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Red lead: understanding red lead in lead–acid batteries

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Abstract

The use of red lead in battery plates is not very well known to a large segment of the lead–acid battery industry. Historically, it was used in pasted and tubular positive plates in order to improve their formation time and enhance deep-cycle performance. Although the use of red lead has diminished over the last few decades, many companies are again considering the use of red lead in their plates. This article aims to give manufacturers a solid knowledge of the properties of red lead, including production and handling methods. Further, it presents an understanding of the influence in battery production, battery performance, and the cost-saving potential of red lead usage. The first part of the article is intended to explain the chemical and physical properties and fields of usage of red lead. The most widely used red lead product specifications for the battery industry are presented and explained. In the second part, the typical equipment for the production of red lead is reviewed. Raw material requirements, material handling equipment, a red lead furnace and milling are presented and discussed. The reader is taken through the production of a typical batch of red lead. Operating charts, process control data and system photos will help to understand the production process. The final part outlines an overall view of process requirements and identifies stages in lead–acid battery production that will be influenced by the use of red lead.

Keywords: Charging efficiency; Formation; Furnace; Lead–acid battery; Red lead; Reserve capacity

1. Chemical and physical properties of red lead

Red lead (Pb_3O_4), also known as minimum, trileadtetroxide or lead orthoplumbate, is normally a fine, dry, brilliant red colored solid usually used in the form of a powder. It can also be wetted and agglomerated into pellets. In contrast to other lead oxides, the lead atoms in red lead occur in two different oxidation states, i.e. Pb(II) and Pb(IV). Together with oxygen, they are arranged in a tetragonal/pseudo-Brookite type of ionic lattice (Fig. 1) [1].

Red lead is sometimes confused with the tetragonal form of leady oxide (α-PbO), which also has a red color, but actually is the raw material for the production of red lead. Red lead forms through an oxidation process when α-PbO is heated to around 450–500 °C, but decomposes to yellow litharge (β-PbO, orthorombic) when temperatures exceed 500 °C at atmospheric pressure, i.e.

$$3\alpha\text{-PbO} + \tfrac{1}{2}O_2 \rightarrow Pb_3O_4 \rightleftarrows 3\beta\text{-PbO} + \tfrac{1}{2}O_2 \qquad (1)$$

The process of converting lead oxide to red lead can be stopped at nearly any percent of oxidation, but industrially three qualities are common.

- Red lead of 25 and 75% are mainly used in lead–acid batteries, especially in stationary and traction batteries; red lead is also used in tubular plate batteries (see Tables 1 and 2).
- Red lead of 85, 97 and 98% (pigment grade) are used in protective paints but today's main applications are crystal glass, television tubes and glazes (see Table 3).

It is important to note that there are two common practices to characterize red lead. One gives the combined weight percentage of PbO_2 and PbO, while the other uses the PbO_2 amount only. Either way, the analysis is usually done with a wet chemical method or physically by X-ray defraction (see Table 4).

2. Production of red lead

2.1. Process steps

The most common method of red lead production is by a two-stage process. First, leady oxide is produced either by a

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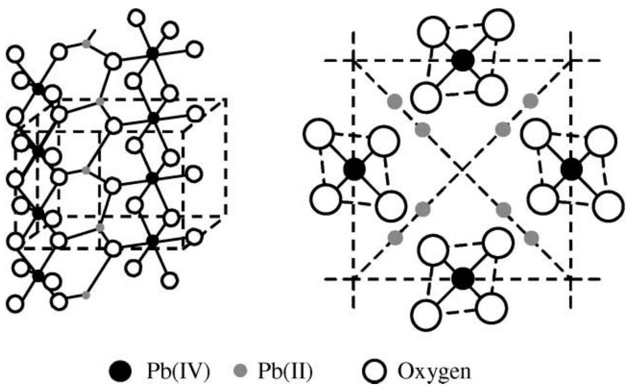

Fig. 1. Crystal structure of red lead [1].

Barton-pot or ball-mill process. In the second step, the leady oxide is oxidized further to red lead inside an oxidation device, most commonly a furnace. After the desired percentage of red lead has been reached, it is discharged and ground in a low-impact hammer mill to adjust final material specifications in particle size, particle-size distribution, acid absorption, and apparent density (see Fig. 2).

Table 1
Physical and chemical red lead data [1,2]

Characteristics	
Molecular weight	685.57
Color	Brick red/orange
Crystal structure	Tetragonal/pseudo-Brookite
Density	9.1 g cm^{-3}
Melting point	500 °C
Mohs hardness	2–3
Water solubility	6.86×10^{-9} g l^{-1}
Dielectric constant	20
Electrical conductivity	$\sim 10^{-12}$ Ω^{-1} cm^{-1}

Table 2
Battery grade red lead specifications [2]

Properties	Pb_3O_4	
Pb_3O_4 (wt.%)	25	75
PbO ($\alpha + \beta$) (wt.%)	75	25
Pb (wt.%)	2.5 maximum	0.5 maximum
Acid absorption (mg g^{-1})	170–200	200–230
Apparent density (g cm^{-3})	1.2–1.5	1–1.2
Median particle size (μm)	3.0	2.0

Table 3
Pigment grade red lead specifications

Properties	Pb_3O_4 pigment grade
Pb_3O_4 (wt.%)	85, 97, 98
Color	Brick red/orange
Apparent density (g cm^{-3})	0.9–1.2
Median particle size (μm)	2.0

Table 4
Different red lead characterization

Pb_3O_4 (%)[a]	PbO_2 (%)[b]	Pb_3O_4 (%)	PbO_2 (%)
5.0	1.7	55.0	19.1
10.0	3.5	60.0	20.9
15.0	5.2	65.0	22.6
20.0	7.0	70.0	24.4
25.0	8.7	75.0	26.1
30.0	10.4	80.0	27.8
35.0	12.2	85.0	29.6
40.0	13.9	90.0	31.3
45.0	15.7	95.0	33.1
50.0	17.4	100.0	34.8

[a] Total amount of red lead in mixture (wt.%).
[b] Amount of PbO_2 only (wt.%).

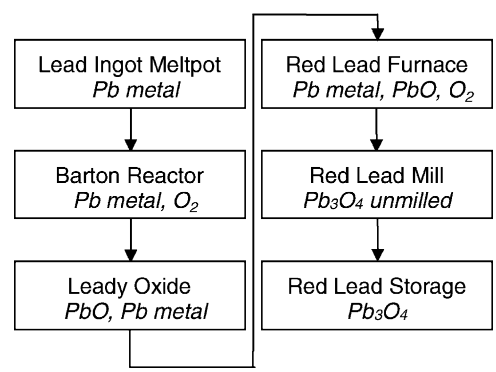

Fig. 2. Schematic of red lead production process.

2.2. *Raw material*

Historically, yellow litharge (100% β-PbO, 0% Pb) was the raw material for the red lead production. Today, most industrial manufacturers of red lead use leady oxide as feed material. The free-lead content of the feed material can range from 5 to 30%, which makes the production equipment for red lead an ideal solution for out-of-specification material from Barton-pots or ball-mills.

2.3. *The red lead furnace*

Different equipment for the production of red lead has been developed and used over the years. Nearly all of it has incorporated the same basic principle of an oxidation process that requires lead oxide, oxygen, temperature, and time. One of the most widely used devices is the furnace, either gas or electrically heated. The following description outlines the operation of the electrically heated red lead furnace produced by eagle oxide.

The electrical red lead furnace is a refractory-lined batch oven with a totally enclosed reaction chamber (Fig. 3). It has a vertical drive shaft that supports and turns agitator arms to stir the batch lying on top of a furnace pan. The batch temperature is controlled by electric heating elements

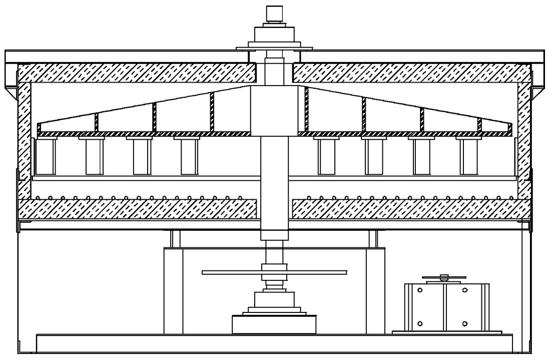

Fig. 3. Electrically-heated red lead furnace produced by eagle oxide.

located below the reaction chamber, mostly used during the pre-heat stage of the process. The raw material is introduced through the sidewall or the top of the furnace by a screw conveyor. Temperature control inside the furnace is accomplished by an actuated butterfly valve in the exhaust stack. The furnace is under negative pressure during operation.

2.4. The four-step production process

The operation of the red lead furnace is a batch process that is divided into four sub-processes.

2.4.1. Pre-heat

Before the first batch, the furnace must be pre-heated to operating temperature. This is accomplished with electrical heating elements. Once a batch of leady oxide is inside the furnace, the output of the heating elements is greatly reduced (or off), because the exothermic reaction generated by the oxidation of Pb to PbO supplies sufficient heat for the oxidation process. After discharging the finished product, the efficiency of the furnace design allows the pre-heat time to be less than 2 min between batches.

2.4.2. Furnace charging

Leady oxide is charged into the furnace by a screw conveyor at an adjustable feed rate so that a constant heat rate is produced by the exothermic conversion of free-lead. High reaction temperatures favor β-PbO formation, therefore, it is important to avoid these conditions in order to maintain a satisfactory production rate. Since the feed material is introduced into the furnace at ambient temperature, the reaction temperature at the beginning of the batch decreases (see Fig. 4). During this period the heating elements keep the furnace pan hot in order to bring the material up to reaction temperature.

2.4.3. Reaction

Once charging has stopped, the reaction time begins. During this step, the material 'cooks' inside the furnace. The free metal oxidizes, forming PbO, and causes the reaction temperature to increase [3], i.e.

$$Pb + \frac{1}{2}O_2 \rightarrow PbO, \quad \Delta G^\circ = -190\,\mathrm{kJ/mol} \qquad (2)$$

The batch stays inside the furnace until the desired percentage of lead(II) oxide has oxidized to red lead, i.e.

$$3PbO + \frac{1}{2}O_2 \rightleftarrows Pb_3O_4 \qquad (3)$$

2.4.4. Furnace discharging

During the reaction period, the charge is tested periodically. As the desired amount of red lead is reached, the material is discharged into a screw conveyor and conveyed into a storage tank (Fig. 5). After the reaction chamber temperature recovers, the furnace is ready to be re-charged.

2.5. Red lead milling

Red lead is milled or ground to adjust customer specifications in particle size, particle size distribution, acid

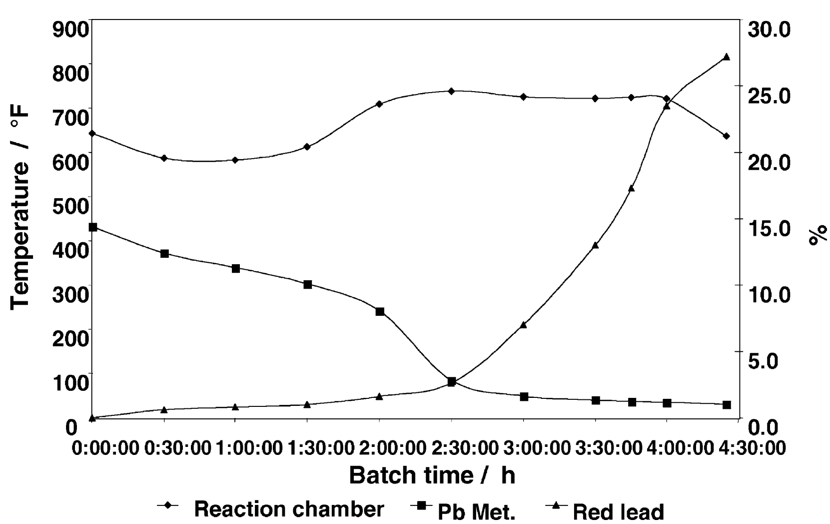

Fig. 4. A 25 wt.% red lead batch.

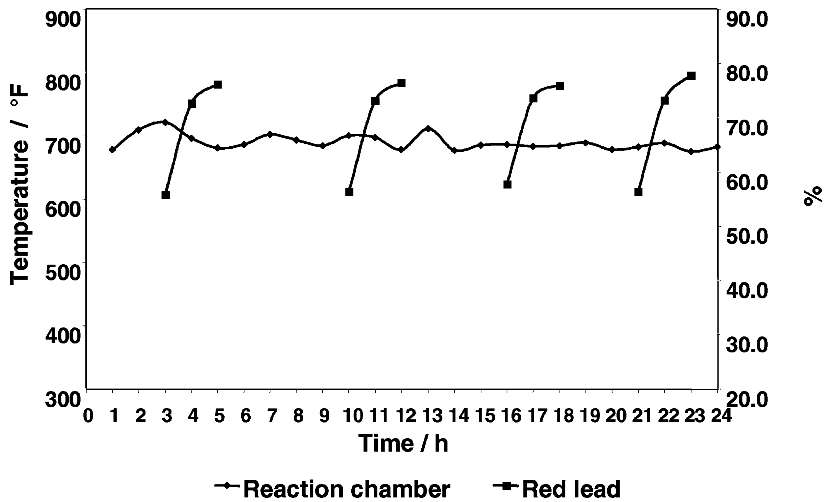

Fig. 5. A 75 wt.% red lead batch repeatability.

Table 5
Batch information for typical red lead specifications

	Batch size (kg)	Batch time (h)
25 wt.% red lead	2700	4–5
75 wt.% red lead	2700	5–6
Pigment grade	2700	12–14

absorption and apparent density. For this last step, a low impact hammer-mill provides enough grinding effect to achieve typical specifications.

2.6. Different red lead qualities

The batch sizes and times for the three primary red lead qualities are listed in Table 5. Batch duration and sizes vary, depending on customer specifications, in β-PbO and free-lead content, apparent density, acid absorption, etc.

3. Influence of red lead in lead–acid batteries

3.1. Changes in pasting, curing, formation and performance of positive plates

Technically, paste-mixing, curing and formation equipment remain the same when leady oxide is substituted with red lead in the active material. There are some red lead characteristics, however, that very positively influence the manufacturing and quality of positive lead–acid battery plates, especially in stationary, traction and valve-regulated (VRLA) batteries.

A recent project of the advanced lead–acid battery consortium (ALABC) conducted by Tudor Battery of Spain concludes that: 'the effect of red lead is clearly seen from the beginning, by improving the electrical performance at all rates and temperatures and not having any detrimental effect ...' [4]. The positive influences of red lead can be summarized as follows.

3.1.1. Oxide stability

With less than 2% of free lead left in the red lead, the oxide experiences little or no further oxidation. The oxide composition is stable and predictable for long periods of time. There is no need for multiple laboratory analyses to verify characteristics after manufacturing or shipping and storage.

3.1.2. More efficient formation

Under the right conditions, red lead can be transformed into $\beta\text{-}PbO_2$ in pasting according to the reaction [5]:

$$Pb_3O_4 + 2H_2SO_4 \rightarrow \beta\text{-}PbO_2 + 2PbSO_4 + 2H_2O \quad (4)$$

This reaction results in the presence of small $\beta\text{-}PbO_2$ seed crystals [6] that promote a more efficient transformation of the entire active mass. Thus, the use of red lead in upstream processes can save valuable time and energy in the formation process.

In addition, red lead increases the content of PbO_2 during formation (at lower temperatures of formation), as shown in Fig. 6 [4]. Because of the higher capacity of red lead batteries, the coulomb and energy efficiency is improved, as demonstrated in the fast charge test conducted in the ALABC project [4] (see Fig. 7).

3.1.3. Higher initial capacity

It is believed that $\beta\text{-}PbO_2$ crystals have a greater discharge capacity than $\alpha\text{-}PbO_2$ [4]. Specifically, $\beta\text{-}PbO_2$ crystals are finer and are thought to have greater electrochemical activity and therefore provide higher effective initial capacity to the battery [7].

Since red lead forms $\beta\text{-}PbO_2$ crystals, its use improves the initial capacity especially for stationary and industrial batteries, as well as for VRLA batteries. In Fig. 8, the authors of

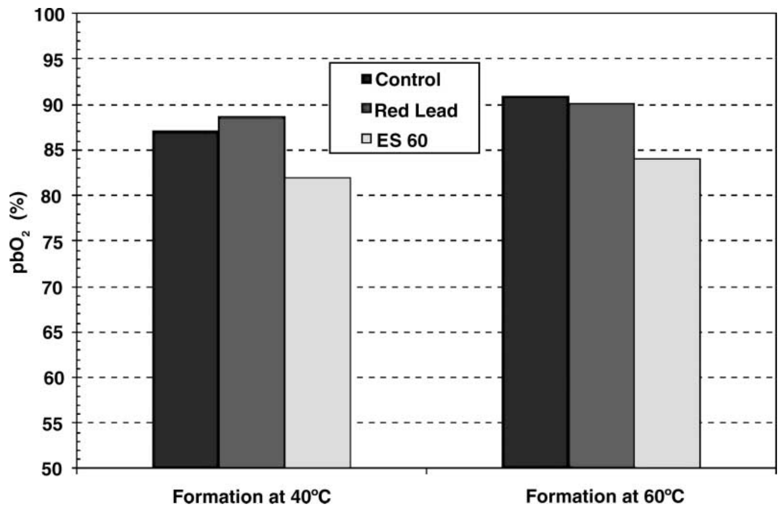

Fig. 6. Increase in PbO_2 content after formation.

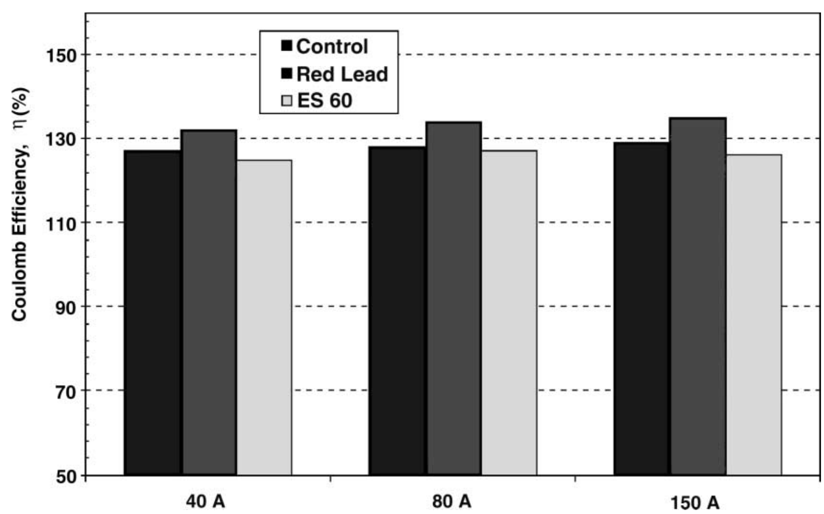

Fig. 7. Charging efficiency (fast charge tests at 40 °C).

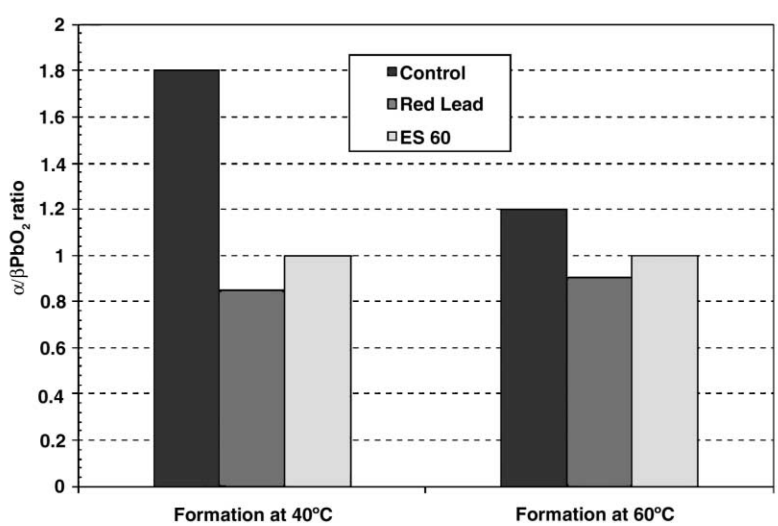

Fig. 8. PbO_2 ratio in positive active mass.

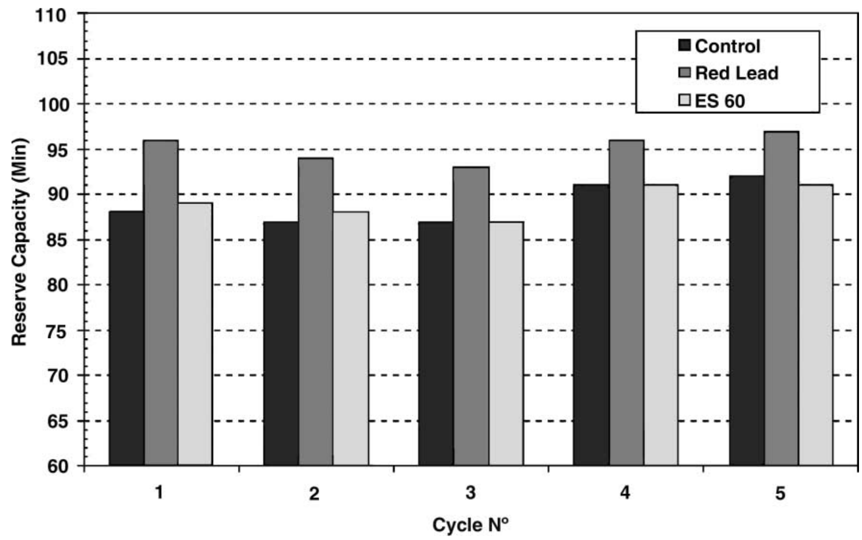

Fig. 9. Initial reserve capacity.

the ALABC project [4] demonstrate the effect of red lead addition on the α-PbO_2:β-PbO_2 ratio after formation.

3.1.4. Reserve capacity and cycle life

Due to the higher initial capacity of batteries manufactured with red lead, the reserve capacity also increases. The ALABC study [4] shows increases in reserve capacity and cycle performance using red lead as an additive in positive plates (see Figs. 9 and 10). The report notes: 'the capacity obtained from the red lead prototypes was significantly higher than that obtained from the standard ... batteries'.

3.1.5. Easier curing control

With less than 2% of free metal left in red lead, the curing process is more predictable. The exothermic heat associated with free lead oxidation is eliminated. This makes it easier to manage the thermal energy in curing and thereby manage the size and shape of the resulting tribasic (3BS) and tetrabasic (4BS) lead sulfate crystals [6]. This is especially important for 4BS curing where recent studies have found that the control of 4BS crystal size is critical to good formation efficiency and battery capacity.

3.1.6. Reproducibility and conformity

With hardly any free metal in the paste mix material, the reproducibility in pasting and curing is greatly improved. Normally, parts of the free metal lead already start to oxidize during paste mixing and continue in pasting and curing. The amount of metal lead being oxidized at each step varies and as a result, characteristics of finished plates show variability, as do cells built of these plates.

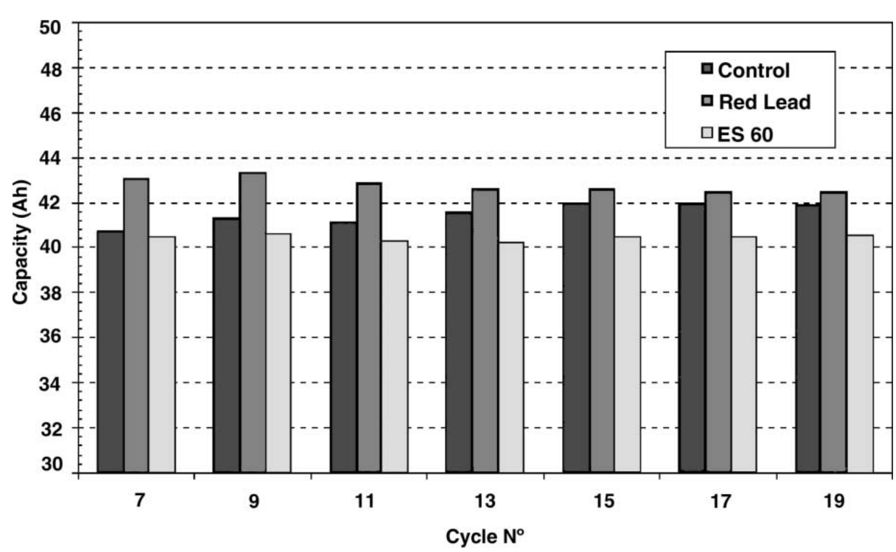

Fig. 10. Capacity and cycling behavior.

3.1.7. Red lead with high β-PbO content

Lead oxide with higher β-PbO content is favorable for stationary and traction batteries since it results in more 4BS crystals after curing and therefore adds to their high cycle-life requirements. Red lead furnaces can be adjusted to produce material with certain amounts of β-PbO. Consequently, the 3BS:4BS ratio adjustment in pasting and curing is more controllable with the use of red lead.

3.1.8. Increased production efficiency

- A shorter curing time will result in faster production, smaller inventory and less storage space. It will also reduce the amount of curing equipment that is needed.
- Better reproducibility provides higher plate-to-plate conformity, fewer rejections, and improves the overall quality.
- With a shorter formation time, the electricity consumption is lowered and less formation equipment is needed. Additionally, smaller amounts of fumes and gases are produced.

3.2. Application differences between 25 and 75 wt.% (or greater) red lead

The battery industry uses red lead in two different ways:

(i) a high percentage red lead (>70 wt.% Pb_3O_4) can be blended into the paste mixture (typically 10–35 wt.%) to produce the desired amount in the finished plate; or
(ii) the paste is directly made from a lower percentage red lead (∼25 wt.% Pb_3O_4) which is substituted for leady oxide in the paste mix batch.

Either way, paste mixing and plate processing are very similar to those with conventional leady oxide. Higher oxidized red lead has smaller particle sizes and higher acid absorption. As a result, more improvements in plate performance are obtained when a mixture of higher oxidized red lead is used in the paste mix.

4. Conclusions

- The process of making red lead has greatly improved. Today, it can be better controlled and, thereby, increases the production rate and makes the equipment cleaner and easier to use.
- With program logic control, a man machine interface and modem dial-up options, state-of-the-art equipment is readily available.
- Red lead can be used to improve initial capacity, reserve capacity and cycle life of batteries.
- The cost/benefit ratio for the application of red lead has altered over the last years and could presently favor the benefits. With today's higher expectations towards lead–acid batteries, red lead could increase the battery quality and become an alternative to installing additional curing and formation equipment.
- Conveyed either mechanically or pneumatically, the material handling of red lead is similar to that for leady oxide and is both simple and clean.

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