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A low-temperature technique for recycling lead/acid battery scrap without wastes and with improved environmental control

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Abstract

A low-temperature technology for recycling battery scrap without producing wastes is suggested for battery plants with small production capabilities. The required reagents are available and their consumption is minimum. Simple and compact equipment is used. The generation of dust and the volume of the process gases are both minimal and are effectively removed by a filter-ventilating unit that has been developed by the ELTA company. Finally, the proposed technology does not require large investment for its realization.

Keywords: Recycling; Lead/acid battery scrap; Environment

1. Pyrometallurgical processing of lead

At present, lead is produced by the pyrometallurgical treatment of both primary and secondary materials. In the main, reduction shaft melting is employed. Coke is used as both a fuel and a reducer. About 80% of secondary lead supplies are processed in shaft furnaces, both in Russia and abroad. The proportion of secondary metal in the total production of lead is increasing steadily and now accounts for 50–60% in industrially developed countries. In addition to shaft melting, both rotary furnaces and electric furnaces are also used. A major drawback with pyrometallurgical methods of lead production from primary and secondary materials is the copious emission of both gas and dust. This is caused by high temperatures, the degree of lead dispersion, and the high volatility of lead and all of its compounds.

2. Environmental concerns

Lead is one of ten metals that pose extreme environmental hazards. The high volatility and toxicity of lead compounds result in the integration of two process chains in the pyrometallurgical process, namely lead smelting and gas cleaning. Gas cleaning requires very expensive equipment to protect the environment. For each tonne of smelted lead, it is necessary to clean 30 000–40000 m^3 of process gases and 150 000 m^3 of exhausts. For a typical lead plant, these amount to millions of cubic metres of gas per hour. The main pollutants are dust, lead and sulfur dioxide. The dust contains large quantities of lead sublimates that are composed of particles with diameters of less than 1 μm. In addition, large quantities of lead slag are generated and their recycling and utilization is a separate problem. The pyrometallurgical recycling of unbroken battery scrap is especially complicated; it gives rise to the exhaust of organic-resinous materials and sulfur compounds from the combustion of rubber cases. In a number of countries, environmental requirements have questioned the advisability of using high-temperature technologies. The general introduction of strict health regulations for the permissible level of lead in gases and other products that are emitted to the environment has forced the development of alternative methods for lead production. Thus, new techniques for recycling secondary lead without (or with minimal) wastes and with the least danger to the environment are required.

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3. The ELTA lead-recycling process

3.1. Technology of the process

Given the present economic situation in Russia, it is advisable to create small and middle-sized plants for the recycling of secondary lead, especially from battery scrap. The ELTA company has responded to the challenge by developing a recycling technique without the production of wastes and with the application of hydrometallurgical, electrochemical and low-temperature (600–700 °C) metallurgical processes (Fig. 1).

The main stages in the ELTA technology are as follows. After removal of electrolyte, battery scrap is hand-broken in order to sort separators and cases from lead–antimony grids and the oxide–sulfate paste. The positive plates are separated from the negatives, and the two plate types are recycled in two parallel streams. This is because it is necessary to produce lead that is free from antimony impurities.

The separation of the battery grid alloy and the oxide–sulfate plate material is performed in a hammer mill, where crushing of the grids and knocking out of the oxide–sulfate paste takes place. The major part of the alloy is separated on a mechanical riddle. Small, residual pieces of the lead–antimony alloy are flattened slightly and separated from the oxide–sulfate mixture on a second riddle. The lead–antimony alloy is remelted at 400 °C in a pot and is then poured out in pigs that are marketable products.

The crushed oxide–sulfate mixture is transported to a desulfurization unit. The main problem with desulfurization is the removal of sulfate ions and the conversion of all of the lead to the oxide (or hydroxide) form. It is advisable to use a hydrometallurgical process for the extraction of lead from the oxide–sulfate fraction. The application of alkaline solvents (e.g., carbonate,

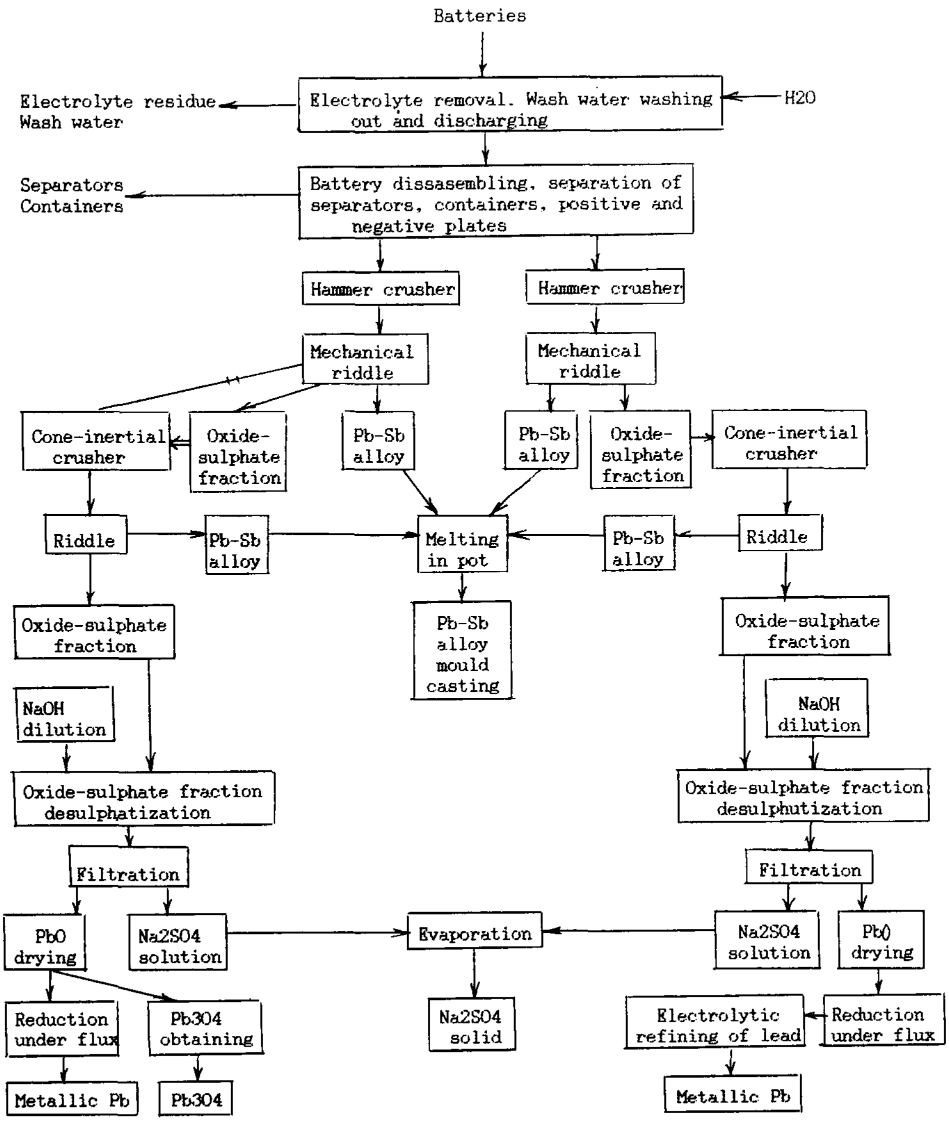

Fig. 1. Proposed technology for recycling lead battery scrap.

hydrocarbonate, hydroxide of alkaline metals) offers the best procedure. Compounds of lead dissolve sufficiently well in these solvents and standard-quality steels can be used to fabricate the equipment. The most promising approach is desulfurization with solutions of sodium hydroxide.

Desulfurization is performed in an enamel reactor. After completion of the process, pulp from the reactor is transported to a vacuum filter (either by a pump or by gravity), where the solid and the liquid phases are separated. The filtered, precipitated sludge is then washed. The solid phase (sludge) is $Pb(OH)_2$. It is removed from the filter, loaded on metal pallets, and dried in a reverberating electric furnace. This results in the formation of PbO, a material that can be used for the production of lead and anti-corrosive paint ('red lead').

The product from the desulfurization process (viz., PbO) is exposed to reduction at low-temperature (650–760 °C) melting under a layer of melted flux. The latter consists of equal amounts of potassium chloride and sodium carbonate. The process gases do not contain SO_2. The melting is performed as follows. The flux is first melted in a metal pot. Then, lead oxide and charcoal are loaded under the layer of melted flux. The consumption of flux is 1–2%. The following marketable products can be obtained from the desulfurization process: (i) crystalline sodium sulfate, which is used in the production of a number of detergents; (ii) crystalline barium sulfate, which is used in the paper and pulp industries and in the production of rubber, ceramics, mineral paints and batteries. Sodium sulfate is obtained by evaporation, while barium sulfate is precipitated by reaction with barium hydroxide–sodium sulfate solutions (Fig. 2). The resulting suspension of barium sulfate is transferred to a settling tank and mixed thoroughly. As the suspension settles, the formation of crystals of barium sulfate takes place. The residual liquid (sodium hydroxide solution) is returned to the desulfurization process. The solid barium sulfate is treated with hot water and, after mixing, the suspension is filtered on a vacuum filter and dried. The reaction between the water solutions of barium hydroxide and sodium sulfate is completed in 15 s.

In the author's opinion, the technological approach of tying up the sulfate ions as the sparingly soluble compound, barium sulfate, is a more appropriate method for removing sulfur from solution than the evaporation of sodium sulfate. This is because, first, the evaporation process involves a large consumption of electricity and, second, the barium sulfate process generates sodium hydroxide which can be used again for the desulfurization of lead sulfate.

Therefore, in the suggested technology, hydrometallurgical conversion/desulfurization of the paste from battery scrap to lead oxide is combined with low-

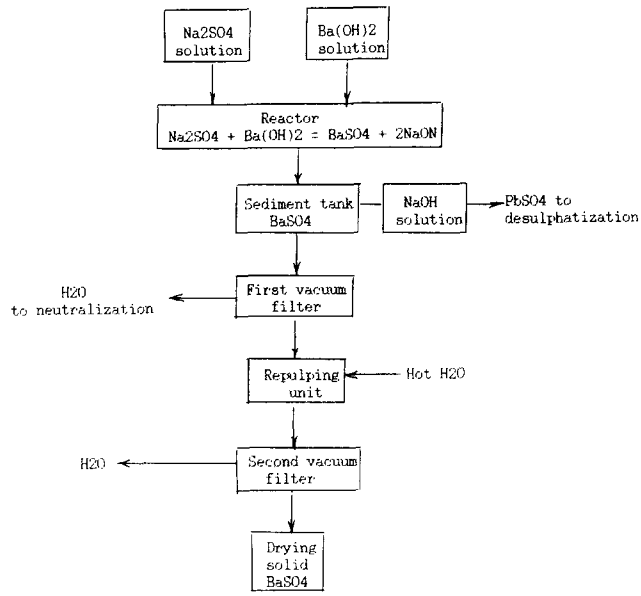

Fig. 2. Extraction of marketable products from the desulfurization process in recycling lead battery scrap.

temperature metallurgical reduction of this lead oxide to lead by carbon under a layer of melted flux. This approach provides optimum environmental conditions in both small and middle-sized plants for recycling battery scrap, and does not involve significant investment and energy consumption.

3.2. Environmental advantages

The technological circuit for shaft melting with gas cleaning is absent in the proposed ELTA scheme for recycling battery scrap. The ecological advantages of the process are as follows.

(1) The generation of dust is reduced markedly due to the application of hydrometallurgical technology for the conversion of lead sulfate to lead oxide.

(2) Smelting of lead–antimony alloy is performed at 400 °C; at this temperature, the vapour pressure of lead is negligible.

(3) Reduction of lead oxide to metallic lead proceeds under a layer of melted salt flux at a temperature not higher than 700 °C and does not release any pollutants to the atmosphere. The process gases do not contain sulfur dioxide.

(4) The marketable product of the technology is barium sulfate, which is completely precipitated from the solutions. Sodium sulfate can also be totally extracted from the solutions during evaporation.

(5) Unlike pyrometallurgical recycling of battery scrap, slags are completely absent.

At present, when prices of energy in Russia are liberated (i.e., there is no State control), comparative economical evaluation of different technologies is difficult. It should be noted, however, that the consumption of natural gas for recycling 1 tonne of secondary lead is: (i) 24–25 m^3 for shaft melting; (ii) 60 m^3 for electric melting; (iii) 12 m^3 for reduction melting under the layer of flux. These rates are related to the process of recovering metallic lead and do not consider the energy that is required for environmental protection. The consumption of energy for the cleaning of process gases and exhausts is extremely large for high-temperature technologies (i.e., shaft melting and electric melting) and cannot be compared with the energy consumption for the technology proposed here.

It should be noted that ELTA is a developer and manufacturer of a filter-ventilating unit (FVU) that is highly effective in extracting aerosols from the air in battery plants and other industrial operations. The FVU removes 99.9% of all solid particles with diameters >5 μm. The procedure involves combining a cyclone element with a filter cassette for fine and coarse filtration. The maximum productivity is 1600 m^3 per hour. The lifetime of the filter cassette is >6 months. By using a filter-cassette made from synthetic fibre materials that do not contain chlorine compounds and carcinogenic compounds, it is possible to burn the material at temperatures of 400–500 °C. This filter unit is used successfully in a number of Russian plants.