)+ 3.5H_2O(l) \quad (4)$$

Thermodynamic calculations have shown that reaction (4) is exothermic ($\Delta H°_{298}$ = -3042.6 kJ/mol). Physical and mechanical properties of obtained materials are presented in Table 1.

Table 1. Physical and mechanical properties of material containing spent alkaline battery electrolyte

№	**Composition**			**Compressive strength, MPa, after 27 days**
	Slag, %	Sand, %	Spent alkaline electrolyte, % of slag	
1	70	30	0	20.5
2	70	30	3	21.5
3	70	30	4	21.0
4	70	30	6	25.3
5	70	30	8	25.4
6	70	30	10	25.4
7	70	30	12	13.2
8	70	30	15	12.5
9	50	50	0	11.5
10	50	50	2	12.3
11	50	50	4	13.0
12	50	50	6	12.8
13	50	50	8	8.7
14	50	50	12	7.8
15	50	50	15	7.0

Addition of 3 to 10 % spent alkaline battery electrolyte into slag-alkaline system increases material strength up to 24 %, as compared to the reference sample and it amounts 25.4 MPa. Aqueous extracts from obtained materials do not contain contaminants.

As a result, each method of recycling can be estimated by the PQ-method in interval from 0 to 1, which gives possibility to conclude which recycling method of spent battery electrolyte is most advantageous. Preliminary calculations show that PQ-index of proposed technological approaches exceeds PQ-indices of currently used technological approaches.

Conclusions

4. Studies have shown that spent battery electrolytes (acid and alkaline), which are dangerous for the environment, can be recycled by application as additional components for production of either phosphate or blast-furnace slag and alkaline binding systems, which are based on spontaneous exothermic chemical reactions.

5. Resulting products of such reactions have low solubility product values, and it allows concluding that deactivation of spent battery electrolytes is based on blocking them in artificial stone, which represents a useful and environmentally safe product.

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