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PROCESSING OF EXHAUST LEADEN-CADMIUM GALVANICELEMENTS

REPORT 1. PRINCIPLES AND PROCESSES OF PROCESSING

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The results of researches are resulted on the reagent processing of exhaust leaden-cadmium galvanic elements and accumulators which serve as the second raw material for electrical engineering industry. The method of processing is developed zero-emission, energy- and resourses economy, ecologically safe, at the same time remaining maintenance of lead, does not exceed cadmium and their connections ecological standards. Chemical and technic processes are analysed, the offered is improved methodology and the general chart of technology of processing of leaden-cadmium galvanic elements and accumulators is developed.

Key words: agrarian machines, accumulators, galvanic elements, technogenic safety, technology of processing, utilization

Formulation of the problem. Absence is in Ukraine of legislation and specialized organizations from processing of galvanic elements and accumulators, that chemical sources of current (CSC), resulted in a volume, that CSC is exhaust throw out in an environment together with other offcuts. For the burial place of exhaust CSC (in the scales of Ukraine are ten of millions of units) grounds which eliminate taking away of metallic components of CSC (lead, tin, zinc, cadmium and other) in an environment are needed. The losses of metals here compare to the charges them on making of CSC.

In the case of burial place of exhaust CSC there is alienation of earths, contamination of bytoxic matters—by heavy metals which appear at destruction of CSC atmospheric and ground waters. An exit from this situation is the exhaustive processing of exhaust CSC welcome back of toxic materials in the sphere of productions of, which takes a place in foreign countries, where legislative acts and organizations are on collection and processing of exhaust CSC.

Annual requirements of Ukraine in metals for electrochemical industry substantial enough, which is why processing of exhaust CSC(as technological offcuts) actually and expedient from the economic and ecological points of view. For this purpose pick up or develop such method of

utilization of exhaust CSC, which answers requirements on the indexes of safety of the Ukrainian and world ecological standards.

Analysis of the last researches and publications the decision of problem is founded in which. The analysis of scientific and technical and patent literature shows that a universal ecologically safe and economic acceptable method of processing of CSC is not. The pyrometallurgical apply in world practice, physical and chemical and reagents methods of processing of exhaust CSC. Failings and advantages of these methods in detail are described before [4].

Purpose and task of researches: a study of possibility of processing of exhaust leadencadmium galvanic elements and accumulators (general name of LCE) is that development of keeping resources and ecologically safe technology which enables to turn the components of LCE in the sphere of production taking into account their ecological standards, and also to improve ecology of environment.

The results of studies. LCE, due to their high specific power-hungryness (in 1.5–2 times higher than at nickel-cadmium, leaden, iron-nickel accumulators), capable to work at low temperatures. They are applied in electric cars, aerospace technique, electronic and domestic devices. There are grounds in relation to the increase of their production on a prospect and, as a result, is growth of amount of exhaust LCE.

The electrochemical chart of SKE is attributed to the group of acid chemical sources of current and describe so [2]:

(-)
$$Cd \mid H_2SO_4 \mid PbO_2 (+)$$
.

Process which forms a current passes for reactions:

$$PbO_2 + Cd + 2H_2SO_4 = CdSO_4 + PbSO_4 + 2H_2O$$
.

The products of exhaust LCE is a plastic corps and active mass: cadmium, dioxide of lead, sulfates of cadmium and lead and sulphuric acid.

Ecological standards (after Ukrainian classification normative documents of DK 004-2003) foresee maximum the possible concentration of cadmium and lead in an environment: PDKCd and PDKPb in waters, accordingly, 0,001 mg/dm 3 and 0,010 mg/dm 3 in soil – PDK_{Cd} = 3 mg/kgand PDK_{Pb} = mg/kg[5].

For the decision of the put purpose we are offer the reagents method of processing of exhaust LCE, based on different ability of cadmium, lead and their connections to formation of complexes, attitude toward acids, meadows and solubility. Researches conducted on the laboratory setting [4].

LCE is exhaust ground down and dissociated the ground up plastic air separation from active

mass. After it mixture of cadmium, oxide of lead (IV) and sulfates of cadmium and lead was dissolved in 60 % sulphuric acid. Thus there were reactions:

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Cd + H_2SO_4 = CdSO_4 + H_2\uparrow

PbO_2 + H_2SO_4 = PbSO_4\downarrow + H_2O + 0.5O_2\uparrow
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Use of sulphuric acid with a concentration over 60 % inadvisable, as goes down solubility of sulfate of cadmium [3].

The mixed solution of sulfates of cadmium and lead and gaseous mixture of hydrogen and oxygen appears as a result of these processes; last in future it is possible to utillize for different technical aims. For the division of cadmium and lead solution of sulfates of these metals is filtered and get sediment of sulfate of lead, in solution there is a sulfate of cadmium which after stoichiometrical treatment settles solution of hydroxide of sodium as hydroxide of cadmium.

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CdSO_4 + 2NaOH = Cd(OH)_2 \downarrow + Na_2SO_4
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Sediment is filtered and gets solution of sulfate of sodium, which evaporate, crystallize and dry. Cadmium from sediment of hishydroxide is returned in the sphere of production of CSC as metallic cadmium on reactions:

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t0  Cd(OH)_2 \downarrow = CdO + H_2O \uparrow \\ CdO + H_2 = Cd + H_2O \uparrow, \\ or in the sphere of galvanic production as an electrolyte of Na2[Cd(OH)_4] \\ 2NaOH + Cd(OH)_2 \downarrow = Na_2[Cd(OH)_4] \\ surplus
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An alternative reagent for a selection a cadmium is 25 % water solution of hydroxideto the ammonium with which a cadmium forms an ammoniacal complex [Cd(NH3)₄](OH)₂, which is utillized in a galvanic production. From asediment of sulfate of lead get commodity products – lead in a free kind or oxide of lead (IV) on reactions:

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PbSO<sub>4</sub>↓ + Na2CO<sub>3</sub> →PbCO<sub>3</sub>↓ + Na<sub>2</sub>SO<sub>4</sub>
concentr. solution
PbCO<sub>3</sub> = PbO + CO<sub>2</sub>↑
PbO + H<sub>2</sub> = Pb + H<sub>2</sub>O↑
PbO + 0,5O<sub>2</sub> = PbO<sub>2</sub>.
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It follows notices, that a division of mixture of littlesoluble is in water of sulfate

and does not cause the carbonate of lead the special difficulties, as their works of solubility differentiate substantially: product solubility PbCO₃« PbSO₄.

In the process of work on every stage of researches conducted an analysis on maintenance of cadmium, lead and their derivates by physical and chemical methods [1]. Analyses testify that remaining maintenance of lead and cadmium on the indexes of safety answers the ecological standards of Ukraine and recommendations of worldwide organization of health and European

Union.

Development of technology of processing of LCE was executed on results laboratory researches of the separate stages, taking into account the features of their flowing on the basis of the conducted researches: the stages and chemical featuresof process of processing of LCE are presented in a table, flow-chart of utilization – on to Fig.

Optimum laboratory terms of processing of LCE: temperature -20-25 0 C, expense 60 %sulphuric acid -3 mols on 1 mol of component of active mass which dissolves, speed of serve of water suspensoids of active mass in sulphuric acid -2 ml/min, expense of hydroxideof sodium -2 mols on 1 mol of matter which is besieged, number of turns of mixer -350-400 min⁻¹.

Stages and chemistry of process of processing of LCE

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Stages of process	Results
There is a vitriolization of cadmium and dioxide of lead at	$Cd + H_2SO_4 = CdSO_4 + H_2 \uparrow$
sulphuric acid	$PbO_2 + H_2SO_4 = PbSO_4 + H_2O + 0.5O_2\uparrow$
Division of lead and cadmium by filtration	sediment of PbSO ₄ , solution of CdSO ₄
Receipt of carbonate of lead	$PbSO_4 \downarrow + Na_2CO_3 = PbCO_3 \downarrow + Na_2SO_4$
Filtration of solution is with sediment of carbonate of lead	sediment of PbCO ₃
	solution of Na2SO ₄
Drying and calcinacion of sediment of carbonate of lead	PbO and CO ₂
Proceeding in the oxide of lead (II) by hydrogen in free	$PbO+H_2 = Pb + H_2O$
lead	100+112 - 10+1120
Besieging of sulfate of cadmium hydroxide of sodium	sediment of Cd(OH) ₂
	solution of Na ₂ SO ₄
Filtration of solution is with sediment of hydroxide of	sediment of Cd(OH) ₂
cadmium	
Drying and calcinacionof sediment of hydroxideof	CdO and H ₂ O
cadmium	
Proceeding in the oxide of cadmium by hydrogen	Cd and H ₂ O
Evaporation, crystallization and drying of solution of	crystalline Na ₂ SO ₄ and H ₂ O
sulfate of sodium	

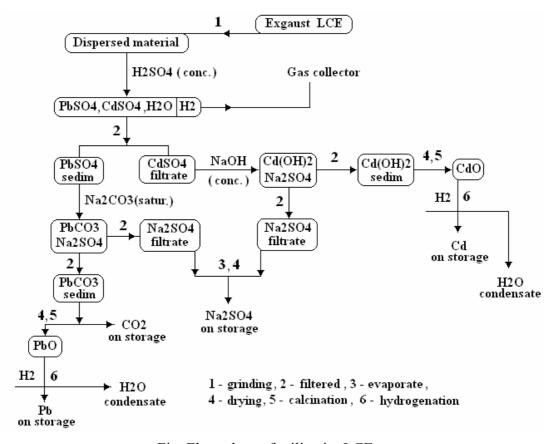


Fig. Flow-chart of utilizationLCE

Conclusion. The results of researches are resulted from the reagents processing of exhaust leaden-cadmium galvanic elements (LCE) which are the second raw material for electrical engineering industry. The method of processing is developed zero-emission, keeping energy and resources, ecologically safe; besides remaining maintenance of lead, cadmium and their connections does not exceed ecological standards. The chemical processes of utilization are analysed, flow-chartof processing of LCE is developed. Non-metal products of galvanic elements are the second raw material for processing of industry other industries.

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