

Spent electrolyte from lead-acid battery utilization

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Introduction

With increasing life standards, the amount of waste generated by households and industry and its management is growing a serious problem. Polish waste management is regulated by Waste Management Act [1]. According to this act, recycling of waste is priority in waste management, and, when impossible, disposal, with lowest possible harm to environment is recommended. When considering recycling or disposal method, Best Available Technologies (BAT) recommendations should be taken into consideration.

Currently Parliament debate on the adoption of new law, the transposition of 2008/98/WE Directive [2]. New regulation is expected to increase of the waste recovery. According to draw, certain types of wastes could lose the status of the waste when recycled and meet the following criteria:

- the substance or object is commonly used for specific purposes
- there is a market for such a substance or object
- the substance or object fulfills the technical requirements for the application of the specific purposes and meets the existing legislation and standards applicable to products
- the use of the substance or object will not lead to harm for human life, health nor for the environment.

One of the hazardous wastes are lead batteries, coded in Regulation of the Environment Minister on waste catalog [3] as I60601*. Act on battery and lead-acid battery [4], has obliged battery manufactures to provide system for collecting and recycling of spent batteries. According to the National Waste Management Plan 2014 [5], recycling rate for lead-acid batteries should achieve at least 50% and recycling yield of at least 65% by 2014.

Lead-acid batteries are the largest group of currently used batteries. Annual world production is about 360 mln batteries with total weight of over 6840 mln tones [6]. After relatively short life period (3 ÷ 5 years), they become hazardous waste due to content of sulfuric acid and toxic lead and its compounds. Electrolyte from spent batteries with concentration of sulfuric acid about 10-25% is contaminated with heavy metals, which difficult finding buyers for such product. Therefore, removing heavy metals (mostly Fe, Zn, Cd, Sb, Pb) and processing electrolyte into other product is mostly desirable.

Processing of lead-acid batteries in Poland is conducted by Orzel Bialy SA and Baterpol SA, both conduct recovery of lead. Their technologies differ in the way of preparing a batch and treating of used electrolyte [7]. In Baterpol the latter is used in desulfurization process, where lead sulfate paste is combined with a mixture of sodium carbonate and sodium hydroxide, converting the lead sulfate to lead. Sodium sulphate, crystallized from obtained in this process solution, can be used for household chemicals. In Orzel Bialy SA, solid fractions of electrolyte are separated by filter press, purified solution is either sold or neutralized with lime slurry and directed to sedimentation ponds.

Waste sulphuric acid is also generated by chemical industry and nonferrous metallurgy. Commonly used method of this hazardous waste disposal is reacting it with calcium hydroxide; obtained gypsum with heavy metals stabilized in form of hydroxide is filtered and disposed on

landfills. Difficulties in stabilizing of pollutants is related to differences in composition and properties of waste acid, depending from process of obtaining thereof. For example, in processing of benzol, waste acids are contaminated with organic compounds. Process used in Petrochemia-Blachownia SA allow to close the loop of sulfuric acid. Contaminated H_2SO_4 is thermally decomposed; as a result of the gas combustion is generated batch of raw materials containing SO_2 which is converted to SO_3 in the catalytic bed, condensed and cooled to obtain pure acid.

Alternative method for recovery of sulphuric acid may be diffusion dialysis. The driving force of this process is concentration gradient between two solution compartments containing contaminated acid and deionized water, divided by an anion exchange membrane. The SO_4^{2-} and H^+ ions are diffused across the membrane into the water whereas retentate is mostly of metal salts, blocked due to their charge and the selectivity of the membrane. The diffusion dialysis was used for sulfuric acid recovery in aluminum surface processing [9], from titanium white waste liquor [10] and rare earth sulfate solution [11].

The problems of heavy metals disposal are also found in industrial wastewater treatment processes. The choice of treatment method depends on concentration and form of metal ions, composition and variation of sewage as well as on investment and operating costs of installation.

The most common and relatively cheap method of removing large amounts of these impurities is precipitating the metal in an insoluble form as hydroxides, sulfides or rarely carbonates or phosphates. Sludge is then removed by means of sedimentation or filtration.

The stability of sludge during storage is important issue due to deposition restrictions. As a result of pH change, metal hydroxides can resolubilize; this raises the need for special preparation and monitoring of landfills. Poorly soluble sulphides are far more stable, but difficult to separate by sedimentation or filtration due to their structure. In sulphide precipitate formation, homogeneous nucleation predominant on crystal growth, leading to fine or colloidal crystal formation. Better structure of precipitate can be obtained when chelating compound of sulphur is used as precipitating agent [12, 13]. Sodium thiocarbonate have shown the high efficiency in metal ions precipitation, similar to a widely used sodium sulfide, and even higher arsenic removal efficiency [14]. Due to its price, however, it is recommended for the purification of waste water with a specific composition.

Solubility of metal hydroxides and sulfides depends strongly on pH. The composition of solution also affects the solubility: in multiple ions solutions, solubilities of individual compounds are altered. As result, the purification of such sewage may require multi-stage process. Appropriate choice of the precipitating agent, its concentration and pH of the sewage allow to fractionate heavy metals, facilitating their recycling.

Experimental

Laboratory-scale studies on heavy metal removal from spent electrolyte from lead-acid batteries were conducted.

Materials

Lead-acid battery waste with sulfuric acid concentration of 15.3% and heavy metal content as given in Table I was used in the

study. Magnesium oxide containing 96% MgO and sodium sulphide $\text{Na}_2\text{S}\cdot 9\text{H}_2\text{O}$, as 100g $\text{Na}_2\text{S}/\text{dm}^3$ solution were used as precipitating and neutralizing agents.

Table I

Metal content of the examined lead-acid battery waste

Compound	Al	As	Cd	Co	Cr	Cu	Fe	Hg	Mg	Mn	Ni	Pb	Sb	Zn
Content, ppm	170	8.4	100	5.3	8.2	59	6800	0.02	1200	160	120	5.3	72	1800

Methodology

The study has focused on purification of waste acid form lead-acid batteries by precipitation of heavy metals; obtained sludge was separated by filtration.

Three methods of acid treatment were compared:

- Hydroxide method (A): metal hydroxides were precipitated in a single step with MgO, which was both precipitating and the neutralizing agent, at pH of solution about 7
- Mixed method (B): metals were precipitated in two steps. Firstly, in acidic environment (pH about 3) with Na_2S , then in neutral pH with MgO
- Sulphide method (C): metal were precipitated in two steps with Na_2S ; firstly in acidic medium, (pH was adjusted to about 4 with addition of MgO) and the second precipitation was conducted in neutral pH.
- After sludge filtration, obtained purified solutions of magnesium sulphate were concentrated, heptahydrate was crystallized and separated from mother liquor.

The metal content in solutions and in the product (magnesium sulphate) was determined by means of ICP-OES. The magnesium content in the solutions and in the product was determined by EDTA titration with eriochrome black T as indicator.

Results

One-step method of hydroxide precipitation with MgO as precipitating agent (A) resulted in large volume of easy to filtrate sludge. However, relatively low dissolution rate of MgO in acid solution was observed. The highest degree of utilization of magnesium, introduced as MgO was shown in method B – about 76%.

The precipitation of metal sulfides with Na_2S lead to much smaller quantity of sludge, however fine form hampered its filtration. Use of an excess of precipitating agent should be avoided, due to the possibility of soluble sulfide complexes formation, remaining sulfide ions in the effluent, and releasing toxic hydrogen sulphide in an acidic environment.

In all the methods, maintaining pH was difficult, due to acidification of the solution as a result of iron oxidation, present in solution at high concentration. To eliminate this problem, pH adjustments were necessary.

Figure 1 shows a graphical comparison of obtained metals degrees of removal by three tested acid purification methods.

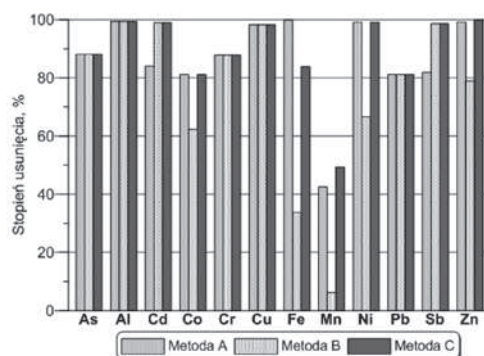


Fig 1. Comparison of metal removal from lead-acid battery waste by proposed methods

As expected, precipitation of metals as sulfides led to better removal of heavy metals (Cd, Cu, Sb, Zn) than hydroxide precipitation. However, in the latter case, higher removal of Fe and Zn, the major contaminants of the solution, was obtained.

Among methods used in the study, the best results were obtained by using:

- a two-step sulfide precipitation (Method C), and
- single-step precipitation of hydroxides (Method A).

The advantages of method C are: smaller quantities of waste sludge obtained and the smallest amount of Cd, Cu, Zn in the final product. An significant advantage of hydroxide method (A) is only single step of filtration required and high degree of main contaminants – Fe and Zn – removal. Moreover, only single precipitating agent is necessary and no toxic gas release occurs during this process. The hydroxide sludge, obtained in large quantities is more difficult to secure storage, but may be more suitable for further metal processing in recovery process.

According to obtained results, best method for purification of waste acid contaminated mainly with Fe and Zn is method A - single-step hydroxide precipitation with MgO. This is due to high degree of heavy metal removal obtained in relation to relative simple technology of process. This method allows good quality crystal magnesium sulfate, which may be a tradable product. Well developed crystal form of product was confirmed in photomicrographs (Photo 1).

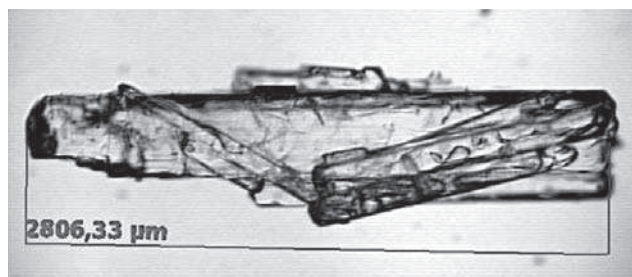


Photo. 1. Microphotography of obtained magnesium sulphate crystal

Table 2

Comparison of metals content in magnesium sulphate obtained from lead-acid battery waste by proposed precipitation methods and requirements of fertilizer regulations

	Content in magnesium sulphate												
	As	Al	Cd	Co	Cr	Cu	Fe	Mn	Ni	Pb	Sb	Zn	MgO
	ppm												%
Method used for waste acid purification:													
Method A	<1	4.4	7.5	<1	<1	2.1	23	76	<1	<1	2.3	4.6	15.95
Method B	<1	3.6	<1	4.6	<1	1.9	4600	160	98	<1	<1	210	15.70
Method C	<1	3.5	<1	<1	<1	1.9	45	170	<1	<1	<1	1.3	14.51
Regulation of Ministry of Agriculture and Rural Development on the implementation of certain provisions of the Act on fertilizers and fertilization of 18 June 2008 - maximum value of the impurities in organic fertilizers and organic-mineral and organic and organic-mineral plant conditioners, mg/kg DM of fertilizer:													
			<5		<100				<60	<140			
Regulation (EC) No 2003/2003 of the European Parliament and the Council of 13 October 2003 Minimum content of nutrients, % (m/m):													
													15.0

Table 3

Comparison of obtained crystalline magnesium sulfate and some commercial product characteristics

Content, %	Manufacturer		MgSO ₄ obtained by method A
	Zakłady Chemiczne Złotniki	Rech Chemical Co. Ltd	
MgSO ₄ ·7H ₂ O	min. 98	min. 99.5	97.6
MgO water-soluble	min. 16	min. 16	15.95
Fe	max. 0.01	max. 0.003	0.0023
Mn	max. 0.005	no data	0.0076
As	no data	max. 0.0004	<0.0001
Heavy metals as lead	max. 0.005	max. 0.001	<0.005

Content of metals in product obtained in method C is consistent with national regulations on fertilizers and mineral plant conditioners, as shown in Table 2. In crystal obtained by method A, Cd content is slightly exceeded (7.5 ppm instead of 5.0). Table 3 summarizes composition of magnesium sulphate obtained from waste acid by proposed method (A) with some commercially available products from manufacturers. Product obtained by proposed method have similar characteristic to available commercial products. It is believed that both Cd and Mn content can be lowered during a further study on optimization of this purification process.

Conclusions

The conducted preliminary study demonstrate that spent acid from lead-acid battery can be purified from heavy metals contaminants to a level allowing to receive magnesium sulfate of quality comparable to that of fertilizer products. Proposed method can be alternative to currently used acid neutralization and disposal of resulting gypsum waste. The most preferred method during laboratory trials was a one-stage hydroxide precipitation with magnesium oxide as precipitating agent, performed at pH of about 7. The degree of purification achieved is 81.0-99.7% for heavy metals except manganese which is removed with yield of 52.5%.

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Translation into English by the Author

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