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Economic considerations of battery recycling based on the Recytec process

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Abstract

The Recytec process is successfully operated on a continuous industrial base since autumn 1994. All the products are regularly re-used without any problems and environmental limits are fully respected. The European Community Battery Directive is valid since many years and only a few countries like Switzerland and The Netherlands have implemented it in national guidelines. In the meantime, battery producers have accepted the necessity of the recycling of mercury-free batteries in order to prevent the contamination of municipal waste streams by other heavy metals, such as zinc and cadmium. Recycling processes like the Recytec process are considered by the battery producers as highly expensive and they are looking for cheaper alternatives. Steel works are confronted with a market change and have to produce less quantities of better quality steels with more stringent environmental limits. The electric arc furnace (EAF), one of the chosen battery destruction techniques, is producing 20% of the European steel. Even if the battery mixes contain only mercury-free batteries, the residual mercury content and the zinc concentration will be too high to insure a good steel quality, if all collected batteries will be fed in EAF. In Waelz kilns (production of zinc oxide concentrates for zinc producers) the situation is the same with regard to the residual mercury concentration and environmental limits. Sorting technologies for the separation of battery mixes into the different battery chemistries will presently fail because the re-users of these sorted mercury-free batteries are not able to accept raw waste batteries but they are interested in some fractions of them. This means that in any case pretreatment is an unavoidable step before selective reclamation of waste batteries. The Recytec process is the low-cost partner in a global strategy for battery recycling. This process is very flexible and will be able to follow, with slight and inexpensive adaptations of the equipment, the trend in mercury content and quantities of c

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1. Introduction

The Recytec process is successfully operated on a continuous industrial base since autumn 1994. All the products are regularly re-used without any problems and environmental limits are fully respected.

The European Community (EC) Battery Directive is valid since many years and only a few countries like Switzerland and The Netherlands have implemented it in national guidelines. In the meantime, battery producers have accepted the necessity of the recycling of mercury-free batteries in order to prevent the contamination of municipal waste streams by other heavy metals such as zinc and cadmium.

Recycling processes, like the Recytec process, are considered by the battery producers as highly expensive and they are looking for cheaper alternatives. The scope of this paper is to present the Recytec process, its evolution potential with regard to mercury-free batteries and to show the reality of the proposed alternatives.

2. Recytec process - present status

Recytec SA started in 1991 with an industrial batch pilot unit with a capacity of 500 t/year. The built-in process steps included:

• one-step thermal treatment (650 °C, inert atmosphere, 1 ton/batch)

- shredding (maximum 10 mm)
- washing and sieving (<2 mm)

• magnetic and inductive separation of washed scraps (ferrous, non-ferrous, inerts)

• anodic dissolution and electrolytic deposition of nonferrous scraps

• chemical dissolution of active mass and electrolytic deposition of zinc, cadmium, copper and nickel

Due to the very bad economic feasibility in relation with the bad quality of used batteries (corrosion), the very low electrochemical yields (high waste energy streams), the remaining mercury concentration after the first thermal treatment and other practical problems, Recytec abandoned the



Fig. 1. Battery recycling process.

hydrometallurgical process steps and replaced them by a second thermal treatment to achieve full demercurization. Instead of 'pure' metals, this process decontaminates the batteries and produces demercurized secondary raw materials, like zinc-manganese powder, iron and non-ferrous scraps, oil, and mercury. The pretreated wastewater is discharged to the local sewage treatment plant for final oxidation of ammonia. The present process scheme is presented in Fig. 1.

The metal scraps are re-used in steel and brass production, the zinc-manganese powder is a secondary raw material for zinc production (Waelz kiln) and the demercurized oil is burned with heat recovery. Depending on its quality, the mercury is sold without any further cleaning or redistilled.

The continuous industrial unit, with a capacity of 0.75 t/h (4000–5000 t/year) of sorted, non-shredded waste batteries is in operation since September 1994. The plant has treated 800 tons of waste batteries since the beginning of 1995 (5 days per week, 3 shifts, 4 workers per shift). The plant has been operated with only one production line during the first two months and is run presently at 68% of its capacity. Due to the high mercury content of the batteries (<1%), it is necessary to prolong the thermal treatment steps in order to reach at least a mercury concentration in the black powder lower than 10 ppm, which is one of the quality criteria for the Waelz kilns.

With this final process scheme, the energy consumption has been lowered by a factor of five and lies near 1.2 kWh/ kg. A part of the waste energy is re-used in the process and for heating purposes of the building.

The batch pilot is used for the treatment of small quantities of 'specialty products' like other mercury wastes (thermometers, amalgams, catalysts, relais) and the pretreatment of special batteries (military applications, big batteries, lithium cell concentrates) and production wastes (air filter bags, active carbon, ion-exchange resins, waste-water sludges, etc.).

The whole plant, including warehouse, maintenance, administration, laboratory and a treatment facility for spent fluorescents and discharge lamps employs 35 people.

3. Recytec process and sorting out

A waste producer is in general not able to assure the quality of his wastes but the waste reclaimer or recycler faces stringent quality criteria for all his outgoing streams. Sorting out by hand or with mechanical and/or electronical devices is needed in all waste activities, in order to achieve a better quality of the wastes to be treated. Potential goals for sorting out of waste batteries could be:

- general quality control
- higher sorting out capacity, lower labour costs
- no other wastes

• no harmful foreign compounds (e.g. compact metal pieces)

- segregation by dimension and weight
- separation of different battery chemistries

• separation of hazardous batteries (lithium cells, Ni–MH rechargeable batteries)

In case of the Recytec process, the first five goals (coarse sorting) have to be achieved for a smooth production. These goals can be reached with a semi-automated mechanical sorting, with a capacity of 3 to 5 t/h and 3 workers. The big blocks are then sorted out by hand in lead/acid, nickel-cadmium and primary batteries. Lithium cells and Ni-MH rechargeable batteries are not separated, if in low concentrations (<5 wt.%). If present in higher concentrations, the mix has to be diluted with other battery types in order to lower the fire risk.

A separation based on the chemistries of the batteries (fine sorting) is not interesting as during the treatment of the produced concentrates, many problems appear which are not observable when treating battery mixes, like higher consumption of chemicals (auto-neutralisation in battery mixes), lower quality of products (zinc content).

Many people in the battery world mention several cheap recycling alternatives if batteries are sorted out into their different chemistries (manganese dioxide, zinc, metal salts producers). But none of these potential re-users are able to accept these products, even if high amounts of selected and mercury-free production wastes are proposed. On the other hand, these potential re-users are in general interested in some fractions of these 'homogeneous' materials.

This means that sorting out by chemistries could be a valuable pre-step before decontamination/pretreatment of waste batteries (mercury, salts, organics) and separation in fine and coarse materials, in order to achieve a better and economic re-use of all the battery materials. The practical and economic feasibility of such a scheme should be analysed jointly by the three potential partners.

Battery producers tried to label the batteries to make automatic sorting-out easier. Labelling could be an information for the consumer, but the experience of recyclers of nickel– cadmium cells shows that the quality of the collected cells is very bad and needs further sorting.

Experience of battery recyclers shows that recently collected batteries are heavily corroded and that labels are often no more legible. Corrosion produces dust (up to 5%), which is presently highly contaminated by mercury, zinc and cadmium. The consequence of this corrosion is cross contamination of all battery types:

- mercury (ppm) 250, range 80–700
- zinc (ppm) 1000, range 300-4000
- cadmium (ppm) 35, range 10–50

Recent controls of imported batteries in Europe have shown up to 15 000 ppm mercury. The problem of mercury will disappear when mercury cells are prohibited and when the mercury content of all produced batteries, including the production in developing countries, which is partly imported to Europe, will lay under 10–20 ppm. The consequence of this observation is that the preparation of mercury-free battery chemistries for specific recycling will not be possible in the near future.

4. Recytec process and the future

4.1. The most frequent question is: batteries are today mostly mercury free, what will happen with the Recytec process in the future?

The national battery recycling programmes are presently not well-defined and the collection rates are very low. In a near future, when the EC Battery Directive will be adapted to a certain reality and in a nation-wide application then the collection rate will raise gradually and the mercury content of collected batteries will fall to its minimum. As a consequence, modular solutions are needed to solve this problem.

The design of the Recytec process units is oriented to this near future. The two units for thermal treatment have the same design for the external part of the oven. This means that, with small changes, it is possible to use this second thermal unit as a first treatment step and to double the treatment capacity.

Practically it is possible to build a first unit with two thermal steps in series, to solve the present problem of mercurycontaining battery mixes and then, when the mercury content is low enough, to transform the second step in a first one.

4.2. The second frequent question is: what will happen when the collected batteries will contain only mercury-free batteries?

At first, what means mercury free? Mercury free regarding the EC Battery Directive is less than 0.025% or 250 ppm. Measurements show that mercury-free batteries contain less than the EC limit, but from the point of view of the re-users of battery fractions, like Waelz kilns or steel works, mercury free is less than 10 ppm.

4.3. The third question is: if we assume that the mercury content of waste batteries is lower than the 10 ppm limit, what will be the future of specific battery recycling?

The metal industry (steel and non-ferrous) will have to achieve more stringent environmental limits in a very near future, like dusts, No_x, dioxins, etc. Steel works, mainly EAFs (electric arc furnaces) are able to destroy batteries. But EAF steel represent only 20% of the steel production (40 Mt/year EAF steel in the EC). The trend of the steel market is to produce in Western countries high quality steel in better environmental conditions. Metals, like zinc, are not accepted in the feedstock in high amounts (<0.2%) due to metallurgical problems and batteries do not represent the only zinc source in steel works. Treating all batteries in EAF steel works would represent a concentration of more than 0.3% in the feed.

This means that a certain pretreatment is necessary before having access to steel works and Waelz kilns. These industries are not a new type of waste incinerators, but metal production processes. The Recytec process is at present time the low-cost pretreatment opportunity for a global battery recycling strategy. Further improvements and simplifications of the Recytec process are planned in the near future.

4.4. The last question is: do you have enough batteries to survive?

The answer is simply yes, because the Recytec process is a very flexible process. The process is able to treat other mercury- or heavy metal-containing wastes like petrochemical catalysts, ion-exchange resins, electronic components, contaminated fraction from industrial site reclamation and a new world appears: pyrolytic treatment of specific organic wastes. All these wastes can be treated with the same type of process units.

5. Conclusions

Recytec has shown a high grade of adaptability to the fast evolution of mercury-containing to the so-called 'green' batteries. During the development process from a industrial batch pilot to a continuous industrial production process, Recytec was able to double the capacity of the industrial unit, to maintain the investment costs in the range of the initially planned level and to lower the energy consumption by a factor of five.

The Recytec process is designed for the treatment of battery mixes. Fine sorting out is not an advantage.

All imagined alternatives for a direct treatment of coarse and fine sorted-out batteries are not presently accessible, due to the fact that collected batteries still contain mercury.

These proposed alternatives will not be able to accept collected batteries, even when they show a mercury content lower than 10 ppm of mercury, due to the fact that the metal industry is facing more stringent product qualities and environmental limits, which are not compatible with the integration in the feed of high amounts of foreign compounds, such as waste batteries presenting negative impacts. But some of the proposed factories are interested in different fractions of pretreated batteries.

The Recytec process can be considered as the low-cost pretreatment step in this new constellation.