Journal of Power Sources, *31* (1990) 281 - 286

TECHNOLOGY FOR TREATING LEAD/ACID BATTERY SCRAP FOR SECONDARY USAGE

N. LYAKOV

Department of Metallurgy, Higher Institute of Chemical Technology, Sofia (Bulgaria)

Lead/acid battery scrap is valuable raw material and its quantity increases every year. It consists of three main fractions:

- metal fraction (grid, combs, pillars, etc.), comprising 30 - 35% of the total weight, with 92 - 95 wt.% lead and 4 - 7 wt.% antimony
- oxide/sulphate fraction (positive and negative paste, slime, etc.), comprising 35 - 45% of the total weight with 68 - 76 wt.% lead and 0.1 - 0.3 wt.% antimony
- organic fraction (ebonite, poly(propylene), poly(ethylene) boxes, poly(vinyl chloride) separators, etc.) comprising 15 - 30% of the total weight.

In addition to these fractions, lead/acid battery scrap also contains the remaining electrolyte, and mixtures of wood, iron, etc.

Lead/acid battery scrap has the following chemical composition: 52 - 65 wt.% lead; 1.5 - 2.5 wt.% antimony; 1.8 - 3.2 wt.% chlorine; 2.8 - 3.2 wt.% sulphur; 14 - 17 wt.% hydrocarbons. The phase composition of the oxide/sulphate fraction is: 50 - 60 wt.% lead sulphate; 20 - 25 wt.% lead dioxide; 10 - 15 wt.% lead oxide. The physical and chemical characteristics of storage battery scrap show that it represents an intricate and hard-to-treat secondary raw materal.

In practice, there are two general methods for treating the scrap:

- direct treatment, either by a pyrometallurgical (separately [1 - 3], or together with other lead-containing products [4, 5]) or by an electrochemical [6] process
- enrichment metallurgical treatment [7 - 10].

Enrichment metallurgical treatment has been applied more widely owing to its superior technical, economic, and environmental parameters. In addition, some of the organic components can be reclaimed. These two treatment methods consist, essentially, of two separate parts: (i) an enrichment process that involves the preparation of the battery scrap for treatment, by separation, of the component fractions; (ii) a metallurgical process that entails the treatment of the metal-containing fractions.

The commonly used method of treatment of lead/acid battery scrap is enrichment in heavy suspension [8 - 10] that is pre-determined by the difference in the specific gravity of the following individual fractions: metal fraction, 10.8 - 11.2 kg dm^{-3}; oxide/sulphate fraction, 7.5 - 7.8 kg dm^{-3}; organic–ebonite boxes, 1.50 - 1.65 kg dm^{-3}; poly(vinyl chloride) separators, 1.15 -

0378-7753/90/$3.50

1.25 kg dm^{-3}; poly(propylene) boxes, 0.90 - 0.93 kg dm^{-3}. The preparatory (enrichment) treatment of lead/acid battery scrap comprises two main operations: (i) crushing; (ii) separation of the crushed material. Both operations need appropriate equipment.

Following research and development work by a group of specialists, equipment has been marketed for crushing storage battery scrap [11] together with additional equipment for separating the crushed scrap. The latter operates under conditions of heavy suspension in water and the oxide/sulphate fraction forms the crushed scrap. These devices are in operation in MP 'G. Dimitrov' in the town of Kardzhaly, Bulgaria.

The equipment for crushing battery scrap has a capacity of 30 tons h^{-1} and guarantees to cope with batteries of various dimensions (up to 500 × 300 × 200 mm) and container materials (ebonite, poly(propylene), poly(ethylene)). The crushed material is granular and is suitable for separation; it is not overcrushed, especially with regard to the poly(vinyl chloride) separators.

The separation device has a drum-type design of special construction to ensure that the formation of a heavy suspension, with a constant and specified specific gravity, is maintained continuously. Control of the specific gravity of the suspension is achieved by supplying water at a given flow rate, together with the crushed battery scrap, and at a set rotation speed of the drum. As a result, there is no need for regeneration and re-circulation of the suspension [8, 9], and the chlorine content of the oxide/sulphate fraction is below 0.4%. The separation device can be used both for separation of the main fractions from the battery scrap (metal, oxide/sulphate, organic) and for separation of the organic fraction into its component sub-fractions: ebonite, poly(vinyl chloride), poly(propylene). The results are shown in Table 1. The separate organic sub-fractions can be re-used in practice. If the battery scrap contains poly(ethylene) boxes, the poly(propylene) sub-fraction also contains poly(ethylene). Granular and secondary poly(propylene) products have been obtained experimentally.

Figure 1 represents, schematically, a technological process line for complete separation of battery scraps. The line gives five enriched fractions,

TABLE 1

Separation of organic fraction of battery scrap

Organic subfraction (%)	Suspension specific gravity (kg dm^{-3})			
	1.0 - 1.1		1.35 - 1.45	
	Light part	Heavy part	Light part	Heavy part
Poly(propylene)	97.85 - 98.90	0.10 - 0.20	0.90 - 1.10	–
Poly(vinyl chloride)	1.10 - 2.10	11.00 - 17.40	98.30 - 98.80	1.90 - 2.20
Ebonite	–	82.30 - 88.90	0.10 - 0.30	97.70 - 98.00

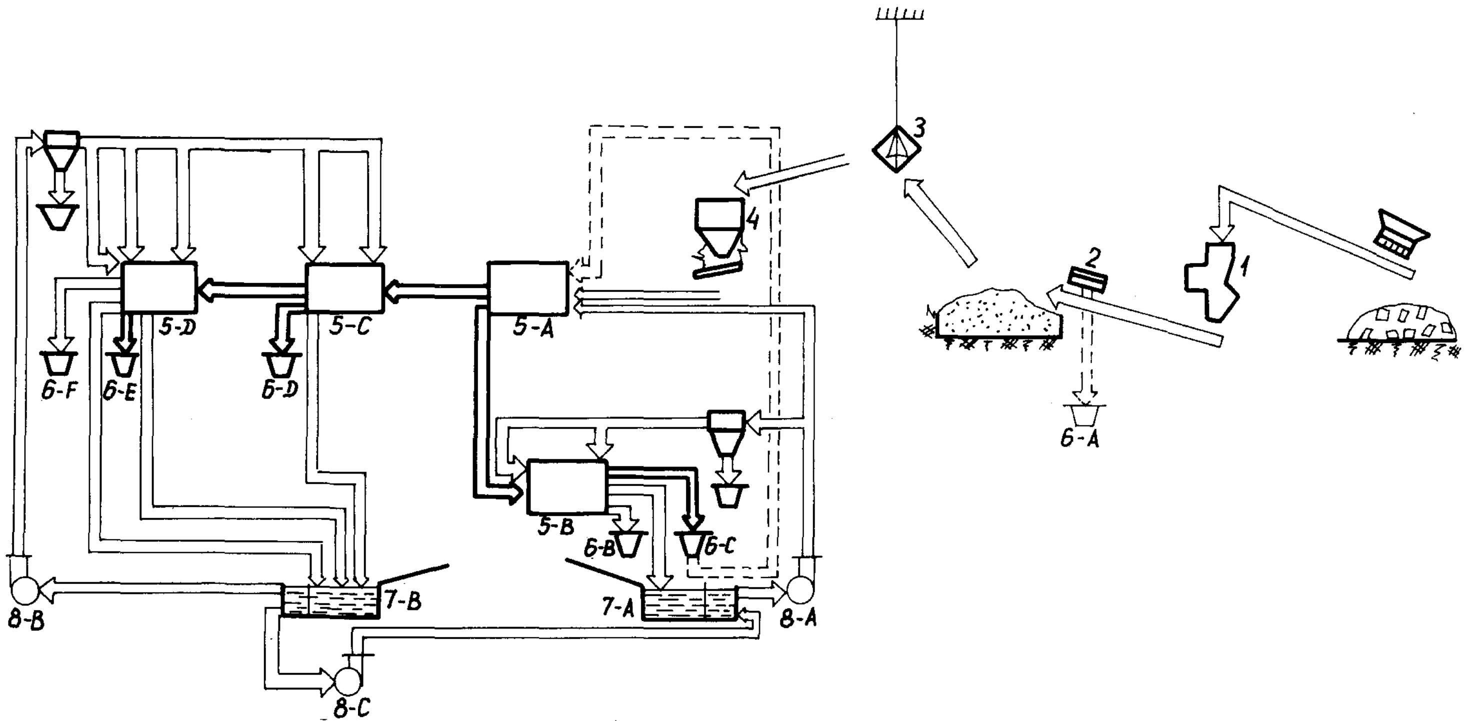

Fig. 1. Schematic of process for treatment of battery scrap.

namely: metal, oxide/sulphate, ebonite, poly(vinyl chloride) and poly(propylene). In the 5-A and 5-B separators a specific gravity of 1.80 - 1.90 kg dm^{-3} is maintained, while in separators 5-C and 5-D specific gravities of 1.35 - 1.45 kg dm^{-3} and 1.00 - 1.10 kg dm^{-3}, respectively, are maintained. Separator 5-B is the control separator which carries out the final purification of the metal and oxide/sulphate fractions from the organic fraction. All separators in this scheme are of the same type. If there is not a need to treat ebonite scrap (since the tendency in world battery production is away from the use of this container material), separator 5-C is not included.

Electrolyte-free battery scraps are taken to a storehouse and, after separation of the iron and wooden boxes and inert material impurities, the scraps are separated by means of a platform. The materials are transported to the crushing device (item 1, Fig. 1) using a plate feeder and a conveyor belt. It should be noted that the practice in Bulgaria is to separate the electrolyte from the battery scrap in advance so that the latter is delivered for treatment in a dry state.

The crushed battery scrap of up to 300 mm dimension is processed in an iron-recovering device (item 2, Fig. 1) and then taken to a receiving hopper. The iron scrap is collected in a container (Fig. 1, 6-A). From the receiving hopper, the crushed batteries are fed (with the help of a crane, item 4, Fig. 1) to a hopper with a vibrating feeder (item 4, Fig. 1). The scrap is then taken to a separator (5-A, Fig. 1) where the following two products are obtained:

- light portion, comprising the majority of the organic fraction (*i.e.*, scrap from ebonite boxes, poly(propylene) boxes, poly(vinyl chloride) separators) and a small quantity of the oxide/sulphate fraction.
- heavy portion, consisting of the majority of the metal and oxide/sulphate fractions and a small quantity of the organic fraction.

The heavy fraction is fed to the separator 5-B (Fig. 1) for controlled separation, whereby the content of the organic fraction in the metal and oxide/sulphate fraction is reduced from 5 - 6 to 2.2 wt.%, inclusive of chlorine in the oxide/sulphate fraction up to 0.4 wt.%. Two products are obtained:

- light portion, representing the remaining, insignificant quantities of the organic fraction
- heavy portion, representing a washed-out metal fraction.

The washed-out metal fraction is conveyed to container 6-B and is transported for treatment. The washing water, which contains the major amount of the oxide/sulphate fraction is taken to the precipitating tank, 7-A. The oxide/sulphate fraction is drained at intervals to moisture contents of 15 - 20 wt.%, after which it is transported for treatment. The remaining, insignificant quantity of the organic fraction is fed to container 6-C and is then returned to separator 5-A. The water is involved in a closed circulation cycle using pump 8-A, and it is cleared by a conical precipitator, from which the hard phase is taken, at intervals, to the precipitation vat 7-A.

The organic fraction from separator 5-A is fed to separator 5-C where two products are obtained:

● light portion, comprising the poly(vinyl chloride) separators and parts of poly(propylene)/poly(ethylene) boxes and an insignificant amount of the oxide/sulphate fraction

● heavy portion, representing a washed-out ebonite fraction.

The washed-out ebonite subfraction is taken to container 6-D and the washing waters, carrying the oxide/sulphate fraction, are conveyed to precipitating tank 7-B.

The light portion from separator 5-C is conveyed to separator 5-D, whereby two products are obtained:

● heavy portion, representing the washed-out poly(vinyl chloride) subfraction

● light portion, representing the washed-out poly(propylene) subfraction.

The washed-out poly(vinyl chloride) subfraction is fed to container 6-E, while the washed-out poly(propylene) subfraction is taken to container 6-F. The washing water enters the precipitation vat 7-B. With the aid of pump 8-B, the water makes a closed circulation cycle and is cleared by a conical precipitator, from which the hard phase is taken at intervals to precipitation vat 7-B. The oxide/sulphate fraction is in a considerably smaller amount in vat 7-B compared with that in precipitating tank 7-A. The two precipitation vats are connected by pump 8-C.

The main parameters of the existing and operating installation in Bulgaria are as follows:

● crushing capacity: 216 000 tons annually

● one module separation capacity: 25 000 tons annually; number of modules: 2

● working hours: for the crushing section, one shift in 24 h; for the separation section, continuous production

● servicing personnel: 4 persons per shift

● metal content of the organic fraction: up to 0.7 wt.%

● organic content of the metal fraction: up to 2.2 wt.%

● chlorine content of the oxide/sulphate fraction: up to 0.4 wt.%

● lead and antimony recovery: over 99%

● utilities per ton of battery scrap: electricity, 46 kW h; water up to 0.5 m^3; no fuel oil, steam, or compressed air usage

● effluent waters: none

● working station lead concentration: up to 0.05 mg m^{-3}.

Compared with traditional methods for processing lead/acid battery scrap, the facility in MP 'G. Dimitriov' in Kardzhaly has the following advantages:

● simplified and compact equipment at low cost

● there is no circulation fraction involved in crushing since the required dimensions of the material are not critical

● no requirement to dry the crushed material and no need to sift the oxide/sulphate fraction (the paste) from the former; this saves the utility resources and equipment required for these purposes

● the oxide/sulphate fraction has a low chlorine content because the entire quantity of crushed material passes through the separation equipment and the poly(vinyl chloride) fraction, containing 54 - 56 wt.% chlorine [13], is separated to the maximum extent.

● there is no preparation, regeneration, and circulation of the suspension. This removes the need for further equipment and avoids the unpleasant transportation of the heavy suspension; the latter is often accompanied by precipitation from the suspension and blocking of the equipment and the communication channels

● no requirement for washing devices because the washing of the fraction is carried out in the separation device itself

● no need for steam, fuel oil, compressed air

● the water is in a complete recirculation cycle and only small amounts of water are used to compensate the humidity of the enriched fractions leaving the facility

● the facility is serviced very easily and involves a high degree of mechanization and automation.

References

1 H. Niclas, *Metall (Berlin), 9* (1978).
2 R. Fugli, *Bull. SEV/VSE, 76* (1985) 16.
3 V. Mastov *et al., Tsvetn. Metal, 6* (1982).
4 M. Tarasenko *et al., Tsvetn. Metal, 5* (1980).
5 K. Vurm, *CMEA Bull., 14* (1981).
6 *Introduction to Metallurgical Engineering Activity*, Snamprogetti S.p.A., Milan, Italy.
7 G. Fuchs, *Erzmetall., 11* (1971).
8 E. Del Sorbo, *BCJ Convention, London, 1974.*
9 A. Melin, *Vortrage anlasslich de International Recycling Symposiums, 11/12 Nov., 1986, Budapest.*
10 H. Dlaska, *Erzmetal, 33* (7/8) (1980).
11 N. Lyakov *et al., Bulgarian Pat. No. 68,334.*
12 N. Lyakov *et al., Bulgarian Pat. No. 79,749.*
13 V. V. Korshak, *Plastic Mass Technology*, Khimiya Publ. House, Moscow, 1988, p. 105.