

INNOVATIONS AND DEVELOPMENTS IN OXIDE PRODUCTION FOR LEAD/ACID BATTERIES

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Lead oxide production methods

The lead oxide manufacturing process has been known since the second half of the nineteenth century. After the lead/acid battery ceased to be a mere scientific curiosity at the turn of the century, the fast-growing demands for storage batteries by industry in general, and by the automotive industry in particular, motivated further development of the traditional process for lead oxide production. Nowadays, over 30% of the total world production of lead oxide is converted into plate material for lead/acid batteries. Of the numerous patented processes, only three basic methods have survived, and these have been further developed by various companies worldwide.

Barton process

In this process (patented in 1908 by G. Barton), molten lead is converted into oxide in a so-called reaction pot or reactor. Within this reactor, an agitator stirs the lead, and blown, or sucked-in, air oxidises the lead droplets. The air stream then carries the lead oxide to a collecting system.

Screen-mill process

In this production method, lead cylinders, formed by a rotating casting machine, are fed into a mill drum. The lead cylinders are converted into oxide by means of oxygen added to the process. The operation is based on the principle that the product falls through holes in the drum shell and is then calibrated by sieves. The lead oxide is collected in the funnel of the outside wall and passed to a lead-dust separator. The air is filtered and returned to the mill.

Shimadzu process

Again, lead cylinders are used as feed stock. However, the air stream carries the oxide directly to the collecting system instead of via a sieve-calibration system, as employed in the screen-mill process.

Heubach–Barton system

Because the Barton process has a fairly high output rate and the energy demand per tonne of lead processed is comparatively low, the majority of oxide-plant manufacturers have concentrated on overcoming the disadvantages of the process. These are:

(i) low acid absorption; on average, this does not exceed 160 - 180 mg H_2SO_4 per g oxide;

(ii) fineness of particle size; some manufacturers have tried to prevent this by incorporating a post milling stage in a hammer mill;

(iii) fairly low specific surface area ($\text{m}^2 \text{g}^{-1}$); this has an adverse effect on the reactivity of the oxide.

The improved Heubach–Barton process produces battery oxides with average and maximum acid absorption values of 200 and 230 mg of H_2SO_4 per g of oxide, respectively. The output has increased from 0.77 to 0.82 to 1.0 t h^{-1} . Due to a recently developed dosing control system, good uniformity of product has been obtained, *i.e.*, within $\pm 2\%$ of specification.

The PbO content can be varied between 65 and 99.7 wt.%. An automated ingot feeder system, controlled by level indicator switches, results in a minimum in labour requirements: one unskilled operator is capable of managing between 4 and 5 Barton pots simultaneously. The combined chain–roller feeder is normally designed to carry 20 ingots, or approximately one tonne of lead. The feeder is controlled by a level indicator switch to ensure a minimum of oscillation in the melting pot temperature; this is achieved by feeding an amount of lead to the melter equal to that consumed by the Barton reactor. Through this, the energy consumption of the melting unit is kept at a very steady level.

In order to maintain the physical and chemical characteristics of the oxide within the desired specification, the approach of Heubach is to control the supply of liquid lead into the reactor to as near a constant value as possible, and to regulate the reaction temperature through variation of the air flow. The latter is achieved by means of automated inlet devices that are supported by false-air nozzles within the system. With this arrangement, the desired quantity and quality of the oxidised material is extracted with a high degree of uniformity. The fineness and uniformity of the product are guaranteed by close control of the temperature, the residence time of the oxide in the reactor, and the flow-rate of the air. If coarse particles of the oxidised product are fed back to the reactor, then the relation of liquid lead, sub-oxide, and oxidised material is disturbed. This makes it impossible to achieve the tight control of the oxidation process that is necessary for the production of oxide with the desired high quality.

Because the reactor floor is fabricated from heat-resistant stainless steel, the need for replacement through wear is no longer experienced. The agitator has to be removed approximately once each year; this is accomplished through a manhole (located above floor level) without having to dismantle the main shaft. Such an arrangement has resulted in a marked

reduction in maintenance costs. The agitator, mainshaft, and shaft foot are also constructed from a heat-resistant stainless steel. The three over-dimensioned bearings of the shaft guarantee an uninterrupted (24 h per day) production sequence.

The oxide collection system comprises a high-performance cyclone and a horizontally arranged, flat-bag filter with polyvinyl chloride spray-coated filter fabrics. Dust collection is initiated by a pressure differential regulator that controls a separate vibrator-impulse fan in an off-line chambered filter arrangement. With the latter, one selected chamber is cleaned off-line while the remaining parts or chambers remain on duty. This has the advantage of saving energy by operating the system only when necessary. The filter surface load is designed to guarantee a lifetime of two to three years. The horizontal arrangement of the filter bags facilitates easy maintenance operations. With this type of filter design, a maximum emission through the exhaust stack of 0.5 mg Nm^{-3} guaranteed.

Heubach HBS mill system

Through the development of the Heubach HBS mill, the advantages of the three above-mentioned oxide processes are combined, namely:

- economy and reliability of the Barton process
- quality of the Shimadzu mill oxides
- production capacity of the screen mills.

The average acid absorption capacity of 270 - 280 mg of H_2SO_4 per g of HBS oxide exceeds the values of all the three alternative processes. The production capacity of 1 t h^{-1} at 70 wt.% PbO content exceeds any other system. The reliability is superior to all other processes due to sophisticated automation that allows operation without supervisory personnel.

In the HBS system, the liquid lead from an oil, gas or electrically heated melting pot is cast into cylinders in two casting machines that each have a capacity of 1.5 t h^{-1} . This arrangement has been chosen because studies have shown that the size and shape of the lead pieces influence the configuration of the oxide particles and allow supervision-free operation over a long period of time. The cylinders (each weighing 100 g) are stored in a standard-sized bin that is located on the top of the mill inlet opening. Load cells regulate the filling level of the mill and continuously control the raw material necessary to maintain the desired load.

The conversion of the lead cylinders into battery oxide takes place by abrasion with accompanying partial oxidation. The control equipment of the HBS system adjusts the process parameters, *i.e.*, lead feed, filling level, air supply, and air- and water-cooling. The oxidised material is removed from the mill pneumatically by an exhaust fan arranged behind the oxide collection system. In contrast to other milling plants, excessively large particles are not returned to the HBS mill; this is because the process control determines, both sensitively and precisely, that only fine and very fine particles with the selected degree of oxidation are removed.

The six most important parameters of the mill operation are recorded on a six-colour plotter for subsequent review and monitoring.

Concluding remarks

Manufacturers of automotive (car-starter) batteries require a highly reactive oxide for the negative plates. On the other hand, a more dense oxide is required for the plates of industrial batteries. Thus, it would appear that an oxide milling plant should be used in the former case, and a Barton plant in the latter. Nevertheless, the major battery manufacturers in F.R.G. continue to employ mill oxide for both types of batteries.

If investment in a new plant or replacement of an obsolescent one is inevitable, then the management must compare the economic advantages of either process. This involves a comparison of the following cost generating parameters.

(i) *Initial costs.* The initial costs for a Barton plant with a high technological standard and securely-dimensioned, vital elementary parts (such as drive motor, gear, shaft, agitator, and reactor bottom) are only slightly lower than the initial costs for a ball-mill plant.

(ii) *Operating costs.* Although a Barton plant requires continuous supervision, one person can operate up to four reactors provided the ingot feeder is automated.

The energy consumption for a Barton plant is about 80 to 90 kW h t^{-1} , and for a mill it is about 95 to 105 kW h t^{-1} if cylinder casting is included. Should it be possible to supply the battery manufacturer with cylinders as raw material, instead of ingots, then the energy consumption for a mill would drop to $70 - 75 \text{ kW h t}^{-1}$.

Mill supervision is only needed during cylinder casting. Over a two shift period, one operator, without supervision, can control six casting machines for three mills and produce sufficient cylinders for a week-end operation.

(iii) *Maintenance costs.* Over two years of constant operation, the maintenance costs of a mill will be slightly lower (about 10%) than those of a Barton pot. After two years, the filter bags in both plants must be examined thoroughly and possibly changed. The major maintenance on a Barton pot would be to weld up the worn out edges of the agitator, to change the roller bearings and, more frequently (depending on ambient temperature, humidity, etc.), to change the V-belts of the main drive gear. Major maintenance work on a mill could possibly involve the change of coupling bolts.

The dross removed from the surface of the melting pot and any area where the liquid lead comes into contact with air represents 1 - 1.5% of the

TABLE 1
Physical and chemical data of Heubach lead oxides

| | Heubach system | |
|---|----------------|--------------|
| | Barton HBS-IV | Mill HBS-I |
| Average acid absorption (mg H ₂ SO ₄ g ⁻¹) | 180 - 210 | 260 - 280 |
| Average particle size (μm) | 4 | 2 |
| Average BET-surface area (m ² g ⁻¹) | 1.2 - 1.4 | 2.4 - 2.8 |
| Average Scott-density (g l ⁻¹) | 1.4 - 1.6 | 1.2 - 1.4 |
| Average compacted density (g l ⁻¹) | 3.6 | 2.9 |
| Reactivity | good | excellent |
| Spread in PbO-content (%) | ±2 | ±1 |
| Degree of oxidation (%) | 60 - 80 | 60 - 80 |
| Guaranteed output (kg h ⁻¹) | 650/1000 | 250/500/1000 |
| Operation start/stop | Optional | Optional |

total raw material input to a Barton plant. The dross should not be thrown into the reactor if a high-quality oxide is desired because it disturbs the mass relation between molten lead droplets, sub-oxide, and oxidised material. Dross can be fed into a mill without causing any operational problems. Therefore, material losses in a mill are negligible.

In conclusion, a comparison of the characteristics of oxide produced by the Heubach-Barton and mill systems are given in Table 1.