



Lead oxide technology—Past, present, and future

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Abstract

In the earliest lead/acid battery, active material was formed electrochemically on the surface of a sheet of lead, which also served as the plate itself. Since that time, lead compounds (i.e., litharge, red lead, leady oxide) have been used to form the active mass, with better efficiency and performance. Many lead oxide production methods have existed, the predominant two are the ‘ball mill’ and the ‘Barton pot’ processes. These, and other methods, produce oxides with characteristics which are unique to each. The oxide properties of particle size and shape, surface area, crystal structure, purity, and degree of oxidation, can potentially, individually or in combinations affect the battery. With today’s manufacturers making mixed product lines that range from deep cycle to automotive lead acid to valve-regulated lead/acid (VRLA) batteries and everything in between, lead oxidation machinery and processes must be able to respond accordingly to produce materials that meet appropriate specifications. Oxide equipment and operating technique is improving in response to those characteristics that the ongoing research by industry indicates are or will, in the future, be beneficial to overall battery performance. © 1998 Published by Elsevier Science S.A. All rights reserved.

Keywords: Lead oxide manufacture; Barton pot; Ball mill; Litharge; Red lead

1. Introduction

Lead oxide compounds have been commercially available for about as long as lead has been refined and used. The earliest uses were for pigmentation and as additives to glass and ceramic glaze formulas. Demonstrated in 1860, Gaston Planté’s secondary lead/acid cell involved the anodic formation of PbO_2 on sheets of lead in a slow, tedious process where reversal of the electrical charge converted the lead to the electrochemical components. Subsequent developments by Faure and Tudor for pasting lead oxide compounds on plates and grids dramatically improved both the time required to form the active mass and, due to greater quantities of active material, the capacity of the secondary cell. These developments created a market in the emerging lead/acid battery industry for large quantities of lead oxide. It was also the impetus for researchers to identify and understand the properties of these compounds, their effect in the lead/acid battery system, and which characteristics optimized that system.

Early production methods converted pure lead to an essentially 100% oxidized product by thermal processes. In

batch furnaces (Fig. 1), the lead was melted then stirred (at first manually, and thus in later improvements, mechanically) in order to allow oxygen from ambient air to react with it. The exothermic reaction that took place therein provided sufficient heat to form lead monoxide which generally was a mixture of two crystal structures (Table 1)—yellow, orthorhombic (β -PbO or α -PbO) and red tetragonal (γ -PbO or α -PbO). When discharged from the furnace, the agglomerated material had to be milled in some fashion to make it suitable for use by battery manufacturers in pasting their plates. Action in roller mills tended to increase the amount of α -PbO, whereas hammer milling tended to maintain the relative ratio of α -PbO: β -PbO as discharged from the furnace. Battery builders had preferences toward one or the other of these products, based upon how each felt a particular crystal modification performed in their product. Milled material could be returned to a similar type of furnace process and converted to red lead (Pb_3O_4), which was also used in paste mix formulations by early manufacturers [1].

Economics stimulated investigations of faster, and more productive methods to produce lead oxides for battery use. In 1898, G.B. Barton patented a process where molten lead was stirred mechanically in the presence of air and steam,

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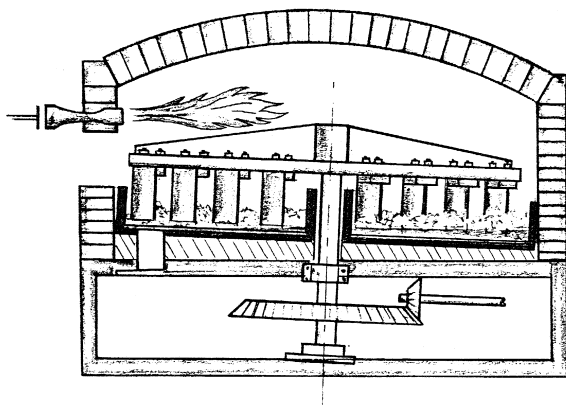


Fig. 1. The litharge reverberatory furnace.

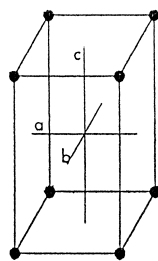
and the resulting oxide continuously transported away for collection via an air stream drawn through the process chamber. This process became commonly known as the Barton Pot (Fig. 2). Another oxide production method

involved the adaptation of a ball mill (commonly used for wet or dry grinding of ores, pigments, and other materials by the action with iron balls into a large rotating chamber) by using lead balls tumbling against one another. In a 1926 patent, G. Shimadzu described this process where friction created sufficient heat to oxidize the outside surface of these lead balls as the horizontal cylindrical mill turned; the oxide dust was carried away by a stream of air for collection (Fig. 3). Both the above methods produced a partially-oxidized product which contained a wide ranging percentage of free metallic particles. Barton material was initially used as feed for litharge furnaces since it was discovered that conversion of the remaining free lead to PbO was rapidly accomplished. The production time of lead monoxide was reduced from 30 h per batch in the above-mentioned furnace process, to about 3–4 h with the Barton and furnace processes combined. It was soon found, however, that these so called ‘leady’ oxides could be used directly in paste formulations and, by about 1925, they were rapidly replacing litharge and red lead.

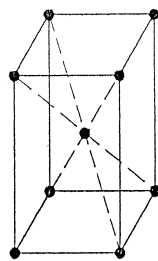
Table 1

The crystal structure of lead monoxides

System	Characteristics	Essential symmetry	Axes in unit cell	Angles in unit cell
Tetragonal (α -PbO)	Two equal axes and one unequal axis mutually perpendicular	One 4-fold axis	$a = b \neq c$	$\alpha = \beta = \gamma = 90^\circ$
Orthorhombic (or rhombic) (β -PbO)	Three unequal-axes mutually perpendicular	Three mutually perpendicular 2-fold axes, or two planes intersecting in a 2-fold axis	$a \neq b \neq c$	$\alpha = \beta = \gamma = 90^\circ$

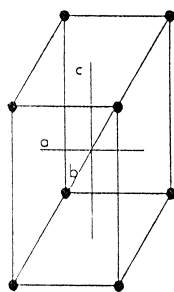


Simple

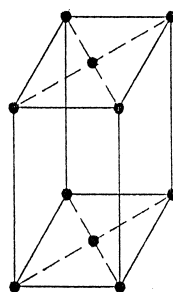


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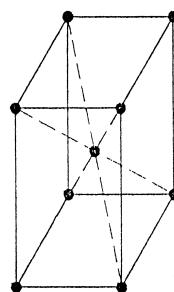
TETRAGONAL



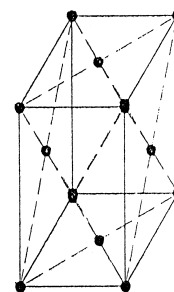
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End face-centered



Body-centered



Face-centered

ORTHORHOMBIC

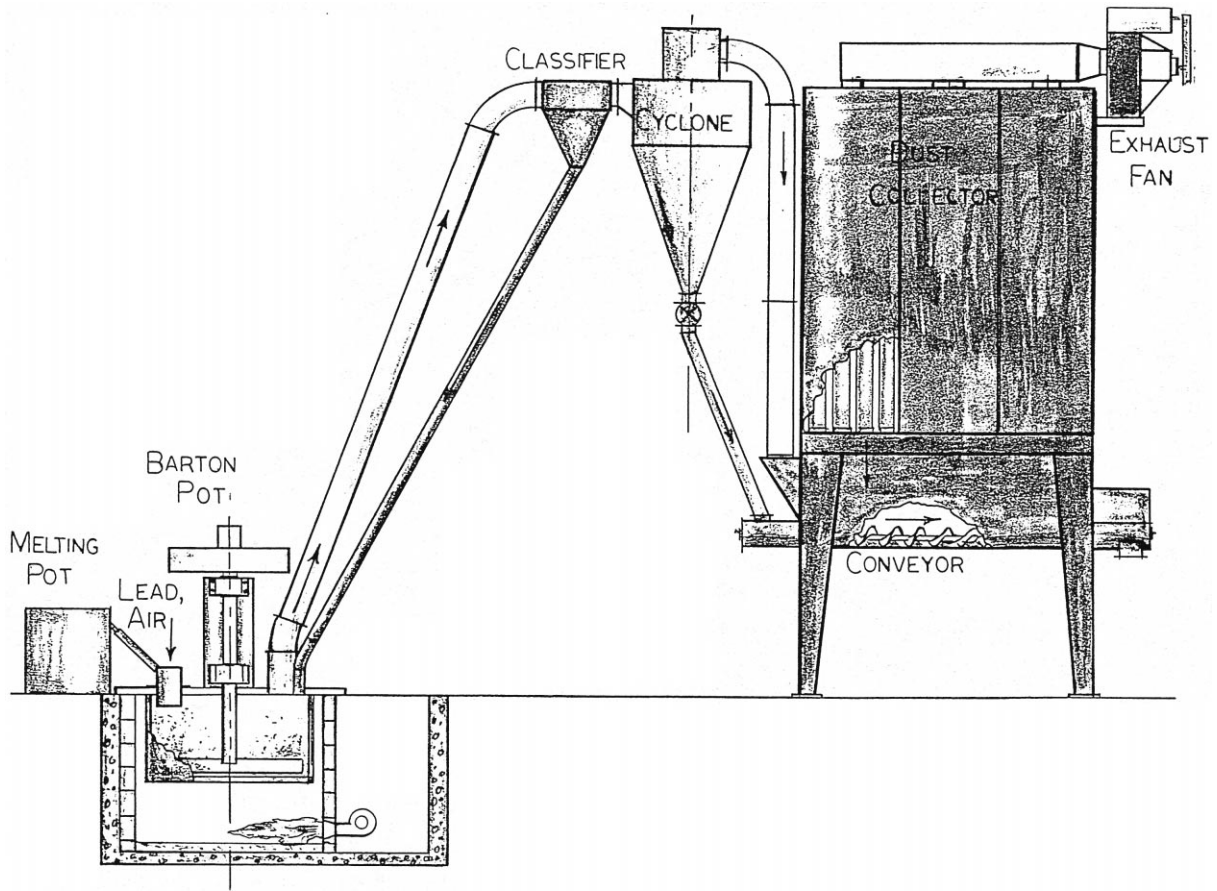


Fig. 2. Barton pot system.

Other methods have been and, in some cases, are still used to produce commercially lead oxides that, due to cost and other considerations, are no longer used in the lead/acid battery. Rotary tube furnaces, molten litharge furnaces, and lead-fume chambers are among those processes [2]. Of the above thermal process for the manufacture of lead oxide compounds, the two that today produce the vast majority of battery oxide are the Barton and

ball-mill processes, the mechanical principles of which will be discussed later.

2. Battery lead oxides

The physical characteristics, chemical properties and reactivities of lead oxide will vary with the method of

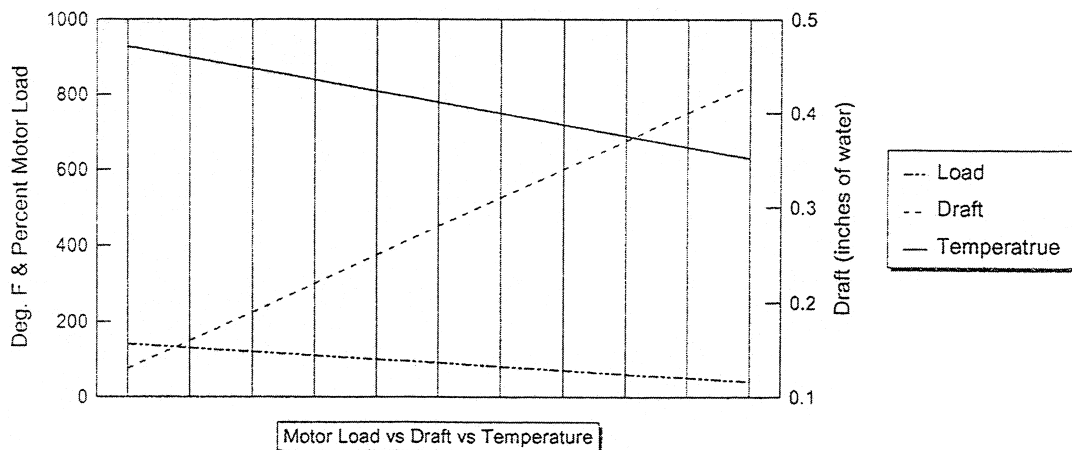


Fig. 3. Basic interactive relationship in a Barton pot.

production, the conditions used during manufacture, the purity of raw materials, and the subsequent material-handling procedures.

Thermal manufacturing techniques generally fall into three categories based upon the temperature range in which the oxide is formed. Low-temperature processes (e.g., ball mills) operate below the melting temperature of metallic lead (327.5°C). Moderate-temperature processes (e.g., Barton pots, litharge and red lead furnaces) are those operating between the melting point of lead and that of lead oxide. High-temperature processes (molten litharge furnace systems) operate above the melting point of lead oxide (886°C). The β -PbO form of lead monoxide forms exclusively above 510°C, whereas α -PbO is the oxidation product formed below the melting point of lead. Processes in which a transitional temperature range of 340 to 510°C occurs, both forms of PbO may be found. Therefore, ball mills produce a product that is essentially 100% α -PbO, while Barton (molten metal) systems are capable of producing materials with varying and controlled ratios of α -PbO: β -PbO that depend upon the selected operating parameters. The PbO crystal structure is of significant interest the plate pasting, curing [3] and formation steps. During pasting and curing processes, β -PbO favors the formation of the tetrabasic lead sulfate (4BS) while α -PbO favors the production of tribasic lead sulfate (3BS). Studies indicate that 1BS yields more α -PbO₂ after formation, which improves the mechanical integrity of the positive plate and may provide longer cycle life. By contrast, 3BS leads to produce β -PbO₂, which is a finer material that results in higher initial capacity but possibly shorter service life.

Beyond the simple molecular formulas of PbO, Pb₃O₄, and PbO₂, research has identified the existence of more complex, non-stoichiometric lead oxide compounds that exhibit some inconsistent and variable properties [4]. The explanation for these inconsistencies is that the heavy lead cation distorts the large and much lighter oxygen anion and thereby causes crystal structure defects not associated with binary compounds of elements with less difference in weight and size. The difference in size between the atoms of lead and oxygen causes inefficiencies in the packing in the crystal lattice and allows unfilled positions to be present. Oxides of lead appear to have structural defects over a wide range of compositions and are affected by certain aspects of the processing conditions. Commercial products, manufactured under less than optimum conditions when compared with those made in the laboratory, are more likely to contain these defects. It has been suggested that the voids within the defect crystal structure of some lead oxide compounds may make it possible for impurities to be taken up and, thereby, affect the behavior of the compound or other compounds that are subsequently formed. Whether tied to the crystal or as separate contaminants, certain impurities in battery oxide have a detrimental affect on battery performance. Therefore, it is important

Table 2
The chemical impurities in lead oxide

Material	Composition (wt.%)		
	ASTM designation: B 29–92	Flooded battery	Valve-regulated battery
Antimony (Sb)	0.0005	0.001	0.0005
Arsenic (As)	0.0005	0.001	0.0005
Tin (Sn)	0.0005	0.001	0.001
Copper (Cu)	0.0010	0.0015	0.001
Silver (Ag)	0.0025	0.005	0.0025
Bismuth (Bi)	0.025	0.03	0.025
Zinc (Zn)	0.0005	0.001	0.001
Tellurium (Te)	0.0001	0.0005	0.0001
Nickel (Ni)	0.0002	0.0005	0.0002
Iron (Fe)	0.001	0.001	0.001
Cadmium (Cd)	–	0.001	0.001
Manganese (Mn)	–	0.0005	0.0001
Selenium (Se)	–	0.0005	0.001
Thallium (Tl)	–	0.01	0.01
Lead by difference	99.97	99.97 to 99.99	99.99

that only soft lead with trace elements within specific limits are used to manufacture lead oxide for battery use [5] (Table 2).

Lead oxides combine readily with carbon dioxide and moisture to form various carbonates, basic carbonates, and hydrated products. Exposure to air and humidity increases the formation of these compounds. Other factors that can influence the properties of lead oxide compounds are photo-sensitivity, semi-conductivity [6], and susceptibility to static charge. When collected for laboratory analysis, oxide samples should be kept in sealed containers to minimize these influences until tests are to be performed. Oxide products should also be handled and stored in such a manner as to minimize exposure to ambient conditions.

3. Lead oxide manufacturing processes

Control of the oxidation process in the Barton and ball-mill systems of today is somewhat improved over earlier times when the ‘sound’ from the equipment and the motors indicated the material loading inside the system and, based upon how good an operator’s ear was, just when to adjust a lead-feed valve or introduce another ingot of lead. Measurements of process temperature were often made in an equally ‘sophisticated’ manner, i.e., by observing the ‘sizzle’ of spit on a hot lid or shell. Draft readings were made with a wave of a hand across the air inlet that, in essence, symbolized the magic art of battery oxide manufacture at that time. Modern electronics, sensors, data collection, and improvements in machinery design have provided these systems with the hard data and equipment necessary for an operator to control the process rather than the other way around. Even though new technologies have aided both processes by improving product

Table 3
The relationship of various lead compounds and conditions

Precursor or condition		Product
<i>o</i> -PbO (orthorhombic)	$\xrightarrow{\text{H}_2\text{SO}_4}$	PbSO ₄ ·4PbO
<i>t</i> -PbO (tetragonal)	$\xrightarrow{\text{H}_2\text{SO}_4}$	PbSO ₄ ·3PbO
PbSO ₄ ·4PbO	$\xrightarrow{\text{Charge}}$	α -PbO ₂
PbSO ₄ ·3PbO	$\xrightarrow{\text{Charge}}$	β -PbO ₂
PbSO ₄	$\xrightarrow{\text{Charge}}$	β -PbO ₂
Pb ₃ O ₄	$\xrightarrow{\text{Charge}}$	β -PbO ₂
2PbCO ₃ ·Pb(OH) ₂	$\xrightarrow{\text{Charge}}$	β -PbO ₂
PbO-M (orthorhombic)	$\xrightarrow{\text{Charge}}$	β -PbO ₂
PbO-L (tetragonal)	$\xrightarrow{\text{Charge}}$	PbO _{1.91}
Pb	$\xrightarrow{\text{Charge}}$	α -PbO ₂
High density paste	$\xrightarrow{\text{Favors}}$	α -PbO ₂
Low density paste	$\xrightarrow{\text{Favors}}$	β -PbO ₂
High forming acid gravity	$\xrightarrow{\text{Favors}}$	β -PbO ₂
Low forming acid gravity	$\xrightarrow{\text{Favors}}$	α -PbO ₂
High current density	$\xrightarrow{\text{Favors}}$	α -PbO ₂
Low forming temp.	$\xrightarrow{\text{Favors}}$	α -PbO ₂

quality and consistency, debate as to the best production method for battery lead oxide continues and centers primarily on particle shape, size distribution, and crystal morphology (Tables 3 and 4).

3.1. Barton-pot process

The principles of operation for a modern Barton system are similar, irrespective of the supplier of the equipment,

in so far as the process and major control parameters are concerned. Nevertheless, specific operating settings and equipment design features can affect the characteristics of the end product.

In the Barton process (Fig. 2), pure lead is melted in a crucible, then introduced to the reaction vessel (pot). A rotating paddle in close proximity to the bottom of the vessel skims molten lead into fine droplets which oxidize rapidly as air is drawn through the pot. The oxidation process is exothermic and, thereby, generates the heat which is necessary for sustaining a continuous reaction as more lead is introduced (Fig. 3). Process temperature is critical in determining the degree of oxidation and crystal morphology of the finished product. Only a small amount of oxide is in the reactor at any given time (approximately 100 to 125 kg for the average sized unit). The air stream, generated by a motor-driven fan, conveys oxide from the reactor for collection. The air exhausted is passed through a filtration system to remove residual dust. The process control parameters typically monitored are:

- reactor temperature
- reactor load
- system air flow
- temperature of lead melt crucible.

Often, additional measurements are made on indirect parameters to provide better overall control of system performance.

As the reactor paddle spins, the droplets of molten lead created take on a roughly spherical or granular shape, (Fig. 4), and then oxidize while more or less retaining this form—a defining characteristic Barton oxide particles. Many

Table 4
Comparison of Barton pot and ball mill oxides

Characteristic	Barton pot	Ball mill
Particle Size	3 to 4 mm median diameter	2 to 3 mm median diameter
Stability/reactivity in air	Generally more stable	Generally high. Can cause storage and long-distance transport problems
Oxide crystal structures (wt.%)	5 to 30% β -PbO (typ.), remaining balance α -PbO	Essentially 100% α -PbO
Acid absorption (mg H ₂ SO ₄ /g oxide)	160–200 (unmilled, up to 240 with hammer milling)	240
Surface area (m ² g ⁻¹)	0.7	2.0–3.0
Free lead content (wt.%)	Approx. 18 to 28	Approx. 25 to 35
Paste mixing characteristics	Makes a softer paste which can result in easier pasting	Makes a slightly stiffer paste which can require careful control
Paste curing	Average curing rate	Slightly faster curing rate
Battery performance	Enhances battery life but can result in lower initial capacity	Batteries have good initial capacity but possibly shorter life
Deep cycleability	Usually good	Sometimes good
Process control	Can be more difficult, but recent improvements in control technology are much better	Easier, more consistent oxide
Typical production rate (kg h ⁻¹)	300 to 900	Possibly up to 1000
Investment considerations	Lower initial and operating costs. Compact in size, relatively quiet, costs less to maintain, uses less energy to run	Higher initial and operating costs. Requires more space, noisy, costlier to maintain
Energy use (KW h/ton)	Up to 100	100 to 300 +
Environmental aspects	With well-engineered environmental systems (including baghouse and storage), existing emissions standards can normally be met	

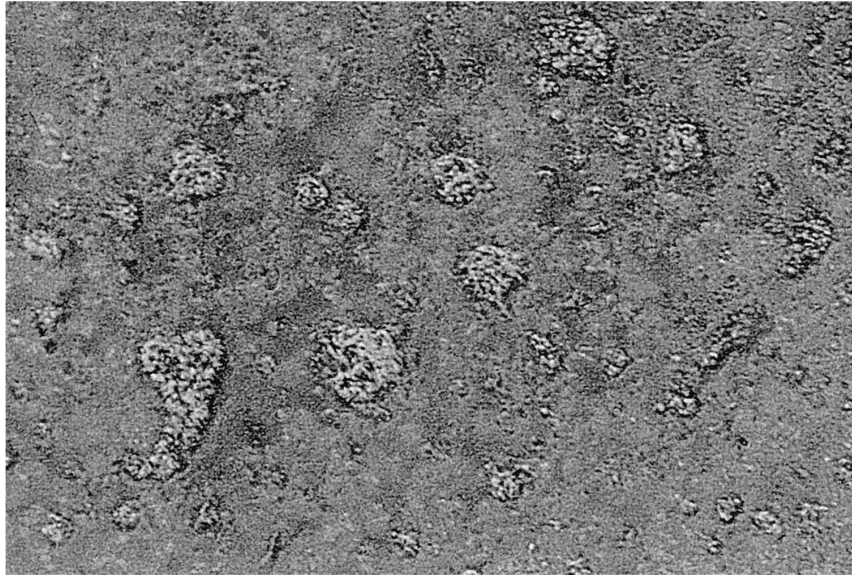


Fig. 4. Photomicrograph of Barton-pot oxide.

different factors affect the size of the particle. Some of these are:

- production rate,
- velocity of the air stream as it exits the reactor,
- depth of the reactor vessel,
- location at which the oxide is drawn out of the reactor,
- paddle design,
- paddle speed,
- method and type of additional classification.

Newer Barton designs generally incorporate the above

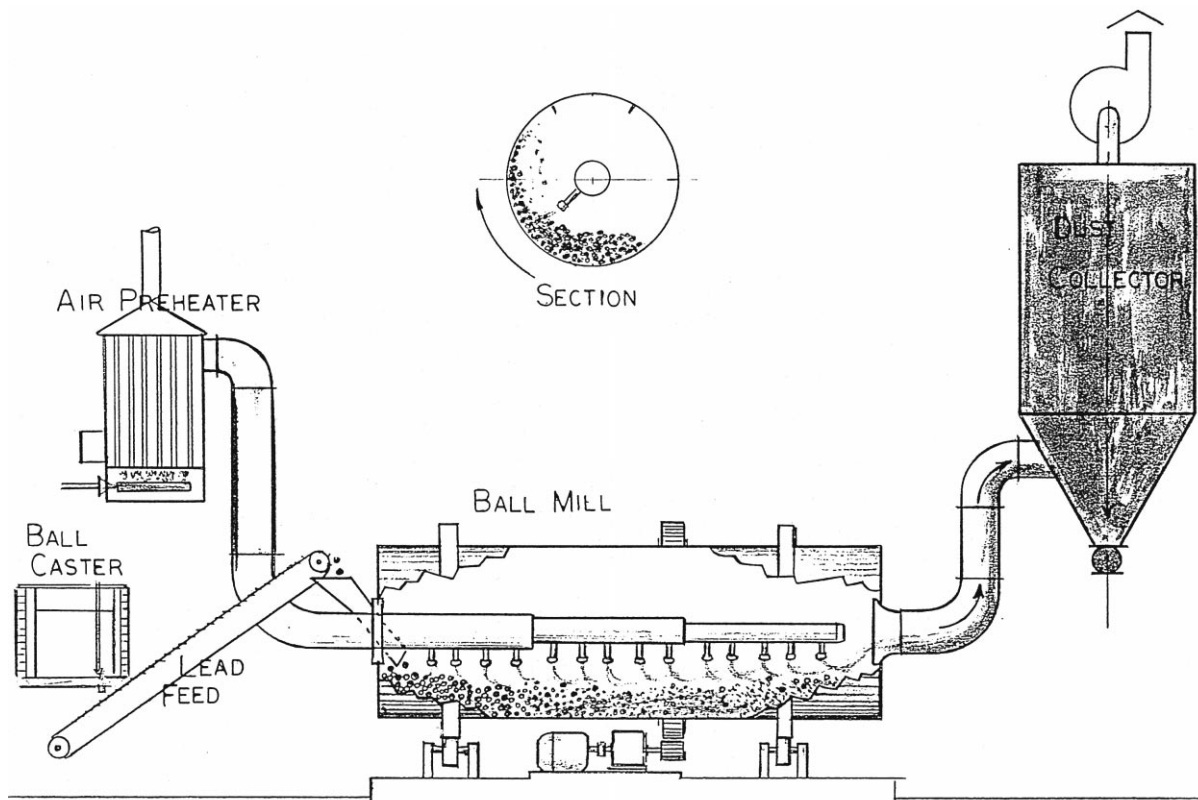


Fig. 5. Cylindrical ball mill.

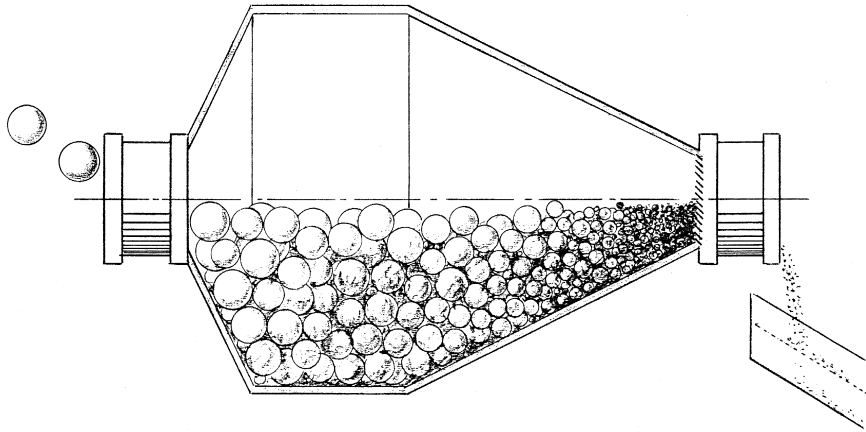


Fig. 6. Conical ball mill.

items in such a way that balances optimum particle diameters with production requirements.

3.2. Ball-mill process

Of the many designs of ball mill that are available, two have become well adapted for the manufacture of lead

oxides—the cylindrical ‘Shimadzu’ type (Fig. 5), and the conical ‘Hardinge’ type (Figs. 6 and 7). Both operate on similar principles and control parameters with slightly different product characteristics which depend upon the mill design used.

In the ball-mill process, the friction of lead balls tumbling against one another inside the mill chamber create sufficient heat to oxidize their surfaces. As attrition and oxidation wear the balls down, new ones are added. The

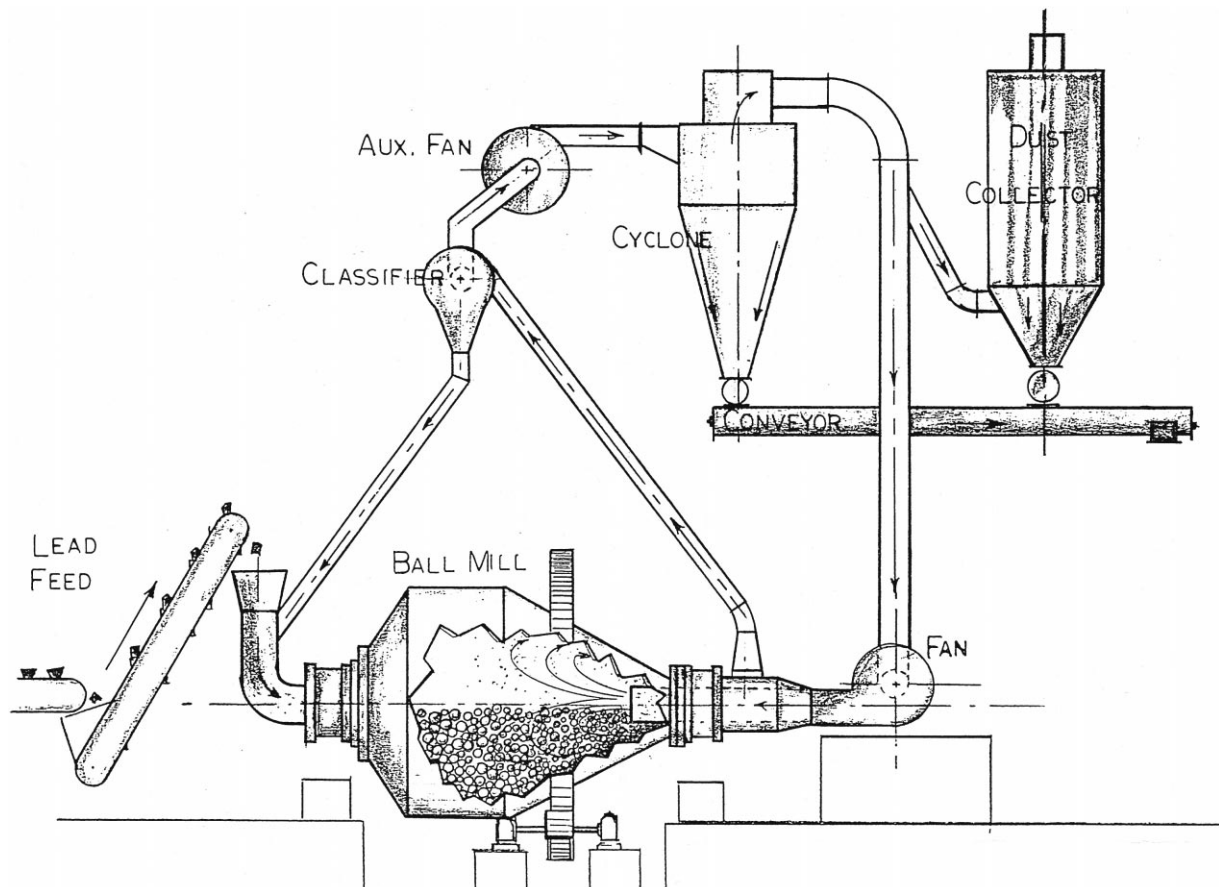


Fig. 7. Conical ball-mill system.

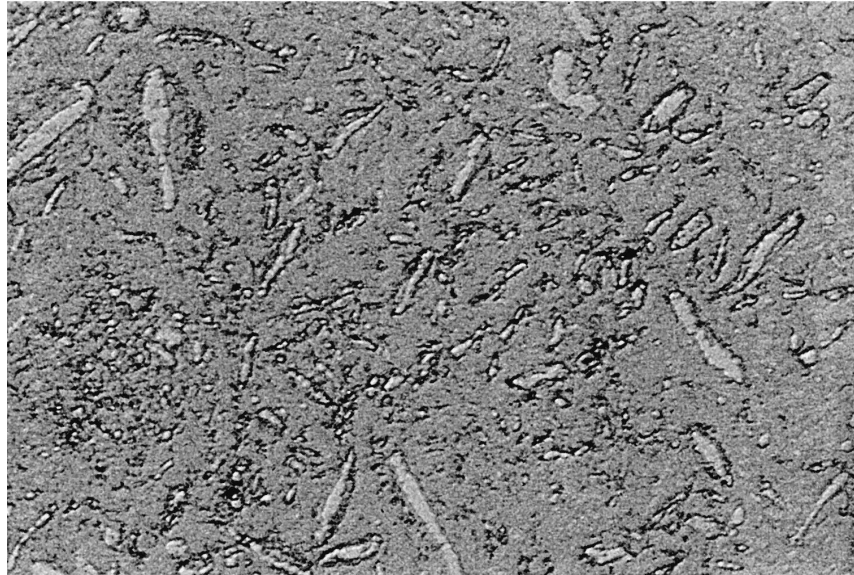


Fig. 8. Photomicrograph of ball-mill oxide.

degree of product oxidation is primarily a function of air flow through the system and, to a lesser degree, the operating temperature of the specific process. Depending upon the size of the system, a ball mill may contain as much as 20 tons of lead during operation. Any temperature adjustments that must be made are in small, incremental steps to avoid losing control of the reaction. Heat regulation and removal from the system is accomplished by drawing cooler ambient air across, and/or spraying water on the outer shell of the mill. Since the system operates below the melting point of lead, the oxide crystal formed is the low-temperature type, viz., α -PbO.

Feed material into the ball mill can be whole 50 kg ingots, ingots that have been ‘chopped’ into multiple sections, or smaller pre-cast balls. Process control parameters typically monitored are:

- mill temperature,
- mill load,
- system air flow.

Additional measurements are made of other parameters to provide better overall control of system performance.¹

The oxide particles generated in a ball mill tend to be uniquely flake and string-like in shape (Fig. 8), due to the shedding action from the ball’s surface. Some factors that influence particle size include:

- mill design (conical or cylindrical),
- production rate,
- residence time in the mill,
- air velocity,

- method and type of additional classification,
- mill speed.

4. Advances in oxide manufacturing and applications

The focus of modern designs of Barton pots and ball mills is to provide a consistent, reproducible product. Advances in the sophistication and affordability of process control systems in recent years has substantially improved machinery performance. Process control costs continue to fall while computing power, speed, software design, interface, data collection and networking systems, etc., become more effective. Present manufacturers of lead oxide equipment can offer an automated system complete with a programmable logic controller (PLC) and interactive touch screen monitor coupled with improved sensors, actuators, etc., at prices relatively unchanged from comparatively simplistic systems of a decade ago. Continuous monitoring of process variables and instant, automatic response to their fluctuation maintain reaction stability in both the Barton-pot and the ball-mill systems, and thus produce a product with a more consistent quality.

Surrounding ambient conditions of temperature and humidity affect the operation of both Barton-pot and ball-mill systems. As these conditions fluctuate daily, and also seasonally, the air drawn through the system impacts the reaction process and product. In order to maintain the oxide within product specification limits, operating settings must be adjusted to compensate accordingly. A few factories have enclosed and air-conditioned the areas that surround their oxide equipment with noticeable improvements in oxide consistency and operating stability. Recent inves-

¹ D. Del Dotto, SMC, pers. comm., 1997.

tigations into the point conditioning of inlet air on both Barton-pot and ball-mill systems, (and then correct to the ambient surroundings during operation) look to offer excellent control of the reaction.

5. Conclusions

Oxide produced by either the Barton-pot or ball-mill process will continue to dominate the available supply of battery lead oxides in the foreseeable future. So, too, will the deliberation as to the advantages or disadvantages of each type. It is more likely to expect that improvements in paste additives, curing, formation, grid design, and/or battery design will factor out differences between these two predominant manufacturing processes. One advance that has been recently reported uses plate-group compression to minimize active material expansion and resultant cracking and shedding [7]. Another explores the strengthening of grids to resist creep when rolled in a specific manner; the rolling alters the lead alloy's mechanical properties [8]. Studies continue to examine active-material additives that will provide better positive-plate porosity and mass utilization [9]. Of course, much other research continues, with promise to be useful generally or to specific aspects and types of lead/acid battery. Continuing improvements in

oxide equipment design are directed at providing the control, flexibility, and reproducibility necessary to manufacture products which meet the characteristics that industry research identifies as beneficial to battery performance.

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