

## LEAD RECYCLING TECHNOLOGY

J. KIRCHER

*Akkumulatorenfabrik Dr Jungfer, A-9181 Feistritz im Rosental, Karnten (Austria)*

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### Importance of recycling

It was only recognized as recently as the 1972 report of the Club of Rome on the predicament of mankind in respect of shortages of natural resources, that uncontrolled consumption of raw materials and energy, as well as accompanying adverse environmental factors, must come to an end. If increased utilization of the known resources continued it was claimed that they would be exhausted in a very short time. Nevertheless, following the discovery of new deposits, as well as improved mining technologies to reduce costs and rising prices for raw material, the predicted lifetime of raw materials had to be corrected continually. It is not only the finite supplies of raw materials and energy but also the rising pollution of the environment that forces more and more public institutions and enterprises to reassess their operations. For these reasons, recycling has become a very important issue.

In every free market, it is the economy that guides the utilization of waste and energy. An exclusively economic judgment of a recycling programme, however, might be fatal as waste would be recycled only if there was a profit for the company. It is therefore necessary to consider recycling from a total point of view that includes protecting the environment and the work force in recycling plants. Most battery companies have experienced an increasing awareness of this fact by the action of legal authorities around the world in issuing local guidelines that are sometimes quite difficult to fulfil.

### Lead-containing secondary material

The life expectancy and recovery rate of lead from various of its products are shown in Table 1. Scrap feed for lead recycling can be placed in one of two categories [1]:

- 'new' scrap — material arising during the manufacturing process
- 'old' scrap — consumers' discards.

At present, changes are taking place in the consumption pattern for lead. Many traditional uses of lead are now in a nett decline (*e.g.*, cable sheathing) or are being legislated out of existence (*e.g.*, lead in petrol). Despite these

TABLE 1

Recovery of lead from various lead-based products (source: ILZSG)

Product	Service life (years)	Product recovery (%)	Recoverable lead (%) <sup>a</sup>
<b>Batteries</b>			
Automotive	4 - 5	at least 90	95 - 97
Traction	5		
Stationary	20		
Sheet	up to 100	80 - 90	98 - 100
Pipe	50	70 - 80	
Cable sheathing	40	50	
<b>Alloys</b>			
Solder	varies with product in which used	20 - 30	
Bearings			
Type metal	indefinite-constant recirculation	5% of annual consumption returned as skimmings and residues from melting operations	98 - 100

<sup>a</sup>Depending on quality of material received.

events, the western world consumption of lead continues to remain at around 4.2 million tonnes. The principal reason for this is the continued growth in the market for lead/acid batteries.

### Systems for secondary lead smelters

Lead is a classic recycling metal. Already, at the turn of the century, recovery of lead from old batteries and industrial waste was of considerable interest. Today, however, recycling of lead is an economic necessity as the production of new lead cannot cover the rising worldwide demand for the metal.

The heterogeneous structure of automotive batteries presents difficulties in recycling. Therefore, the demands to be met by a good recycling system are quite complex and must satisfy not only technological and economic criteria but also must meet stringent environmental standards.

For recycling old batteries the following types of metallurgical plants are mainly used:

- shaft furnace
- short-drum type furnace
- rotary tubular kiln
- electric furnace and some exotic types

## Jungfer shaft furnace

### *General description*

The layout and operation of the Jungfer shaft furnace for processing battery scrap is given in Figs. 1 and 2, respectively. The battery plate groups are separated from the cases and the electrolyte by a slow rotation saw. The lead-containing components, *i.e.*, so-called battery 'scrap', are fed to the shaft furnace. The weak acid electrolyte is neutralized or put through a recycling process. The cases are automatically fed to a cutting mill by a belt conveyor and there cut into small pieces. The polypropylene (PP) and hard rubber granulates are conveyed to a separation unit. There, the crushed material is separated into a PP-fraction and a hard rubber-fraction. These separated fractions are discharged and conveyed to the corresponding dryer and bagged.

The battery scrap contains mainly crude lead, lead oxide, lead sulphate, and organic components. In the smelting furnace the sulphate is converted to lead oxide by the addition of iron. In turn, the oxide is reduced to crude lead. The organic components are burned and therefore serve as an energy supply for the smelting process which must be operated under a reducing atmosphere. This is achieved by the addition of coke (note, coke can be partly replaced by natural gas). It is possible to follow the converter reactions by observing the temperature-drop in the furnace.

Smelting takes place in a shaft furnace. In the charging-unit, the necessary components of the process are mixed and fed to the furnace by conveyor. The preheated combustion air is injected by nozzles. The shaft furnace and its throat are cooled by a primary water circuit that, in turn, is cooled by a secondary circuit in a water-water heat exchanger. The secondary cooling circuit operates with a cooling tower. The throat is water-cooled in order to provide certain operational advantages. The furnace chamber is lined with refractories and has two tap-openings and stands on rails. In the event of breakdown, therefore, it is possible to remove the furnace chamber for inspection and, if necessary, repair the shaft furnace. A clay seal is used between the shaft furnace and the furnace chamber.

### *Reaction steps*

The highest temperature stage takes place in the nozzle area (1200 - 1400 °C) and results from the combustion of coke and organic components. Carbon is combusted to carbon dioxide by the addition of air. As a result, the high-smelting slag components are liquefied. Sulphur is converted into CaSO<sub>4</sub>.

In the reduction region (700 - 900 °C), the rising CO<sub>2</sub> is reduced by annealed coke, *i.e.*,



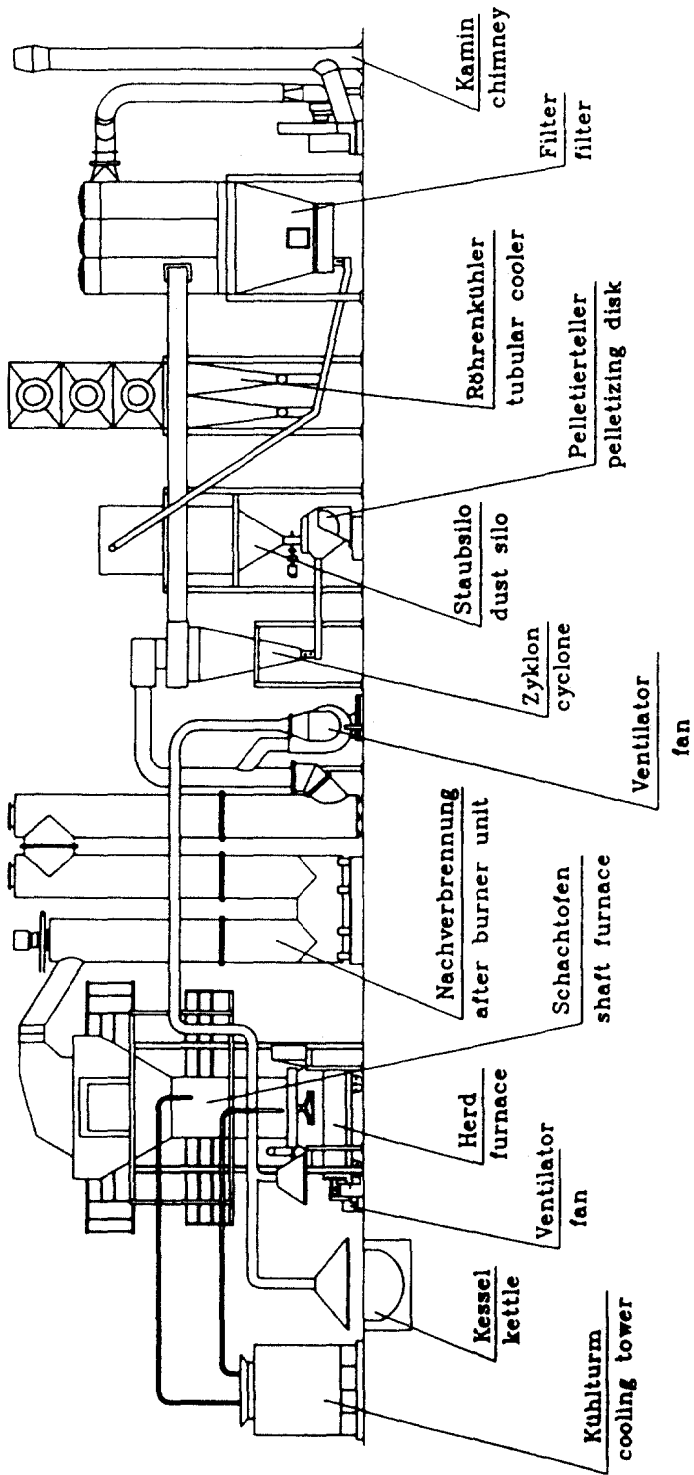


Fig. 1. Flow sheet of Jungfer shaft furnace.

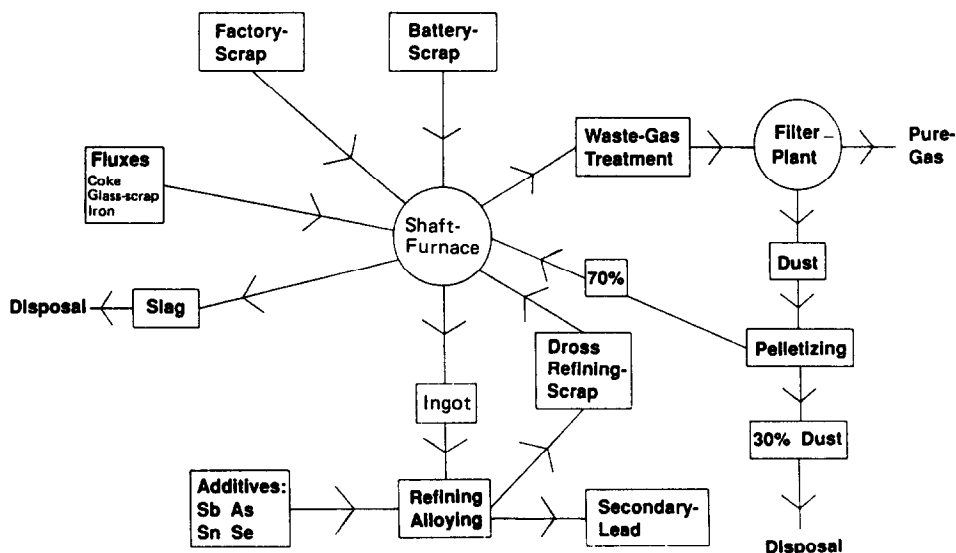


Fig. 2. Flow sheet of secondary lead production using Jungfer shaft furnace.

At the same time, the low-smelted slag components are liquefied, the lead sulphate is converted into lead oxide by iron (eqn. (2)), and crude lead is present as a liquid.



In the reaction region (400 - 700 °C), lead oxide is reduced to crude lead and carbon monoxide:



At this stage, the volatile ingredients of organic components escape.

Owing to the chemistry of lead production, it is essential to maintain a reduced atmosphere within the whole shaft furnace. Carbon monoxide of 3 - 5 vol.% in the waste gas is required.

### *Waste gas treatment*

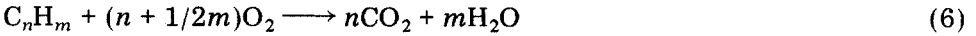
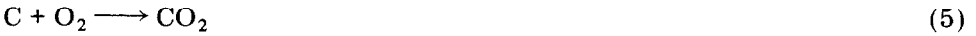
Toxic waste is a major international problem. One of the most effective treatments is to burn it at around 1300 °C, at which point the chemical compounds break down into their constituent and (in theory) non-toxic parts. In the case of the Jungfer system, the dust-containing waste gas leaving the shaft furnace is guided into an incinerator. The waste gas is mixed with combustion air and all combustible components of the waste gas (carbon black, CO, etc.) are burned. A light-oil or natural gas burner is used as an ignition source. The dust is partly molten and can be tapped out of the incinerator; the crude lead is separated from the slag.

Waste gas leaves the incinerator at about 850 °C and passes to a heat exchanger for heating the combustion air of the shaft furnace, thereby

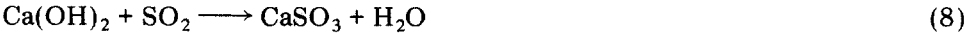
being cooled down itself. The outlet temperature of the waste gas is about 450 °C. To achieve the required waste-gas temperature of 150 °C before entry to the filter, the waste gas is mixed with exhaust air from the shaft furnace area.

All the large particles are separated in a cyclone. The waste gas is cleaned in a bag filter to a maximum of 10 N m<sup>-3</sup> dust content prior to entering the exhaust chimney. The dust separated in the cyclone and bag filter is conveyed to the pelletizing unit where pellets are made with the addition of water.

The waste gas leaving the shaft furnace at 300 °C contains significant amounts of CO, C, cracked hydrocarbons and dust. These components are burned in the incinerator at 1300 °C.



In subsequent steps, dust is separated in a cyclone and bag filter, while SO<sub>2</sub> is converted to calcium sulphite by addition of lime into the waste-gas flow.



The residual SO<sub>2</sub> content of the exhaust gas is <300 mg N m<sup>-3</sup>, and the dust content is <10 mg N m<sup>-3</sup>. The separated dust (containing also calcium sulphite and unconverted lime) is pelletized and recycled to the smelting process.

#### *Handling of slag and crude lead*

Because both the slag and the lead are in a liquid condition, it is necessary to tap both components. With this procedure, slag is run into a mould and solidifies there. The lower part of the slag cone, containing a certain percentage of lead, is cut and recycled to the charging unit. The crude lead is run into oil-heated refining kettles where it is refined and alloyed to meet the required specifications. Samples are taken to the laboratory for spectrometric analysis; the results are available within a few minutes thus enabling the operator to correct the alloy immediately.

#### *Environmental standards*

The emission limits measured inside the chimney are as follows:

Total dust	<10 mg N m <sup>-3</sup>
Organic carbon	<50 mg N m <sup>-3</sup>
Chlorine and chlorides, as Cl <sub>2</sub>	<5 mg N m <sup>-3</sup>
Fluorine and fluorides, as F <sub>2</sub>	<5 mg N m <sup>-3</sup>
Sulphur dioxide	80 tons/year
Arsenic	<1 mg N m <sup>-3</sup>

The emission limits measured within the area surrounding the factory at 1.5 m above ground level are:

Lead	$<0.002 \text{ mg m}^{-3}$
Sulphur dioxide	$<0.2 \text{ mg m}^{-3}$

The ground deposition limit for lead is less than  $0.25 \text{ mg m}^{-2} \text{ day}^{-1}$  as an average over an area of  $1 \text{ km}^2$  surrounding the factory.

## Conclusions

The recycling of battery scrap with the shaft-furnace system is particularly suitable for battery factories of any size, as well as smelters who are seeking a simple and economical system designed to meet the latest environmental standards.

## Reference

- 1 G. L. Rae, *J. Power Sources*, 19 (1987) 121 - 131.