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The Wimmis project

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Abstract

Batrec is operating a plant for the recycling of spent dry batteries with a capacity of 3000 tons per year. The plant is situated in a tourist area of Switzerland and all the strict emission limits are fulfilled. The process yields four products: ferromanganese, zinc, mercury, and slag.

Keywords: Recycling; Spent batteries; Switzerland; Ferromanganese; Zinc; Mercury; Slag

1. Introduction

1994 was the first full production year for the battery recycling plant of Batrec AG, Wimmis, Switzerland. The plant is performing well. No hazardous wastes have been generated and all products are sold. The process, developed by SHI (Sumitomo Heavy Industries Ltd., Japan), was proven for the recycling of metals and metal oxides contaminated with heavy metals and organics [1-3].

The plans for the future are to increase the production capacity beyond 3000 tons annually in order to reduce the recycling cost.

2. Plant and process

The process was designed to achieve the following two goals: (i) to extract the major metal compounds (>95%) of batteries in a reusable form, and (ii) to produce no hazardous wastes.

The process consists of three basic steps, see Fig. 1.

(i) pyrolysis of the organic part of the batteries in the shaft furnace at temperatures of 300 to 700 °C, followed by

(ii) reducing the metallic compounds in the melting furnace at a temperature of about 1500 °C; the metals are either molten (Fe, Mn) or evaporated (Zn), and

(iii) recovery of the gaseous zinc in a splash condenser.

2.1. Pyrolysis

The batteries are fed into the pyrolysis furnace without any pretreatment. The temperature in this shaft furnace varies between roughly 300 °C at the top to 700 °C at the bottom. The batteries pass the furnace within four hours. During this time, the organic compounds are pyrolyzed and the mercury compounds escape into the exhaust-treatment system.

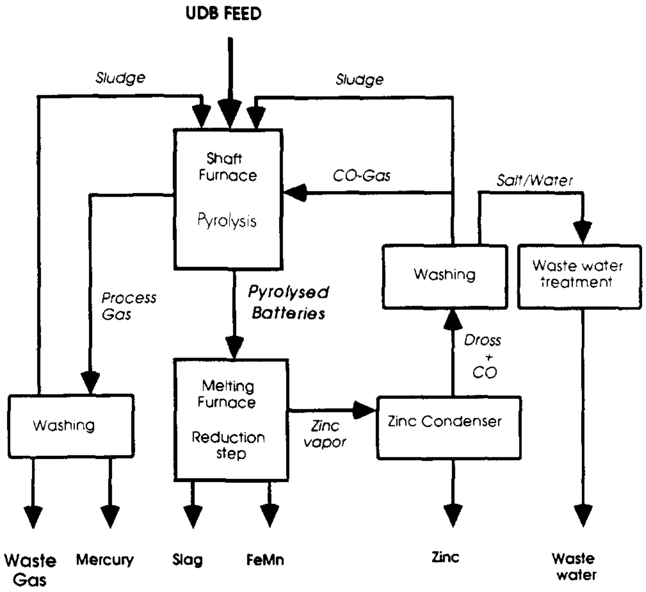

Fig. 1. Flow sheet of the Batrec plant. UDB: used dry batteries.

2.2. Melting furnace

The pyrolyzed batteries are directly fed into the melting furnace. Additives such as coke and magnesium oxide are added. In addition to the melting of metals, the induction furnace serves as a reduction vessel for metal oxides, mainly of iron, manganese and zinc.

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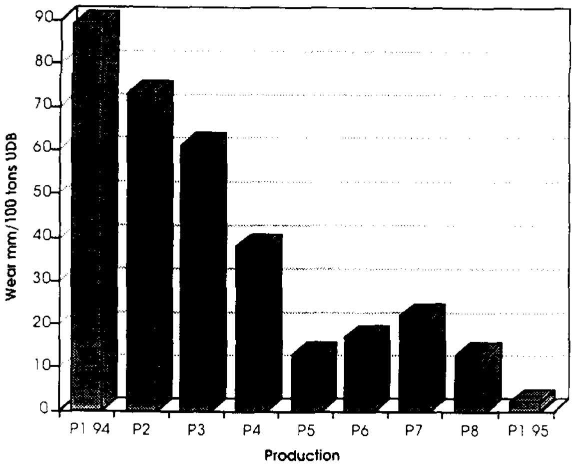

Fig. 2. Wear of bricks during the productions in 1994.

The liquid ferromanganese and the slag are cast into ingots, and the zinc evaporates.

2.3. Splash condenser

The vaporized zinc exits the furnace through a heated duct and enters the zinc condenser. It condenses upon impact with the liquid zinc from the splash in the condenser. The liquid zinc is then cast into ingots.

The waste gas from the condenser is mainly CO. It is, after going through a washing system, used as the main energy supplier for the pyrolysis.

2.4. Exhaust gas

The exhaust gas from the shaft furnace, gaseous mercury and the pyrolysis gas, are post-combusted in the incinerator (1000 °C) and then led through different washing and cleaning steps to the activated carbon filter and the exhaust chimney. The mercury is distilled from the sludges of this system or directly from the process.

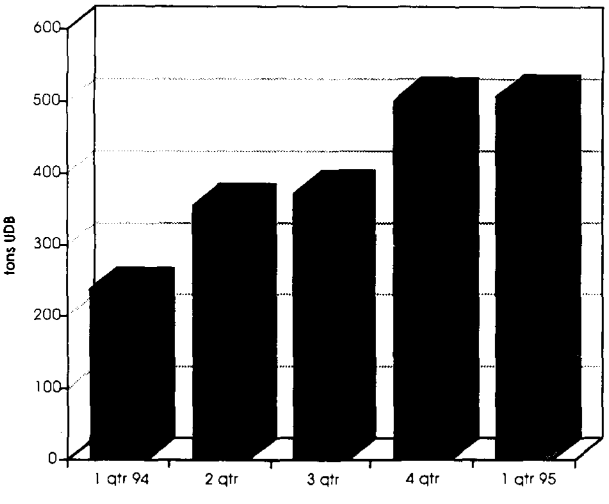

Fig. 3. Production development 1994–1995.

2.5. Sludge recycling system

All sludges and dusts from the gas washing systems as well as the dross from the zinc condenser are returned into the shaft furnace. There they undergo the same treatment as the original batteries. No upconcentration of any kind has been observed so far.

3. Recent plant improvements

Through several modifications of the plant and simplifications in the operation, the productivity was improved. The basic process was not changed.

Following are two examples of improvements:

(i) Lifting of the zinc condenser. Lifting of the zinc condenser improved the working conditions and also reduced the amount of work to handle the zinc. The concurrent modification of the duct between the melting furnace and the splash condenser virtually eliminated the problems of plugging and eliminated therefore the need for periodical cleaning.

(ii) Refractories for the melting furnace. The production has to be interrupted when the refractories in the melting furnace are worn down and have to be replaced. Each period between two changes of bricks is given a 'production number', see Fig. 2.

The use of more sophisticated materials and a controlled slag management improved the life of the bricks significantly. Fig. 2 shows the wear of the bricks during the productions in 1994.

4. Production

The plant recycled 1750 tons of used dry batteries (UDB) in 1994. The increase in a three-month period production is shown in Fig. 3. The goal is to increase the production to 3000 tons of batteries per year by the end of 1995. The plant works 24 h a day, 7 days a week. There are 5 shifts of four people.

5. Products

Four products are recovered: (i) ferromanganese; (ii) zinc; (iii) mercury, and (iv) slag.

5.1. Ferromanganese

Ferromanganese is quantitatively the main product of the process. The content of manganese in the alloy (25–40% depending on UDB) determines the sales prices. All ferromanganese is currently sold to a Swiss steel manufacturer.

Fig. 4 shows a tapping of the melting furnace.

Fig. 4. Tapping of the melting furnace.

Fig. 5. Products of the Batrec process: ferromanganese pigs, mercury, zinc and slag.

5.2. Zinc

The purity of zinc depends on the amount of the Ni–Cd batteries fed because the cadmium also condenses in the splash condenser to form an alloy with the zinc. The value of the recovered zinc reaches 75 to 85% of the London Metal Exchange (LME) price. The amount of zinc in UDBs is approximately 18%.

5.3. Mercury

Mercury is the product with the highest value. It is directly recovered in its metallic form and after chemical treatment and one distillation step reaches a very high purity level (impurities in the ppb range).

5.3.1. Content of mercury in household batteries

From 10 December 1994 to 10 February 1995, a test was conducted in order to determine the approximate content of mercury in household batteries.

For this purpose, button cells and military batteries were sorted out from the mix going into the plant. The only exception were 150 kg of special military batteries, which were recycled in a one-day test. They had a mercury concentration of about 25 wt.% and represented therefore an additional 37 kg input of mercury.

During the entire period, 366 tons of batteries were recycled. The recovered amount of mercury was 132 kg. After the deduction of the 37 kg from the military batteries, the household batteries yielded approximately 95 kg of mercury.

This amount does not represent the precise mercury content in the batteries since a significant amount of mercury is retained in the tubes and pumps of the plant. In order to minimize this effect, the whole plant was cleaned before the test. Another fact that establishes the correlation between the mercury and the batteries that were recycled is the constant level of mercury production throughout the test. During most of the days, between 1 and 2 kg of mercury were recovered.

One may conclude that each 1000 tons of UDBs that are currently collected in Switzerland, contain roughly 250 kg of mercury. It has to be properly recycled.

5.4. Slag

The glasslike slag is the only product which cannot be sold to day and has to be disposed of in a waste deposit. Official laboratory tests conducted by the Institute of Technology of Zurich (AFIF) showed that the slag is leach proof and therefore an alternative use (e.g. in road construction) is feasible. The amount of the slag varies between 2–3 wt.% of the products.

Fig. 5 shows the four products.

5.5. By-products

All by-products from the entire process are reintroduced to the process. The basic slugde arises in the washing line after the zinc condenser and mostly contains zinc oxide. The acid sludge is washed out of the waste gas line after the shaft furnace. One gets about 10 kg of acid sludge per ton UDB. According to an analysis conducted last year this sludge contains up to 64 wt.% of mercury in the dry substance. The mercury exists either as metal, as calomel or several other mercury compounds; it is recovered in a distillation. The distillation residue is recycled into the process.

The refractory bricks of the melting furnace are changed during each maintenance. This means about 15 tons mainly MgO-containing bricks a year. These bricks are entirely reintroduced into the process as slag building additives to the UDB feed. Therefore, the total annual quantity of refractories that have to be disposed is about 8 tons.

6. Emissions

Both waste water and waste gas volumes could be reduced in 1994 by means of simple modifications and improvements

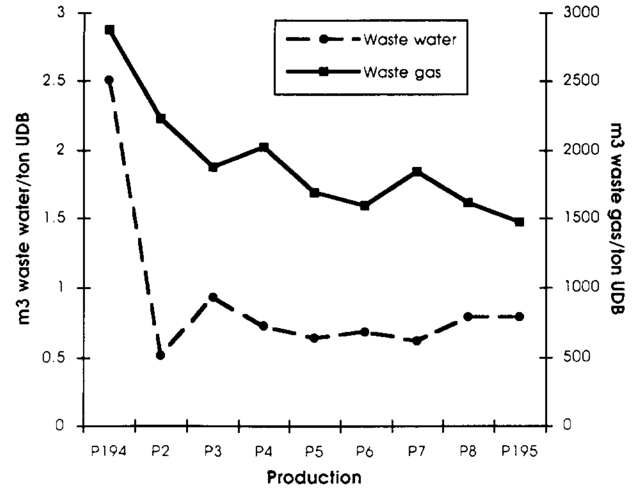

Fig. 6. Reduction of the emissions in 1994.

Table 1
Waste gas measurements

Material	Limit	Value
Carbon monoxide (mg/m^3)		9 ± 7
Nitrogen dioxide (g/h)	1000	720
Nitrogen dioxide (mg/m^3)		1490 ± 150
Total carbon (g/h)	20	< 0.97
Total carbon (mg/m^3)	20	< 2
Mercury (g/h)	0.1	0.042
Mercury (mg/m^3)	0.1	0.087 ± 0.022
Fine dusts (mg/m^3)	20	< 0.5
Dioxins/furanes, minimum (ng/m^3)	0.1	0.002
Dioxins/furanes, maximum (ng/m^3)	0.1	0.017

Table 2
Waste water analysis

Heavy metals	Limit values	Detected values
Mercury (mg/l)	0.01	0.002–0.009
Zinc (mg/l)	2.0	0.24–1.46
Cadmium (mg/l)	< 0.1	0.07
Lead (mg/l)	< 0.5	0.17
Copper (mg/l)	< 1.0	0.19

of the process. Fig. 6 shows this reduction of the emissions over the productions of 1994.

The emissions are continually analysed in order to stay within the Swiss emissions limits. These analyses showed that the effective pollutant concentrations are significantly below the tough Swiss emission limits. Especially dioxins are destructed to a point, where they cannot be measured anymore at the chimney. The dioxin concentrations in Table 1 were measured before the last two active carbon filters. These analyses were even made before the active carbon filters. Table 1 shows the result of such an analysis.

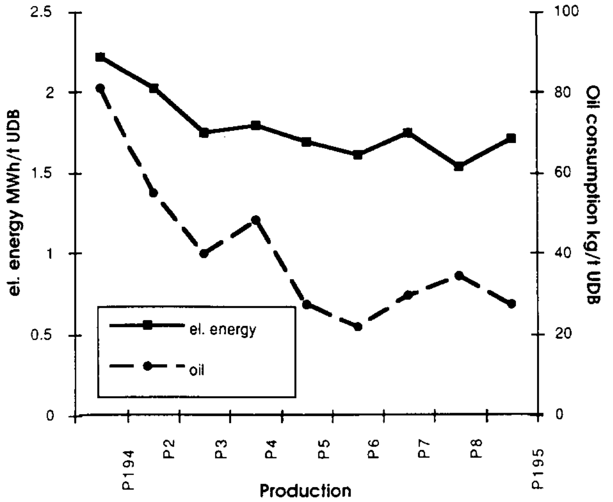

Fig. 7. Energy consumption in 1994.

The waste water is continuously analysed by an independent laboratory. If the limits for the discharge of waste water to a sewage plant cannot be detected, the waste water is given back to the process once again. The discharged water has zinc concentrations (< 2 mg/l) below these of drinking water (3–5 mg/l). Table 2 shows an analysis of the waste water.

7. Energy consumption

A general increase in efficiency of the plant is always reflected by a lower relative energy consumption. Fig. 7 shows the consumption of electric energy and oil consumption of the burners in 1994.

In the course of 1995 an additional CO burner will be installed. The CO gas is a product of the reduction in the shaft furnace and a part is already used in the hot-gas generator. A complete utilization of this energy source is to be desired. This measure will bring a further reduction in the specific energy consumption.

8. Cost development

Recent tests have shown that it is possible to increase the capacity of the existing plant to about 4000 tons without any basic change, such as new furnaces. The increase in the capacity will lead to cost reductions which will decrease the price of battery recycling in the Wimmis plant to less than US$ 4000 per ton.

As the next important step in the reduction of cost, the construction of a new plant with significantly larger capacity is planned. For such a plant, the recycling costs are expected to less than US$ 1000 per ton.

9. Conclusions and outlook

The Batrec plant for the recycling of spent batteries is running well. The process of Sumitomo Heavy Industries, Inc. is proven: spent batteries are transformed into saleable products and no hazardous wastes are produced.

All the strict requirements for the reduction of emissions in Switzerland are fulfilled.

The process has a very high potential for cost reduction when the capacity is increased. This will be the objectives for the next years.

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