

RECYCLING OF LEAD/ACID BATTERIES: THE GINATTA PROCESS

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Introduction

The Ginatta process for the electrochemical recovery of lead from used lead/acid batteries has been described previously [1 - 3], and starting from detailed energy and mass balances involving three years of plant operation, the economic aspect of the process has been deduced. In the most recent work [3] a report was given of tests that defined the operational parameters of the plant. This paper presents new data collected during the past four years together with some new electrochemical aspects and applications of the process.

Characteristics of the Ginatta process

Table 1 provides the technical characteristics of the Ginatta plant in Santena (Italy). In this study, a method of increasing the antimony content of the slimes was considered, and the effects of organic compounds added to the electrolyte to improve lead electrodeposition were studied. In addition, particular attention was directed towards lead recovery from wastes arising from the battery manufacturing plant, with the aim of eliminating all pyrometallurgical lead recovery processes from the fields of battery manufacturing and application.

The process flow-chart is given in Fig. 1. The process is divided into four stages. In the first stage, the spent batteries are prepared and bottom cutting and mounting on anodic plastic frames are undertaken. In the second stage, the batteries are subjected to activation that converts the lead sulphate to lead and lead dioxide. Battery dissolution and lead recovery occur in the third stage. Finally, the electrolyte composition is restored in the fourth stage by using an electrowinning cell with graphite anodes.

The average composition of the spent batteries processed during the past four years is shown in Table 2. At present, almost all of the automotive

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TABLE 1

Technical characteristics of Ginatta process, Santena, Italy

| | |
|-----------------------------------------------|---------------------------|
| Production (t/year) | 4.500 |
| Batteries recycled (kg h^{-1}) | 1.175 |
| Activation tanks | 2 |
| Dissolution tanks | 4 |
| Electrowinning tanks | 2 |
| Number of cathodes per tank | 18 |
| Number of anodes | 19 |
| Frames per tank | 12 |
| Batteries per frame | 40 |
| Electrolyte volume (m^3) | 140 |
| Cathode dimension (m) | 8 strips 0.2×1.8 |
| Anode dimension (dia.) | 0.04 |
| Cathode current density (A m^{-2}) | 400 |
| Cathode efficiency | 0.99 |
| Activation tank voltage (V) | 14.5 |
| Dissolution tank voltage (V) | 3.2 |
| Electrowinning tank voltage (V) | 3.5 |
| Working temperature ($^{\circ}\text{C}$) | 35 - 45 |
| Graphite anode consumption (year) | 2 - 3 |
| Electrolyte composition (g l^{-1}) | |
| Pb | 35 |
| HBF_4 | 180 |

TABLE 2

Average composition (wt.%) of spent batteries

| | |
|----------------------------|-------|
| Sulphuric acid (conc. 22%) | 17.40 |
| Lead grids | 27.31 |
| Pastes | 40.20 |
| Lead connections | 4.90 |
| Antimony | 0.25 |
| Tin, arsenic | 0.09 |
| Poly(propylene) | 6.70 |
| Separators | 2.60 |

TABLE 3

Energy balance (kW h) of Ginatta process

| | |
|-------------------------|-----|
| Activation process | 124 |
| Dissolution process | 370 |
| Reacidification process | 400 |
| Bottom-cutting machine | 12 |
| Water treatment | 1 |
| Fragmentation machine | 5 |
| Auxiliary service | 1 |

SPENT STORAGE BATTERIES

1.000 (609)

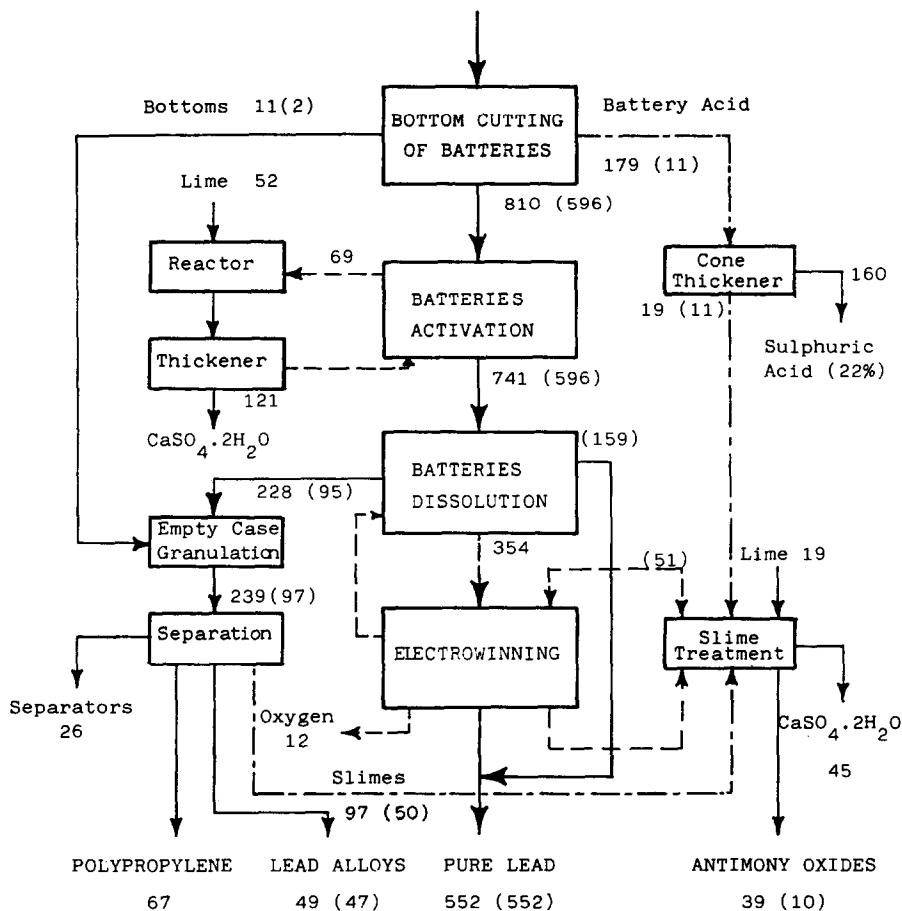


Fig. 1. Process flow-chart. Data in kg h^{-1} for poly(propylene) batteries (lead content in parentheses).

batteries are manufactured using a poly(propylene) case. The average weight per battery of those processed was approximately 12 kg. For a tonne of these batteries, the material balance data reported in Fig. 1 were obtained. The energy balance of the process is reported in Table 3.

It has been verified [3] that battery dissolution in fluoroboric acid (HBF_4) is due to the external current flowing through the electrolytic tanks, and to the short circuits established between the cells of the batteries and

between the positive active material and the grids. The change in electrolyte concentration affects both the electrolyte resistivity and the reaction overvoltage, so that dissolution occurs homogeneously and the process is self-regulating.

It has also been shown [3] that some impurities accumulating in the electrolytic bath inhibit the formation of lead dioxide on the graphite anode by decreasing the oxygen overvoltage. As a consequence, the weights of the anodes used in the electrowinning tanks do not increase with time; antimony exerts this effect to the maximum extent.

The electrochemical behaviour of the impurities obviously affects the lead cathode purity; each metal ion must be studied separately and a determination made of its distribution in both the slimes and the electrolyte. Antimony, which at present is the most important impurity, is present in the electrolyte as a trivalent ion; it becomes pentavalent during the process owing to the high positive potential of the positive plates and the graphite anodes. Thus, antimony is present in the electrolyte as Sb^{5+} , and in the muds as Sb_2O_5 . The latter is formed by hydrolysis or is already present in the positive active material of the batteries.

Treatment of slimes

There is a section in the plant where the slimes resulting from the bottom cutting of the batteries and from the electrolytic cells are treated to increase the antimony concentration. During this treatment, lead sulphate is converted to lead carbonate. For this purpose, the slimes, ammonium carbonate, and water (in a weight ratio 100:25:650) are mixed in a vigorously stirred mixer at a temperature of 60 °C. After conversion, the slimes are leached with the acid electrolyte from the electrowinning cells. An electrolyte enriched in lead ions and a slime enriched in antimony are obtained.

The lead dioxide and the metallic lead react during the leaching of the slimes because of the formation of local electrochemical couples. The dissolution of lead dioxide is favoured by H_2O_2 addition. The electrolyte is passed to the electrowinning cells. After filtration, the slimes have the mean composition reported in Table 4. Figure 2 gives the flow-chart for the treatment of slimes.

TABLE 4

Average composition (wt.%) of slimes

| | |
|-------------------------------|---------|
| Lead | 13 |
| Antimony | 13 - 25 |
| Tin, arsenic and other metals | < 2 |
| H_2O | 13 - 17 |
| Other non-metals | 46 - 58 |

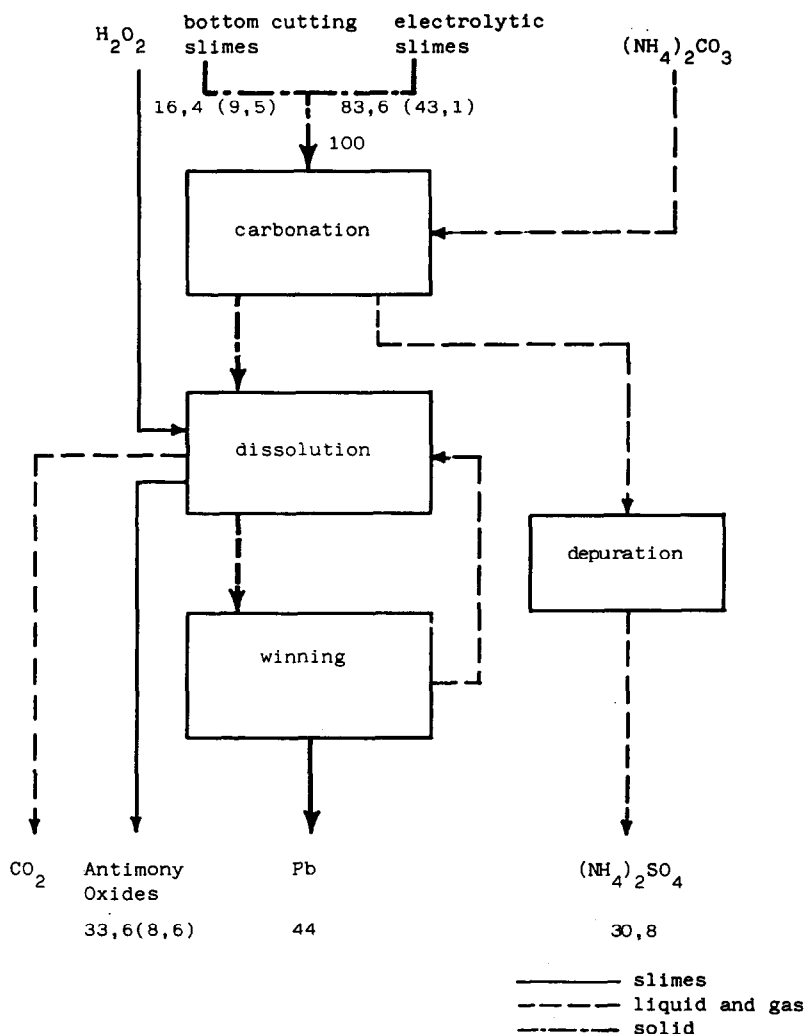


Fig. 2. Flow-chart for treatment of slimes. Data in $kg\ h^{-1}$ (lead content in parentheses).

Processing of inert plates

The fluoroboric electrolyte used in the plant easily dissolves both the inert plates and the lead oxide pastes arising from the battery manufacturing plant. The paste detaches easily from the grids which undergo slight corrosion (2.6% by weight).

The fine metallic lead and the sulphates remain undissolved and constitute, with the inert substances, the slimes that are treated as described previously. Again, the electrolyte comes from the electrowinning cells where

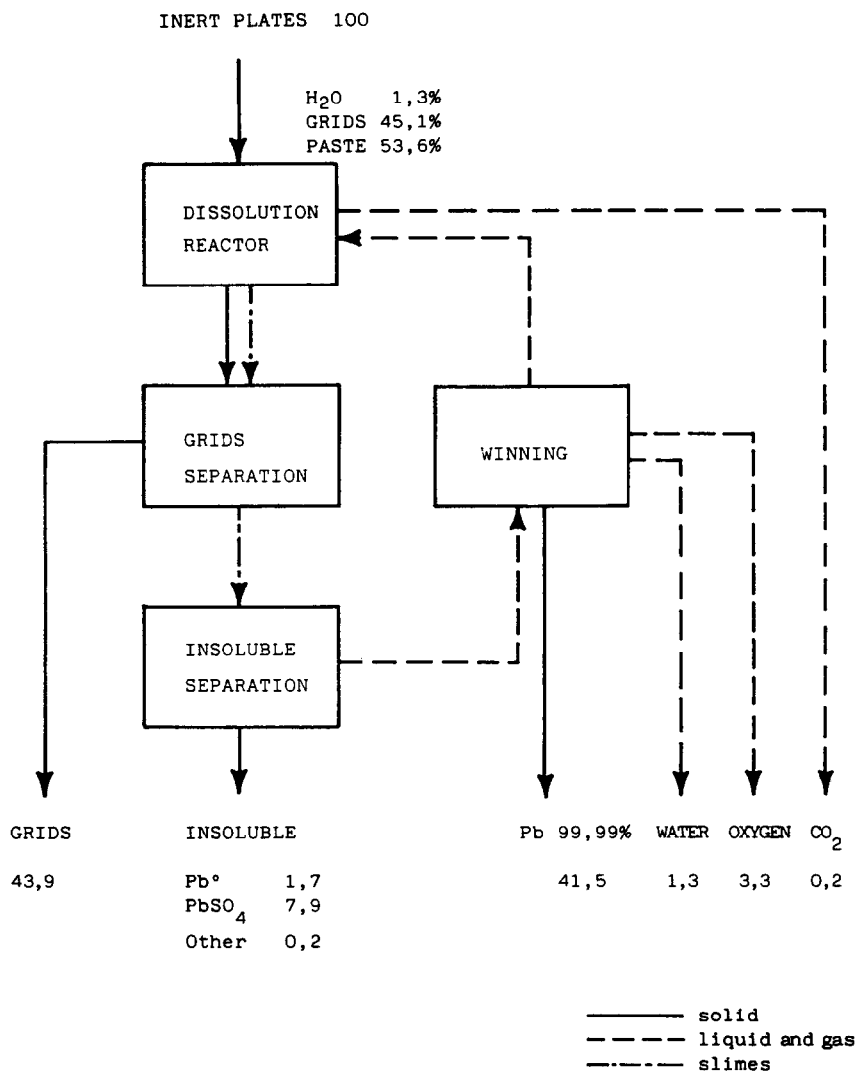


Fig. 3. Flow-chart for treatment of inert plates. Data in kg h⁻¹.

the free acid is more concentrated (Fig. 3). Data for the material balance are also reported in Fig. 3.

Experimental

The principal problems to be solved in the electrolysis concern the behaviour of impurities, the effect of organic substances added to the electrolyte, and the anomalous growth of lead dioxide anodes. Some laboratory

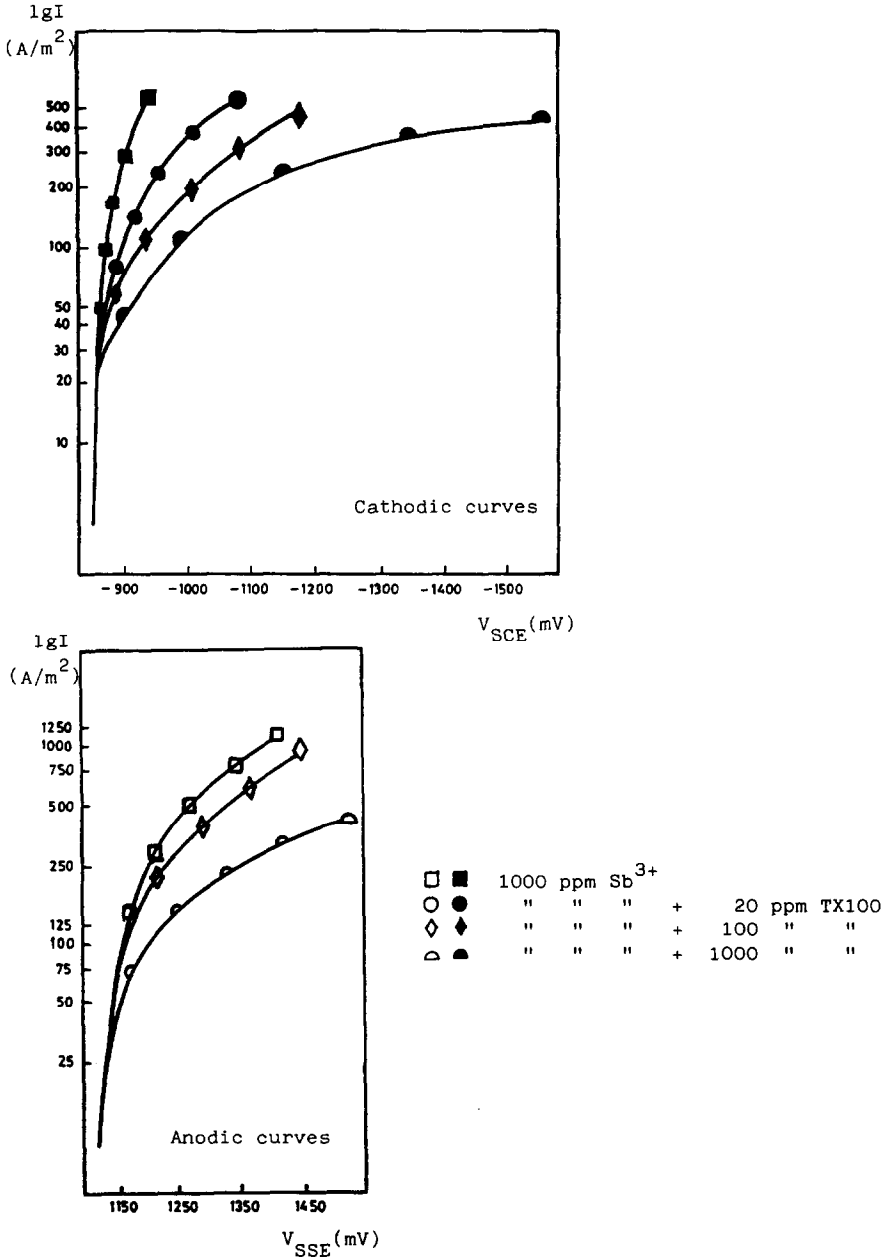


Fig. 4. Cathodic and anodic polarization curves. $T = 32^\circ\text{C}$, HBF_4 20%, $\text{Pb } 30 \text{ g l}^{-1}$.

and industrial tests have been carried out to clarify these aspects. In particular, the behaviour of antimony, the effect of Triton X100, and the repartition of arsenic, bismuth, tellurium and tin between the cathodes and the slimes have been studied.

TABLE 5

Impurities in lead cathodes (ppm)

| | |
|----------|----|
| Antimony | 25 |
| Tin | <5 |
| Arsenic | <3 |
| Copper | 11 |
| Bismuth | 15 |

It is well known that Sb^{3+} ions only can be reduced at the cathode; antimony remains as pentavalent ions in the solution up to a concentration of about 12 g l^{-1} . Chemical analysis of specimens taken from various points of the plant show that a major part of the antimony remains in the anodic slimes within the battery containers at the end of the dissolution. A minor part dissolves as trivalent ions in the electrolyte.

Antimony present in the bath is oxidized at the lead dioxide anodes and exerts a beneficial influence via inhibition of the oxidation of lead ions. The anodes are thus dimensionally stable and the thickness of the dioxide deposited on the graphite electrodes is never greater than 5-6 mm. The pentavalent antimony ions slowly form oxides that precipitate in the anodic slimes of the cells. At the cathodic lead, the amount of the antimony is never greater than 30 ppm; the concentration in the solution during five years of plant operation has been lower than 2 g l^{-1} .

Some organic substances must be used to favour a regular lead electrodeposition; of the various compounds tested Triton X100 appears to have the greatest beneficial levelling action. This compound affects both the cathodic and the anodic process, probably as a consequence of a chemical adsorption on the surface of the electrodes (Fig. 4).

Various tests show that the increase in the anodic potential favours antimony oxidation to pentavalent ions without increasing the dioxide deposition rate. With regard to the cathodic process, Triton X100 favours the growth of very fine-grain deposits. Naturally, this organic substance degrades with time and must always be added to the electrolyte.

In the case of other impurities, only tellurium cannot be eliminated: it discharges with lead in the limiting-current condition. Arsenic, bismuth and tin are present as oxides in the anodic slimes. The purity grade of the cathode is given in Table 5.

References

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- 4 M. Maja, F. Mercandetti, N. Penazzi, P. Spinelli and M. V. Ginatta, *Journées D'Electrochimie '85, Firenze, May 28 - 31*, Abstr. no. 6, p. 40.