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Journal of Power Sources 57 (1995) 27–30

JOURNAL OF POWER SOURCES

The BATENUS process for recycling mixed battery waste

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Abstract

The first large-scale battery recycling facility implementing the hydrometallurgical BATENUS technology is expected to go into operation by 1996. The plant will be situated in Schönebeck/Sachsen–Anhalt, and has a projected maximum capacity of 7500 tons of spent batteries per year. The engineering is being carried out by Keramchemie GmbH and the plant will be operated by Batterierecycling Schönebeck GmbH. The BATENUS process was developed by Pira GmbH, a research institute in Stühlingen, Germany, during a period of five years. This new process combines hydrometallurgical operations in a nearly closed reagent cycle that involves electrochemical and membrane techniques. Effluent emissions are minimized to the greatest possible extent. Process validity has been proven in a series of pilot plant testings. After mechanical separation of the casing materials like ferrous and nonferrous metals, paper and plastics, the subsequent hydrometallurgical recovery yields zinc, copper, nickel and cadmium. The other products are manganese carbonate and a mixture of manganese oxide with carbon black. Mercury is immobilized by absorption on a selective ion-exchange resin. The BATENUS process is a master process for the hydrometallurgical reclamation of metals from secondary raw materials. It has found its first application in the treatment of spent consumer batteries (i.e., mixtures of zinc–carbon, alkaline manganese, lithium, nickel–cadmium cells, etc.). As a result of its modular process design, the individual steps can be modified easily and adapted to accommodate variations in the contents of the secondary raw materials. Further applications of this highly flexible technology are planned for the future.

Keywords: Recycling; Germany; Spent batteries

1. Introduction

The processing of metal solutions using hydrometallurgical techniques is a well-established and efficient method for the recovery of metals from raw materials, e.g. ores. The benefits of hydrometallurgy are: (i) nearly complete recovery of metals; (ii) high purity products; (iii) relatively low energy requirements, and (iv) avoidance of effluent emissions.

However, working with aqueous solutions can often lead to large amounts of more or less contaminated waste water. For this reason BATENUS utilises a combination of proven hydrometallurgical operations like solid–liquid extraction, selective ion exchange and solvent extraction with state-of-the-art membrane technology, i.e. reverse osmosis and electrodialysis with bipolar membranes. This strategy makes it possible to reprocess reagents and thus minimize the emission of salt solutions. Instead of dumping the salt solution, it is split into the corresponding acid and base. Both are recycled into the process as leachant or as neutralizing agent, respectively.

In addition, the BATENUS process consists of a modular and therefore flexible combination of its individual operations. Adjusting the process scheme to varying inputs is an option for future applications.

The first plant working according to this innovative principle is presently going through the official licensing procedure. The expected start of production will be in 1996.

2. Consumer batteries as secondary raw materials

About 775 million items or 26 500 tons of consumer batteries are sold per year in Germany. This tonnage corresponds with the amount of raw materials necessary for battery production. The individual metal demands in tons per annum are:

Iron	8050
Manganese	6300
Zinc	3900
Nickel	630
Cadmium	480
Lead	95
Mercury	17

The environmental impact of dumped battery waste has been discussed over years. An ordinance regarding the collection and recycling of spent batteries has been issued in the Euro-

Elsevier Science S.A.
SSDI 0378-7753(95)02234-8

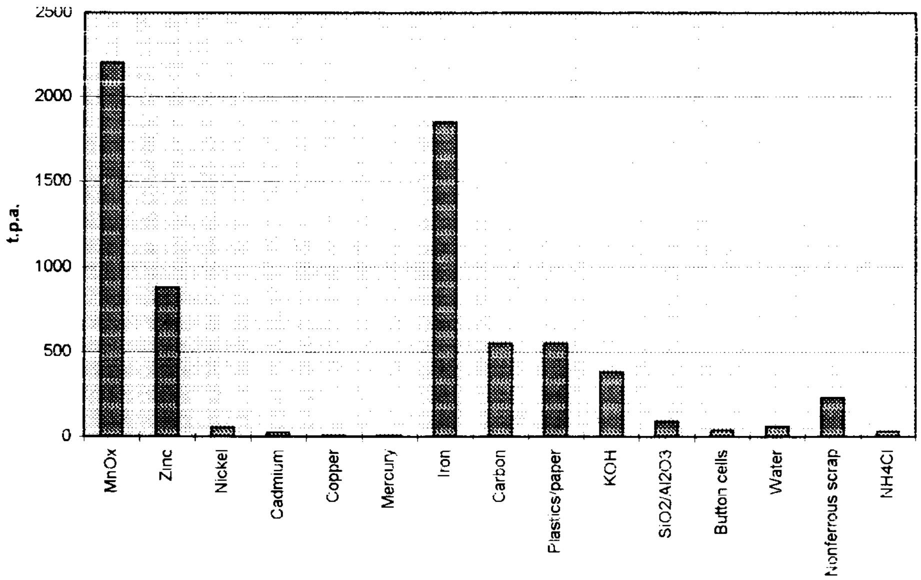

Fig. 1. Composition of the spent batteries before recycling (tons per annum).

pean Community in 1991. Even though this ordinance has not yet been enacted as a national law in Germany, such a regulation is expected for the near future.

In addition to the environmental aspect there is a question of political economic viability. In landfills the raw materials will be lost. Recycling should provide a twofold savings impact (i) of the limited landfill space, and (ii) of raw materials, which would otherwise have to be imported. Generally, jurisdiction prefers utilization of waste to the increase of landfilling.

Consequently, most municipalities and bigger companies in Germany collect all kinds of consumer batteries. This mixture must then be handled as hazardous waste and is subjected to special treatment. But presently, this usually means sorting out the nickel–cadmium and mercuric oxide cells, and then dumping 85% of the batteries, the zinc–carbon and alkaline manganese cells.

3. BATENUS — high innovation standard in recycling

BATENUS offers the possibility of a nearly complete metal recovery from mixtures of spent batteries. This process works:

- in a flexible, modular construction, which can easily be modified
- with a very low sensitivity towards variations of the composition of the input
- forming a nearly closed cycle, thus avoiding effluent emissions
- producing metals of high purity and easily marketable basic materials and chemicals

The BATENUS technology was developed by the R&D institute Pira in Stühlingen, Germany, during a period of five years. The development included process design, laboratory experiments, pilot-plant experiments, testing each individual operation under realistic conditions, and fine tuning of the modular units towards each other.

Keramchemie, in its role as general contractor, is going to erect the first industrial scale BATENUS plant in Schönebeck/Sachsen–Anhalt. This plant will be operated by Batterierecycling Schönebeck GmbH.

4. Energy requirements

An important feature of BATENUS is its economical energy requirement.

The average specific energy consumption in a plant processing 7500 tons per annum (max.) of batteries is about 2500 kWh/t of batteries.

The average specific electrical energy requirement for winning the main process products (zinc, copper, nickel, cadmium, iron, nonferrous scrap, manganese carbonate, manganese oxide) is about 4125 kWh/t of products.

A comparison with well-known figures from established hydrometallurgical nonferrous primary smelters such as: 4100 kWh/t of fine electrolytical zinc, 3150 kWh/t of fine electrolytical copper, or 3400 kWh/t of iron from primary smelter shows that the BATENUS process leads to an acceptable energy balance regarding metals reclamation from secondary raw materials.

5. Nearly complete recovery of resources

A comparison between Figs. 1 and 2 shows that more than 90% of the battery input are transferred into marketable products. These are not only ferrous and nonferrous scrap, both of which are sold to scrap dealers, but also paper and plastics that go to a thermal utilization. A mixture of manganese oxide

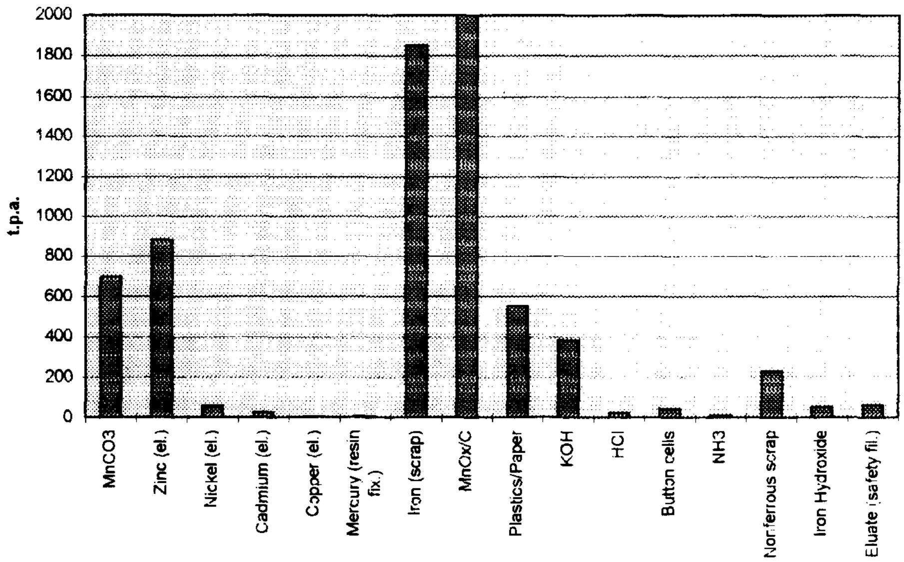

Fig. 2. Composition of the recycling products (tons per annum).

and carbon can be sold to a ferromanganese producer. Moreover, pure metals like zinc, copper, cadmium and nickel as well as manganese carbonate are recovered as basic commercial products.

The residuals of the process are resin-fixed mercury, iron hydroxide and the eluate from an ion-exchanger containing two valent metal ions (mainly alkaline earth and manganese). The overall amount of these products in a plant for the treatment of 7000 tons per annum of spent batteries is approximately 200 tons per annum.

6. Plant description

The flow chart of the BATENUS process for battery recycling is shown in Fig. 3.

6.1. Mechanical treatment

A mixture of batteries are delivered to the BATENUS plant. The first mechanical operation is sieving out the button cells. Those cells are sent to a mercury recovery company.

In a gastight unit, the batteries are shredded. At the shredder exit, a magnet removes scrap iron. After washing, this scrap is sold to a scrap dealer. Paper, plastics and nonferrous metals are separated from the battery contents with the aid of sieves. A further separation yields a paper/plastics portion and a nonferrous scrap portion.

The battery contents are ground in order to get a powder which is led to the hydrometallurgical unit.

6.2. Hydrometallurgical reprocessing

The pulverized battery contents are leached in diluted sulfuric acid. Any potentially resulting exhaust gas is cleaned in a scrubber. Subsequently, the leaching suspension is filtered.

The recovered filter cake, consisting mainly of manganese oxide and carbon black, is washed and dried. This product is sold to a ferromanganese producer.

The filtrate is cleaned of mercury traces by a selective ion-exchanger.

Zinc is extracted from the mercury-free process solution in a multistep solvent extraction. Stripping of the organic phase with sulfuric acid yields a pure zinc sulfate solution from which zinc metal is generated electrolytically.

Copper, nickel and cadmium are successively separated from the solution by selective ion-exchangers. The resins are eluted by sulfuric acid yielding the corresponding sulfate solutions. The pure metals are recovered by electrolysis.

The iron concentration has to be controlled in the nickel eluate. If necessary, iron hydroxide is removed.

At this stage the main process solution contains only manganese and alkaline metal sulfate (as well as small amounts of chloride). Addition of sodium carbonate yields a manganese carbonate precipitate. This precipitate is filtered out and washed with water. After drying this product can be marketed as a raw material for manganese or manganese dioxide production.

The remaining alkaline metal sulfate solution is concentrated by reverse osmosis. Subsequently the concentrate is split into acid and base by electrodialysis with bipolar membranes (EDBM). The acid — sulfuric acid with a small amount of hydrochloric acid — is used as leachant for the battery powder.

A certain portion of both acid and base is concentrated by evaporation. In the evaporators hydrochloric acid is removed from the sulfuric acid and ammonia is removed from the base (sodium, potassium, lithium hydroxide). Whilst the concentrated sulfuric acid is used for regeneration of ion-exchangers, the concentrated base serves as a neutralizing agent in the process.

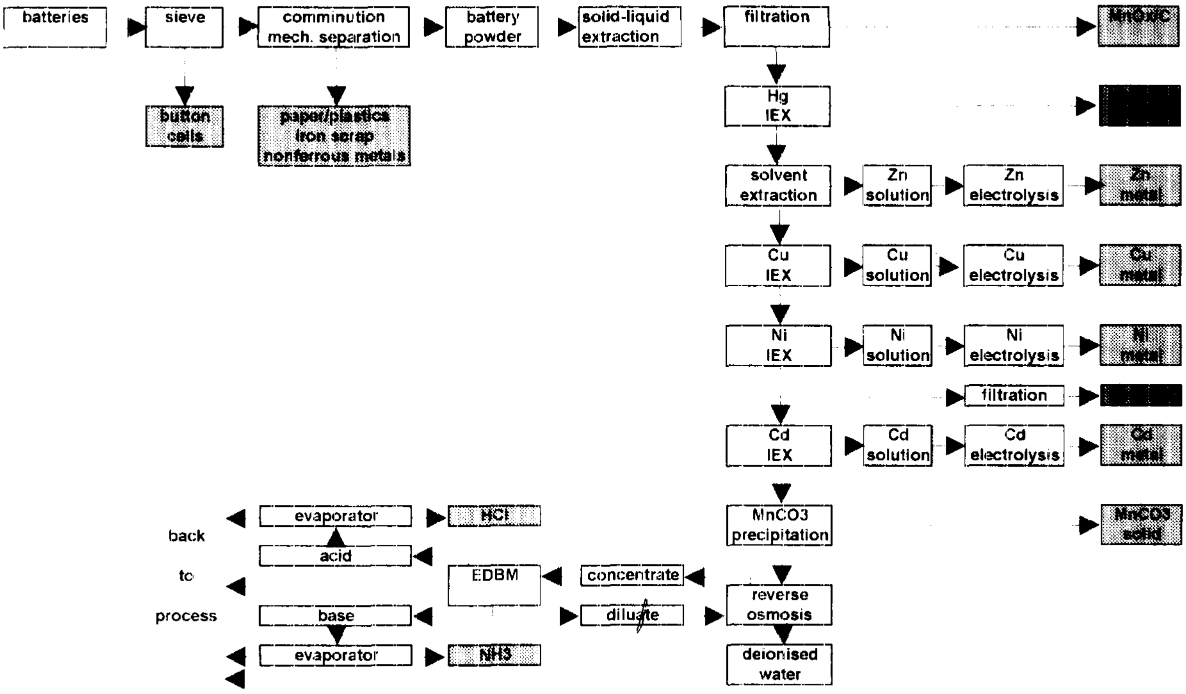

Fig. 3. Flow chart of the BATENUS recycling process.

The diluted salt solution from the EDBM is again concentrated by reverse osmosis. The resulting concentrate is led back to EDBM and demineralized water is recovered for washing purposes.

7. Discussion and conclusions

BATENUS is a recycling process in a nearly closed cycle with relatively low energy requirements minimizing effluent emissions. Resources are recovered to a more than satisfying extent.

First, proven hydrometallurgical operations on the one hand guarantee reliability. Second, utilization of advanced membrane procedures, like electrodialysis with bipolar membranes to a scale which — at least for European conditions — is unique, will lead to a substantial progress in technology.

The first application of BATENUS — battery recycling — for which an industrial facility will be erected this year is only the key for a variety of ecological as well as economical processes. High flexibility in process design due to the modular construction of the individual operations makes this technology a master process for the recovery of products from different secondary raw materials.