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Development and use of a new system for environmentally clean recycling of lead battery scrap

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Abstract

A process for recycling the scrap that arises during battery manufacture is described. The reclaimed lead compounds are used to produce new lead batteries with improved physical and electrochemical parameters. The principle of the method is based on a thermochemical reaction in which the tribasic lead sulfate content of the scrap is converted into tetrabasic lead sulfate at temperatures higher than 400 °C. The thermochemical reactivation and the addition of given amounts of tetrabasic lead sulfate improve not only the cycle life but also the cold-cranking performance and gram/Ampere hour value of the batteries.

Keywords: Recycling; Lead battery scrap

1. Introduction

The world, as a consequence of increased ecological consciousness, has declared war on products that cause, either during use or after wearing out, irreversible environmental and health damage. Unfortunately, electrochemical power sources are high on the list of environmentally polluting chemicals. Therefore, the organizations fighting for a cleaner environment pay special interest to the manufacture and use of these power sources. In highly developed countries, severe regulations are bringing the production, utilization, collection and recycling of most of the chemical power sources under control.

The most widespread electrochemical power source is the lead/acid battery; it represents 65% of all used primary and secondary cells. Nevertheless, this does not cause too much of a problem from the point of view of environmental protection. The reclaim of lead/acid batteries is well established; 100% of junk batteries can be collected and recycled. Indeed, many European countries have introduced this practice already.

A significant part (~10%) of the 2–2.5 million tonnes of secondary lead is obtained from the recycling of lead/acid battery production scrap. The market trends in Europe and all over the world indicate that only those battery companies who run their production without unnecessary expense will survive. Rational operation

includes: maximum active-material utilization and reduction of in-house scrap rates or recycling of them via the normal production flow in an economical way.

2. Precedents leading to Perion-MRH I processes

The development of the so-called MRH production scrap-recycling process began at Perion Battery Factory Co. Ltd. in 1989. Besides the expected benefits of environmental protection, the experiments were initiated by the fact that Perion could save the expenses that were incurred if the factory allowed its production scrap to be recycled by another company.

Since Hungary does not have any junk battery recycling smelter, the authors' company had to export all its lead scrap abroad. This involved significant transport costs accompanied by a complicated licensing procedure. Previously, Perion had recycled a part of its in-house scrap, but this was limited to pasting sludge and lead-alloy scrap. Complete recovery is difficult because the scrap is quite heterogeneous (both in consistency and in phase chemistry) with many different wastes, e.g., leady oxide, soft lead dross, wet paste, and cured-formed positive and negative active material. Nevertheless, as a result of research and development work over many years, a process has been developed

that can solve all these problems. This is known as the MRH I process and is shown schematically in Fig. 1.

3. Perion MRH I process

3.1. Material collecting

Careful collecting, storing and handling are important parts of the process. The materials are of high value, therefore their treatment must be performed as attentively as those of primary materials.

The sludge of the pasters must be collected in a well maintained waste-water system in order to avoid oil or detergent contamination. Scrap plates of pasting, curing, assembly and formation operations are piled on pallets. It is important to keep the positive and the negative scraps separate from each other (red pallets are used for positive plate scraps, blue for negatives).

3.2. Drying

After collecting the sludge of the pasting department and dewatering it with a filter press, it is dried in a

continuous operating oven developed by Perion. The slurry loses ~15% of its moisture. The outgoing powder has only ~0.1 wt.% water. Scrap consisting of wet, cured and formed plates is pre-dried in a standard drying chamber.

3.3. Grid/active-material separation

The separating equipment parts the positive and negative plates into grids and active materials. Conveyors discharge the positive and negative active materials into separate storage systems. If identical lead alloy was used for both plate polarities, then the active material falls into one pot, but into two pots if different alloys were used. Lead pumps deliver the molten lead into casting dies.

During development of the MRH I process, special attention was paid to achieving complete grid and active-material separation. This is because the hard lead remainders would spoil the water consumption and self-discharge of new batteries. Moreover, if active materials remain on the grids they will form a dross that cannot be recycled with this process.

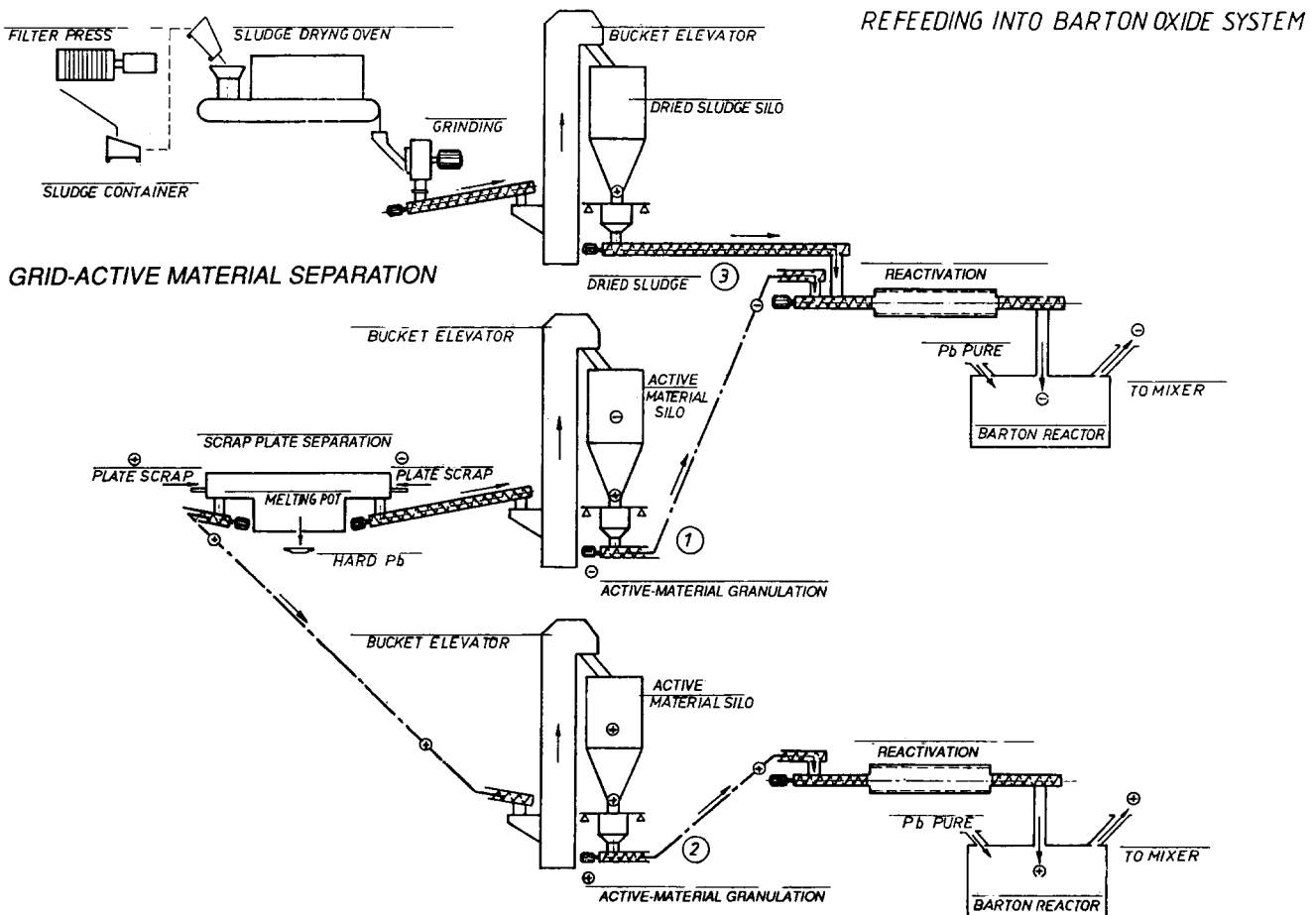


Fig. 1. Operation of Perion MRH I battery-recycling process.

The separated negative active-material scrap is passed with the dried sludge through the pretreating unit into the reactor of the negative oxide system. The pretreated positive scrap passes through its own system.

3.4. Reactivation

The key operation of the MRH I method is the reactivation. The physical and chemical conversions take place both in the pretreating reactor and in the Barton-pot oxide system. These reactions have positive effects on both the active-material parameters and the operation of the oxide system.

4. Results gained with Perion MRH I process

4.1. Quality improvement of leady oxide

The most remarkable result achieved with the process was an increased reactivity of the leady oxide (i.e., better water and acid absorption). An examination of the effect revealed that the pretreated scrap material (termed 'MRH additive') interacts with the lead oxide particles mechanically. This causes a decrease in the average particle size; no large agglomerates are formed and, in addition to the regular, spherical particles, split particles with larger specific surfaces are also produced. The latter clearly account for the enhanced specific surface area and the increase reactivity of the leady oxide.

4.2. Positive effects on oxide system operation

Continuous feeding of MRH I additive necessitated only minor changes in the operating parameters of the oxide system. After reaching thermal equilibrium, significantly less particles stick to the walls or to the cover of the reactor. This results in shorter downtimes, less cleaning, and greater operational safety. Instead of the weekly cleaning conducted previously, only one cleaning per month is now necessary. As a consequence, the output is increased, lead emissions are smaller, and labour costs are lowered.

Typical effects of the quality improvement in leady oxide and the better operating conditions are shown in Fig. 2. It can be seen that not only does the acid absorption increase but also deviations from the average value are smaller, i.e., the oxide is more uniform.

4.3. Better active-material parameters

The more reactive leady oxide has given rise to further benefits. These include: lower paste densities, higher cranking performance and better capacity values. Normally, improvement of the last two parameters would

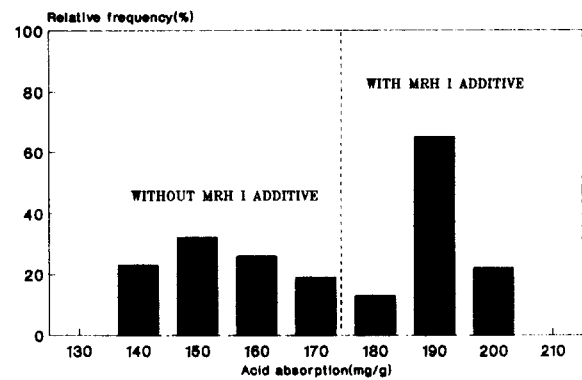


Fig. 2. Frequency distribution of the acid absorption of leady oxide with and without MRH I additives.

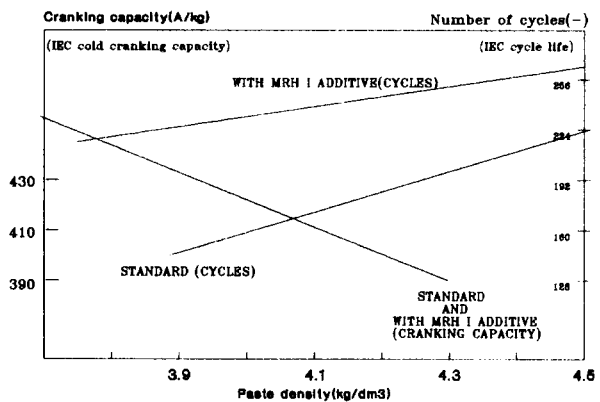


Fig. 3. Effect of paste density on cold-cranking performance and cycle life.

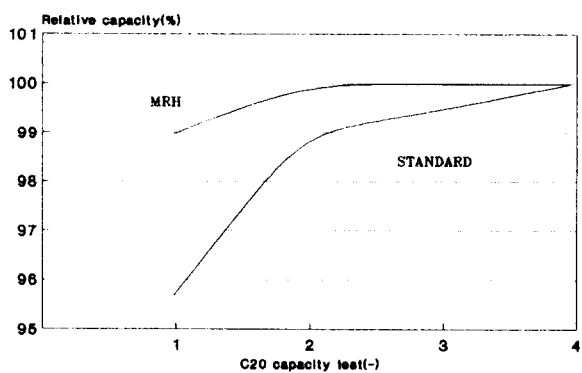


Fig. 4. Formation efficiency for standard batteries and batteries with MRH I additive (first discharges).

cause degradation of cycle life, but with MRH I additive the reverse is in fact observed. For example, addition of MRH I additive to the oxide gives a marked improvement in the cranking-performance/cycle-life relationship (Fig. 3).

The high oxide reactivity and the low paste-density effect also raises the efficiency of plate formation. Fig. 4 shows the results for the first four C/20 capacity tests for active materials either with or without MRH I additive.

5. Application limits for MRH I

5.1. Method cannot be used with ball mills

Experiments have shown that a ball mill and the MRH I pretreating reactor cannot be used together to perform a reactivation that will give a grade of leady oxide that has the benefits discussed above.

5.2. Separate positive and negative oxide systems are needed

If the factory does not have separate oxide systems for both plate polarities, then only the positive MRH I additive can be recycled.

5.3. Limited feeding rates into Barton-pot oxide systems

Tests have been conducted on the thermoequilibrium of the oxide process to determine the optimum ratio between MRH I additive and lead oxide. If the feeding is even, then no problems are experienced up to 25 wt.% of additive. Some manufacturers may have the wish to use MRH I additive for only certain types of battery (e.g., automotive and traction batteries, OE

types, etc.). In these cases, the upper limit of 25 wt.% puts a restraint on the application.

6. MRH II process

This technology has been developed to eliminate the restrictions found with the above MRH I process. A comparison of Figs. 1 and 5 shows that, in the MRH I process, the reactivation of the lead compounds is performed in separate equipment. Also, refeeding into the normal production flow is joined not to the oxide system but to the paste mixer. With this method, there is no need to separate the positive and negative oxide production. Moreover, it no longer matters whether the oxide is produced in a Barton-pot system or in a ball mill, and the thermal equilibrium of the Barton-pot system does not limit the feeding rates of the MRH additive. In flat-plate production, it is possible to achieve a maximum ratio of 75 wt.% MRH II additive and 25 wt.% standard lead oxide ratio without impairing battery performance.

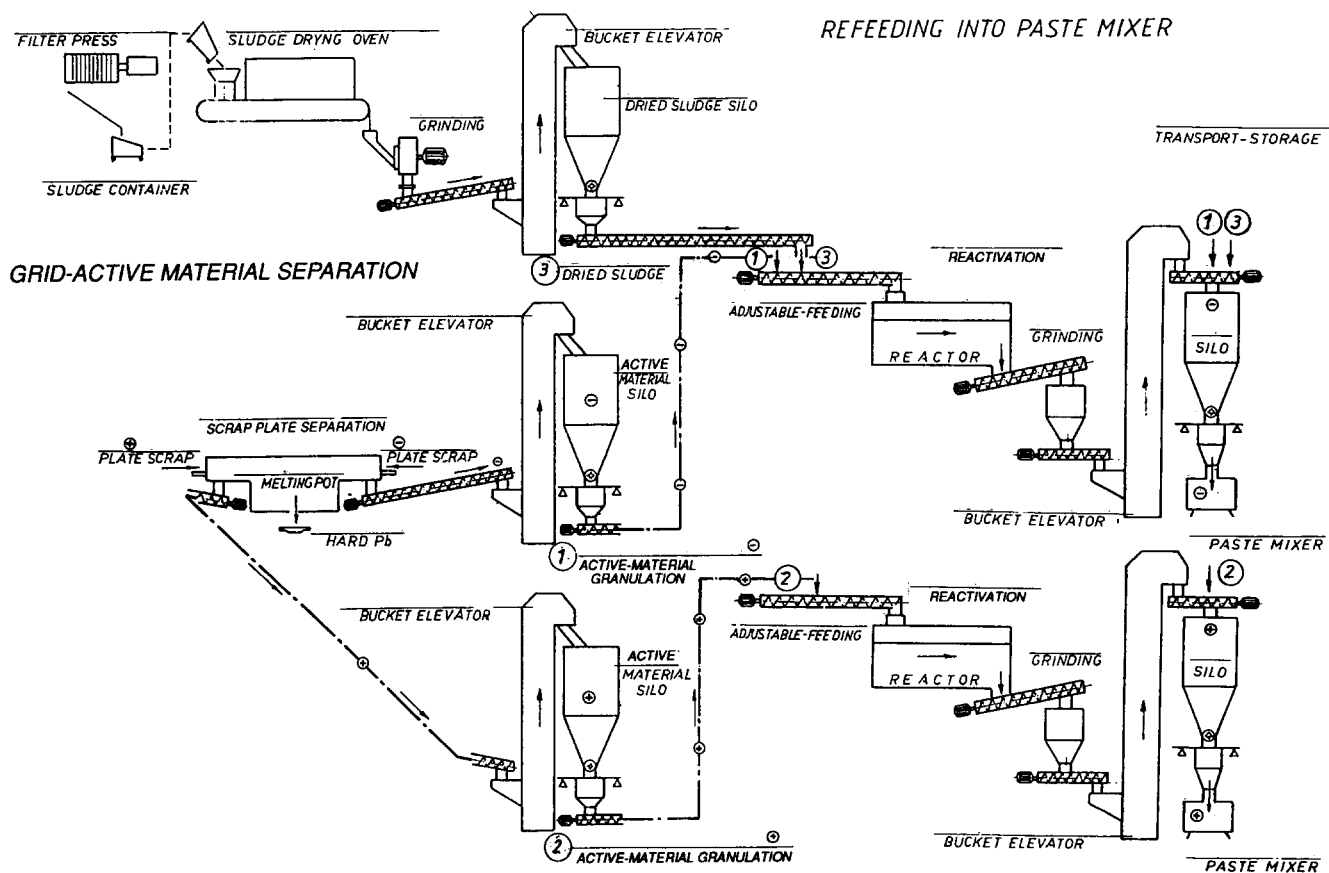


Fig. 5. Operation of the Perion MRH II battery-recycling process.

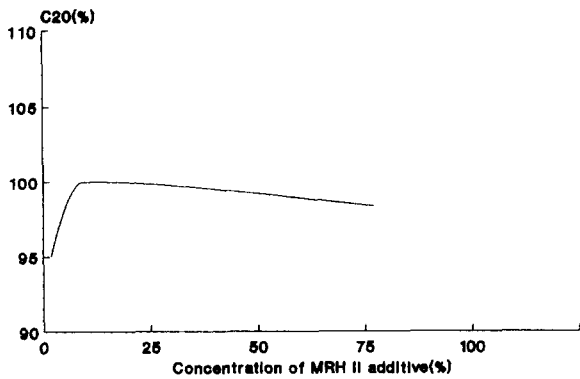


Fig. 6. C/20 capacity (IEC test) of batteries with MRH II additive.

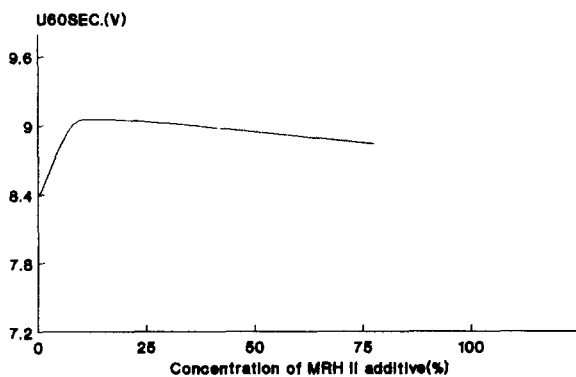


Fig. 7. Cold-cranking performance (IEC test) of batteries with MRH II additive.

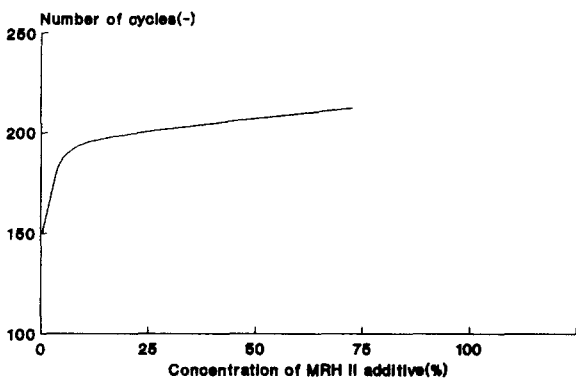


Fig. 8. Cycle life (IEC test) of batteries with MRH II additive.

7. Performance of batteries made with MRH II additive

The data given in Figs. 6 and 7 show that the optimal capacity and cranking performance is achieved with 10 wt.% MRH II additive. (Below 25 wt.% MRH concentration, both MRH additives yield nearly identical results.) If more MRH II additive is used, both battery parameters show a slight decrease, but at 75 wt.% addition, they are still better than the values given by standard active materials. By contrast, as the concentration of MRH II is increased, battery cycle life becomes proportionally longer (Fig. 8).

8. Reasons for positive effects of MRH I and II processes

Investigations have proved conclusively that both the MRH I and II reactivation processes transform the tribasic lead sulfate ($3\text{PbO} \cdot \text{PbSO}_4 \cdot \text{H}_2\text{O} = 3\text{BS}$) content of the additive into tetrabasic lead sulfate ($4\text{PbO} \cdot \text{PbSO}_4 = 4\text{BS}$).

Since the additive feeding rates can be varied, the 3BS and 4BS contents within the active material can be adjusted accordingly. Furthermore, the particle size of the 4BS produced in the MRH process is nearly an order of magnitude less than that of crystals made by traditional methods at 70–90 °C. Presumably this difference in the particle size plays an important role in the phenomenon observed with the MRH additive, namely, that the macrostructural skeleton reinforced with 4BS does not cause any drastic decrease in surface area.

If the benefits offered by the reinforced active-material structure are exploited, it becomes possible to increase the specific surface area by lowering the active-material density (to give better cranking performance and capacity value) while, at the same time, cycle life is extended.

9. Economical features of the application of MRH processes

Exact economic calculations can be made only when precise information on labour and energy costs, scrap rates, etc. is available. It is possible, however, to make a rough estimation. For example, if a factory using 10 000 t of lead per year installs the MRH process, then the annual cost savings can amount to US\$ 1 million.

10. Benefits achieved with MRH in environment protection

The following advantages are to be gained with the MRH scrap reclaiming system.

- (i) All processing lead scrap can be recycled in the battery plant itself; there is no need to take a potential polluting risk through the transport of dangerous wastes.
- (ii) The process has better efficiency compared with the smelting process, therefore substantial lead emissions can be avoided (no lead dross to deposit).
- (iii) The process also reuses the environmentally harmful sulfur compounds as structural material.
- (iv) A better specific coefficient of active-material utilization is obtained and this allows less lead to be built into the battery.

(v) As a consequence of longer cycle life, less junk batteries arise in the same time period.

11. Summary

The present process has been in use at the Perion Battery Factory Co. Ltd. since 1989. It has successfully passed the so-called 'clinical test'. Benefits have passed on to batteries in the form of improvements in cycle life, cranking performance, charge acceptance, water consumption and self-discharge. Improvements have also been made to the recycleability of the additive produced by the process.

Most of the scientific studies have been performed at the Hungarian Veszprém University and at the Research Center of Johnson Controls Incorporation in USA. On the basis of the common tests, Johnson Controls has teamed up with Perion to market the MRH process outside of Europe.

It is very likely that more is to be gained from using MRH-derived 4BS in the positive and negative plates.

In the meantime, the process offers the following advantages:

- technological improvement
- environment friendly operation
- material savings
- quality improvement
- recycling of dangerous wastes

These are all advances that will strengthen the position of battery manufacturers using the MRH processes in competition with other companies, and will help to meet the strict requirements of environmental protection.

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