

## IMPROVING THE CURING OF POSITIVE PLATES FOR LEAD/ACID BATTERIES

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### Introduction

#### *Plate production processes*

Flat positive plates for lead/acid batteries are produced by applying a paste of 'leady oxide', water, and diluted sulphuric acid onto a lead or lead-alloy grid structure. The leady oxide is made by either the Barton-pot or the ball-mill process and usually comprises about three-parts lead monoxide ( $\alpha$ -PbO and  $\beta$ -PbO) to one-part fine lead particles (so-called 'free lead') [1]. The relative amounts of each constituent can be controlled by manipulation of the operation parameters governing the oxide-making process, *i.e.*, lead feed rate, air flow and temperature. Sometimes, the oxide is blended with a minor percentage of red lead ( $Pb_3O_4$ ) as well as with certain proprietary additives that are thought to benefit the manufacturing procedure and/or battery performance.

It has been claimed [2, 3] that during paste mixing, the free lead (and any  $Pb_3O_4$ ) remains largely unchanged. On the other hand, a significant proportion of the PbO converts to basic sulphate. The latter, encompassing the following three varieties, serves to consolidate the paste: monobasic lead sulphate,  $PbO \cdot PbSO_4$  (=1BS); tribasic lead sulphate,  $3PbO \cdot PbSO_4 \cdot H_2O$  (=3BS); tetrabasic lead sulphate,  $4PbO \cdot PbSO_4$  (=4BS). Formation of 1BS occurs either when an excess of acid is used or, in normal paste formulations, when local pH values fall due to poor mixing. Care is taken to minimize the development of 1BS since the compound is harmful to plate performance [4-6]. In summary, the results of published studies [2, 3, 7-20] variously assert that the relative amounts of 3BS and 4BS in the paste are influenced

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by the properties of the starting oxide (composition, morphology, particle size, etc.), the quantities of water and sulphuric acid added, the maximum mixing temperature, the mechanics of mixing (method of acid addition, type of mixer, etc.), and the duration of the process. Of these, temperature is the main determinant: the rate of formation of 4BS is appreciable only above  $\sim 70^\circ\text{C}$  [1, 11 - 14, 16 - 19]. Manufacturers generally find it necessary, however, to keep the temperature below  $\sim 50^\circ\text{C}$  (by using water-cooled jackets or by addition of excess water together with accelerated evaporation under forced air flow) in order to produce a paste with good consistency and plasticity. Thus, at the end of processing, the paste usually consists of a mixture of unreacted starting materials and 3BS.

After application to the grids, the moist plates are 'flash dried' in a tunnel oven (to dry the surfaces and thereby improve handleability) and then placed in a chamber for 'curing' under set conditions of humidity and temperature for a given time [21]. Investigations have shown [2, 6, 13 - 15, 22 - 31] that at least four reactions can occur either separately or simultaneously during the curing process:

- (i) conversion of metallic lead particles to  $\alpha\text{-PbO}$  with the liberation of heat;
- (ii) progressive growth of basic lead sulphate crystals;
- (iii) development of basic lead carbonates (*e.g.*, hydrocerussite,  $2\text{PbCO}_3 \cdot \text{Pb(OH)}_2 = \text{HC}$ ), especially on the surface of the plate material;
- (iv) corrosive attack of the metal grid.

These reactions cause the plate material to harden and form a strong bond with the grid.

The chemical composition of the cured plate is largely dependent on the temperature and humidity conditions applied during the process. At curing temperatures below  $\sim 70^\circ\text{C}$ , the predominant species are 3BS and unreacted  $\text{PbO}$ . As with pastes, 4BS is found to occur at higher temperatures [6, 14, 15, 25 - 30], provided sufficient water is present and sufficient time is allowed for the chemical reaction to develop. Pierson [25] appears to have been the first to suggest that 4BS is formed by direct recrystallization of 3BS. At the termination of plate curing, it is recommended [32] that free lead and moisture contents should not exceed 2 and 1 wt.%, respectively.

The change in phase chemistry at high temperatures and humidities markedly affects the morphological, mechanical, and electrochemical properties of the cured mass. In general, finely-divided crystals of 3BS are replaced by larger crystals of 4BS; both types of crystal have an elongated, prismatic form. As early as 1966, Burbank [23] showed that the latter crystals interlock to provide a rigid network that is maintained during plate formation (*i.e.*, the transition to  $\text{PbO}_2$  is metasomatic) and, consequently, imparts additional mechanical strength to the plate material. On the other hand, the larger crystals slow the formation process and reduce the initial capacity during cycling. The suggestion that the reticular structure in the formed plate is composed of  $\alpha\text{-PbO}_2$  [33, 34], together with the arguments of Pierson [15], have given rise to the popular belief that 4BS favours the formation of this

polymorph. Culpin [35] has recently pointed out, however, that the weight of experimental evidence is against this view. Nevertheless, it has been shown [36] that, when all other physical and chemical characteristics of the plate material are kept constant, the  $\alpha$ -PbO<sub>2</sub> content can exert a beneficial effect on plate cycle life under deep-discharge service, with the optimum  $\alpha$ -PbO<sub>2</sub>: $\beta$ -PbO<sub>2</sub> weight ratio (at the completion of formation) lying in the vicinity of 0.8. In summary, acknowledgement of the importance of cured-plate composition on battery performance has created a rule-of-thumb that 3BS-rich material gives capacity, and is therefore appropriate to the manufacture of automotive batteries, while 4BS-rich material gives cycling capability and should be used for industrial batteries.

### *Optimization of plate curing*

The foregoing discussion demonstrates that the chemical composition and morphological structure of the plate material are both strongly dependent upon processing history, and that these two features are of great importance to capacity and mechanical stability during service. Most battery-makers recognize curing as being the critical stage in the production of pasted plates. As a result, technical know-how is usually kept proprietary and very little information is published on strategies aimed at controlling plate curing in the factory to yield material with preferred chemical species and optimum morphology/porosity. Interestingly, curing processes are also becoming relevant to tubular-plate manufacture, given the increasing trend towards replacing the hazardous traditional method of filling tubes with dry oxide by cleaner, slurry-injection techniques. The latter approach allows a controlled curing stage (as opposed to a simple drying procedure) to be added before the normal pickling process so that the possible advantages of 3BS/4BS formation can be imparted to the tubular-plate material.

Factory experience has shown that it is extremely difficult to regulate the conditions of the curing process, particularly the temperature of the individual plates, so that good consistency of product is obtained. Furthermore, in the interests of gaining greater efficiency in battery manufacture, there is a strong desire within the industry to reduce the period presently devoted to curing (typically 72 h). To date, progress in both areas has been hindered by the absence of a precise and fairly rapid technique for quantitatively monitoring the effects of changes in the process parameters on the phase chemistry of the cured material. This deficiency has now been overcome through the development of a simple and user-friendly X-ray diffraction phase-analysis procedure during CSIRO research studies of lead/acid plate materials [1, 36-40]. The new technique (known as 'PEAKS<sup>®</sup>') provides manufacturers with a universal method for measuring the changes in phase chemistry that accompany *all* stages of plate preparation and service (see below for details). This facility offers both immediate and future economic advantages to the battery industry in that processing problems can be diagnosed at source, product consistency can be monitored, and advanced strategies can be explored for reducing work-in-progress and maximizing

product performance. As an example, this paper describes a campaign in which PEAKS® was used to determine quantitatively the progressive changes in phase composition of wet-filled tubular plates during curing under normal factory conditions. It will be seen that the resulting data have provided new scientific information that will assist attempts to improve the performance of tubular plates through the inclusion of a regulated curing procedure.

## Experimental

### *Tubular-plate production*

The tubular plates were of a 15-tube gauntlet design and were filled by injection of a slurry of blended leady oxide/red lead ( $\sim 4:1$ ), water, and diluted sulphuric acid. The leady oxide was produced by the ball-mill process and, typically, consisted of 68 wt.%  $\alpha$ -PbO and 32 wt.% Pb. After filling, the plates were suspended, without forced drying, in two adjacent rows on a rack; each row contained about 120 plates. The total production run required nine such racks (termed here R1 to R9) and was completed in an 8 h shift. The racks were set aside under ambient conditions during the plate-filling procedure and then were transferred to the curing chamber in the sequence shown in Fig. 1. Five of the racks were fitted with thermocouples that gave readings of the local temperature at successive one-hourly intervals. Samples of material were taken (see below) from plates situated close to these thermocouples. A number of plates residing in the back corners of the chamber (*i.e.*, in racks R2 and R3) and close to the door (*i.e.*, rack R6) were replaced by freshly-filled examples from rack R9 in order to provide a uniform benchmark for comparisons of location effects. After loading, the chamber was sealed and the temperature set to 55 °C. The humidity was provided by the moisture content of the plates themselves, rather than by installing a humidifier in the chamber's air-circulation system.

In summary, the objective of the above strategy was to investigate the influence of the following factors upon the nature of the chemical species produced during progressive stages of the paste-mixing, tube filling, and curing processes:

- (i) paste ageing prior to curing — by comparison of analytical data for samples taken from racks R1 and R9;
- (ii) curing time — by removing samples from racks R1 and R9 at given intervals after placement in the curing chamber;
- (iii) temperature variations within the chamber and, hence, plate location — by comparison of analytical data from racks R2/R3, R1/R9 and R6.

### *Sample collection and preparation*

Plates were removed periodically from the curing chamber and, in each instance, a sample was taken from the centre of the seventh tube (counting from the lug) of the 15-tube array. Further curing of the extracted material was halted by rapid treatment, first with distilled water (to remove acid) and

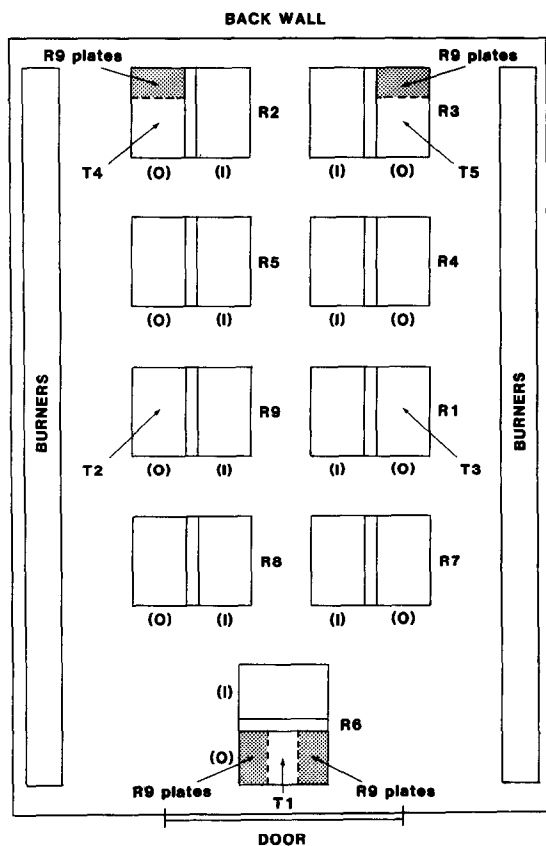


Fig. 1. Arrangement of plate racks in curing chamber. (I) = inner row and (O) = outer row of rack. T1 to T5 indicate positions of thermocouples.

then with absolute ethanol (to remove water), followed by drying in a desiccator [41]. When dry, a portion of each sample was gently ground, using a pestle and mortar, and then pressed into a standard X-ray sample holder appropriate for a Philips diffractometer. Pore-size and surface-area measurements were conducted on selected samples using procedures described previously [1]. The morphology of the cured material was examined with a JEOL JSM-25S III scanning electron microscope.

#### *X-ray phase analysis*

Samples of leady oxide, paste, and filled-tube material at various stages of curing were analyzed by the new X-ray diffraction phase-analysis method, PEAKS<sup>®</sup>, developed [42] in the CSIRO Division of Mineral Products under sponsorship from Pasminco Metals Pty Limited. PEAKS<sup>®</sup> is capable of determining the relative abundance of any of the 11 lead phases commonly

encountered at various stages in the manufacture and service of lead/acid plate materials, *i.e.*, Pb,  $\alpha$ -PbO,  $\beta$ -PbO, Pb<sub>3</sub>O<sub>4</sub>, 1BS, 3BS, 4BS, PbSO<sub>4</sub>, HC,  $\alpha$ -PbO<sub>2</sub>,  $\beta$ -PbO<sub>2</sub>. Except in the case of lead (see below), the accuracy of the method is  $\pm 10\%$  (relative) for each phase. It should be remembered that, in general, PEAKS<sup>®</sup> data refer only to crystalline phases and not to amorphous components [39]; the amount of amorphous material can, however, be determined if a known weight of an absent phase (not Pb) is added as an internal standard or 'spike'. The analytical software has been written for operation on an IBM-compatible personal computer; it is easy to use and simple to learn. The system is driven by a very user-friendly menu that produces a virtually instantaneous analysis on the computer screen. The data can be dumped to a printer or stored on file for access later.

The methodology of PEAKS<sup>®</sup> is based on techniques previously developed at CSIRO [1, 36-40], but requires only the diffraction peak heights rather than their complete integrated intensities. This simplifies significantly the data-collection procedure. The values of the heights (on any arbitrary scale) of 20 diffraction peaks are inputted directly to PEAKS<sup>®</sup> via a keyboard in response to the prompt from a simple menu. The heights may be obtained either from the diffraction pattern (by simple measurement), or from the list of values produced by the diffractometer software itself. PEAKS<sup>®</sup> then corrects the input data for background and peak overlaps, averages the intensities of up to three peaks for each phase, and finally normalizes the data for differences in phase-scattering power using a pre-determined set of calculated 'reference intensity ratios' [37].

In the study reported here, data were collected on a Philips diffractometer with Cu K $\alpha$  radiation over the angular range 5 - 60° 2 $\theta$  and at a scan rate of  $\sim 4^\circ \text{ min}^{-1}$ . Standard PW1710 software was used to provide a list of peak heights and positions on an on-line printer. The peak-height values were then keyed into the PEAKS program that was running on a personal computer adjacent to the diffractometer. The results were disposed to a second printer while the next diffraction pattern was being collected. The raw data were subsequently re-analyzed, with the incorporation of independent measurements of the free-lead content that were obtained a short time later from differential scanning calorimetry and/or wet-chemical methods. This procedure is recommended (though not essential) since the free-lead content is notoriously difficult to determine accurately from X-ray measurements alone [1]. The additional analytical work is not prohibitive as most manufacturers routinely monitor free-lead levels during plate curing.

## Results and discussion

### *Effect of stand time on plate composition*

As mentioned above, the filled tubular plates were set aside under ambient conditions until the production run was completed. Thus, although the paste was taken from the same bulk supply, its residence time in the

TABLE 1

Phase analysis for wet-filled tubular plates (rack R1 in Fig. 1) during increasing stand period under ambient conditions

Stand time (h)	Pb (wt.%)	$\alpha$ -PbO (wt.%)	$\beta$ -PbO (wt.%)	Pb <sub>3</sub> O <sub>4</sub> (wt.%)	3BS (wt.%)	4BS (wt.%)
0	13	12	4	9	59	3
2	17	8	4	10	56	5
4	12	14	4	9	57	4
6	8	12	4	8	64	4
8	14	12	3	8	59	4
Oxide blend	24	56	—	20	—	—

tubes varied by up to 8 h. An investigation was made to determine whether such a delay before curing exerted an influence on the plate composition. Accordingly, phase analyses were conducted every 2 h on samples taken from plates at successive and equal intervals along each of the two rows in rack R1. It was found that there was little difference in composition between adjacent plates in the inner and outer rows. Moreover, the paste had already reached a stable composition during mixing and remained virtually unchanged throughout the stand period (Table 1). At the final stage, the material consisted principally of 3BS (~60 wt.%) and unreacted free lead and oxide, together with a small amount of 4BS ( $\leq 5$  wt.%). Relative to flat-plate types, the tubular design is expected to restrict the access of oxygen to the material and, hence, increase the resistance of lead particles to oxidation. Despite this, approximately half of the free lead reacted during mixing (*i.e.*, from 24 to about 13 wt.%, Table 1). Furthermore, although red lead is generally considered to be inert during mixing, the proportion of this phase was likewise reduced—from an initial value of 20 wt.% in the oxide blend (15 wt.% after other paste ingredients were added) to about 9 wt.% after mixing.

#### *Effect of curing time on plate composition and morphology*

Plots of the quantity of 3BS and 4BS *versus* time, in plates taken from the first (R1) and last (R9) batches after loading into the curing chamber at 55 °C, are given in Fig. 2(a) and (b), respectively. In each case, there is a sharp transformation of 3BS to 4BS. This change in composition commences sooner for freshly-filled plates (probably because a higher moisture level has been retained) and is more rapid when plates are placed closer to the burners (*i.e.*, outer plates). In all cases, the transformation is completed within 24 h.

The quantity of 4BS is in excess of that of the starting 3BS, especially in aged plates. This observation differs from that of Pierson [25] who, for flat plates, found that the 3BS was replaced by an approximately equal

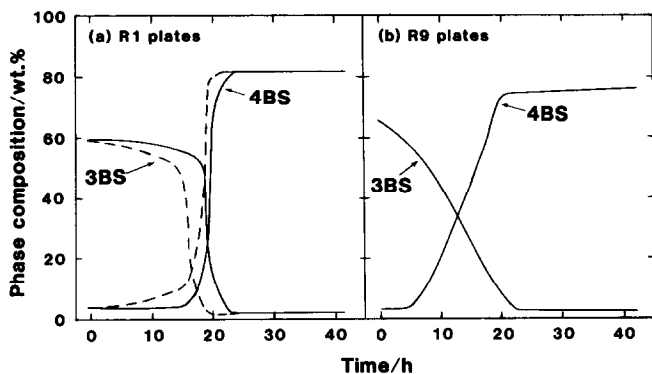
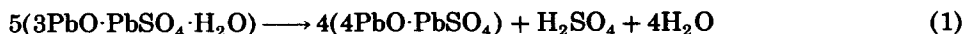


Fig. 2. Change in basic lead sulphate content during plate curing: —, inner plates; ---, outer plates in a given rack.

amount of 4BS, as expected according to the equation [17]:



At the end of curing, it is noted that the contents of Pb,  $\alpha$ -PbO and  $\text{Pb}_3\text{O}_4$  have all declined in the plates contained in racks R1 and R9 (Table 2) relative to the values prior to loading into the curing chamber (Table 1). Thus, the increased yield of 4BS could result from several sulphation reactions initiated by the  $\text{H}_2\text{SO}_4$  released during the conversion of 3BS to 4BS (eqn. (1)), namely: (i) oxidation/sulphation of residual free lead; (ii) reduction/sulphation of  $\text{Pb}_3\text{O}_4$  in concert with reaction (i); (iii) sulphation of  $\alpha$ -PbO. Whether these reactions proceed directly to 4BS, or via an intermediate 3BS phase, remains to be established.

The change in the crystal morphology of the plate material with curing time is shown by the scanning electron micrographs given in Fig. 3. It can be seen that large, elongated, prismatic 4BS crystals (Fig. 3(d)) of length up to

TABLE 2

Phase analysis for freshly-filled plates after curing in different parts of the chamber

Plate location	$T_{\text{max}}^a$ (°C)	Pb (wt.%)	$\alpha$ -PbO (wt.%)	$\beta$ -PbO (wt.%)	$\text{Pb}_3\text{O}_4$ (wt.%)	3BS (wt.%)	4BS (wt.%)	HC (wt.%)
Back left (R2)	75	5	25	8	17	28	12	5
Back right (R3)	70	5	27	12	15	33	3	5
Centre left (R9)	80	1	8	3	5	1	82	—
Centre right (R1)	65	1	9	2	4	2	82	—
Front left (R6)	n.d.	—	21	5	14	—	56	4
Front centre (R6)	72	—	17	4	13	5	58	3
Front right (R6)	n.d.	—	23	2	14	—	57	4

<sup>a</sup> Maximum plate temperature during first 24 h of curing.  
n.d. = not determined.



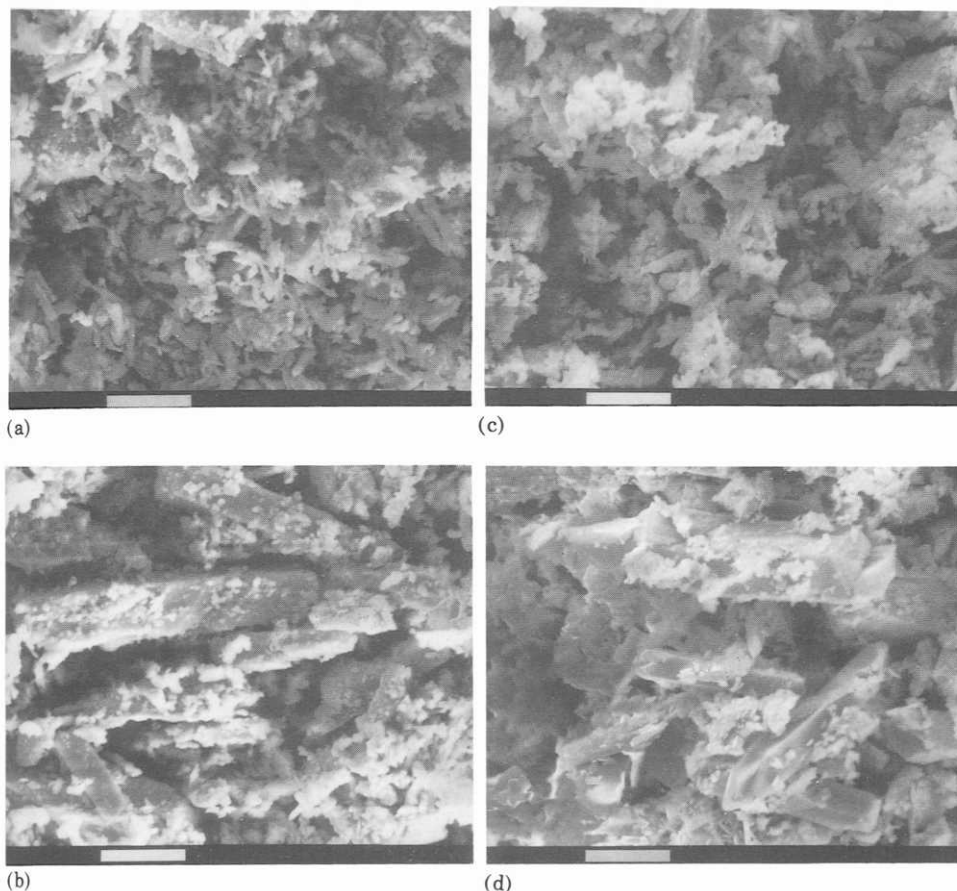


Fig. 3. Scanning electron micrographs of progressive changes in the morphology of cured material with time: (a) 2 h; (b) 18 h; (c) 20 h; (d) 22 h. Phase composition: (a) 65 wt.% 3BS, 4 wt.% 4BS; (b) 50 wt.% 3BS, 23 wt.% 4BS; (c) 25 wt.% 3BS, 58 wt.% 4BS; (d) 2 wt.% 3BS, 83 wt.% 4BS.

35  $\mu\text{m}$  evolve from the initial loose aggregates of smaller ( $< 10 \mu\text{m}$ ), similarly shaped, 3BS crystals (Fig. 3(a)). This observation is in accordance with the studies of other workers [17, 25, 26, 29, 43]. Surface-area and porosity data for the same suite of samples are presented in Fig. 4(a) and (b), respectively. The decrease in surface area with progressive development of 4BS is consistent with the concomitant increase in the average pore diameter. When prepared for flat plates, cured pastes containing 4BS have also been found to have a large average pore diameter [17]. On the other hand, the observed decrease in the total pore volume of material with 4BS-enrichment is opposite to that reported for flat plates [17, 27]. This suggests that 4BS crystals are less impervious and/or form more compact aggregates when produced within the confines of the tubular-plate design.

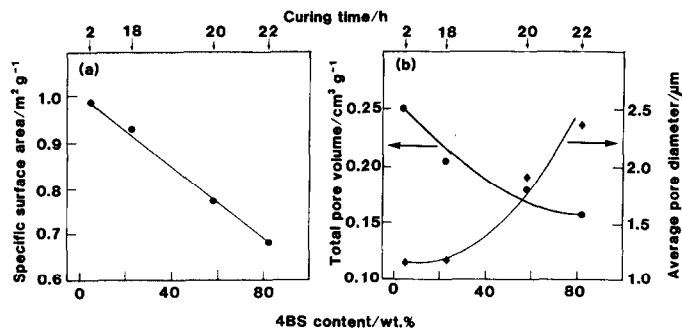


Fig. 4. Surface area and porosity of cured material as a function of 4BS content and curing time.

#### Effect of plate location on plate composition

The data in Table 2 provide a comparison of the end-of-cure phase composition of freshly-filled plates placed in the outer rows of racks in the back two corners (R2, R3), the centre (R1, R9), and the front (R6) of the curing chamber, see Fig. 1. Although all the plates are from the same source (rack R9), and therefore can be assumed to have the same initial phase composition, there are marked differences in the final cured composition with plate location. It is necessary to consider these phase variations in conjunction with the thermal conditions experienced by the plates (Fig. 5).

The initial rise in temperature is due to heating of the chamber as well as to oxidation of the free lead. Comparison of Figs. 2 and 5 shows that the phase transformations within the plate material are completed at about the time the plate temperature reaches a maximum value,  $T_{\text{max}}$ . There is, however, no direct relationship between  $T_{\text{max}}$  and the yield of 4BS (Table 2). This is particularly true at the back of the chamber where only negligible amounts of 4BS are produced despite the plate temperature reaching values in excess of  $70^\circ\text{C}$ . In addition, during the early stages of curing, the plates in this location do not display the sharp temperature peak that is experienced by plates in the centre and front of the chamber (Fig. 5). This suggests that the sharp rise in temperature may be associated with the conversion of 3BS to 4BS, and that the conditions at the back of the chamber are sufficiently different from those prevailing elsewhere to prevent this chemical reaction from occurring to the same extent. (Note, however, published thermodynamic data [44] indicate that the 3BS/4BS reaction is endothermic.) In this connection, it is seen that the  $\alpha$ -PbO,  $\beta$ -PbO and  $\text{Pb}_3\text{O}_4$  contents of racks R2 and R3 are higher at the end of cure than in the paste (*cf.* Tables 1 and 2). One possible reason for this unexpected phase composition is that, without external humidity control, the plates at the back of the chamber dry out rapidly and the temperature remains uniformly high over a sufficient period of time for the 4BS, produced initially during the temperature rise, to be rendered unstable, breaking down to 3BS, PbO and  $\text{Pb}_3\text{O}_4$  (with the assistance of oxygen). This may explain why the  $\beta$ -PbO content is greater in racks R2 and

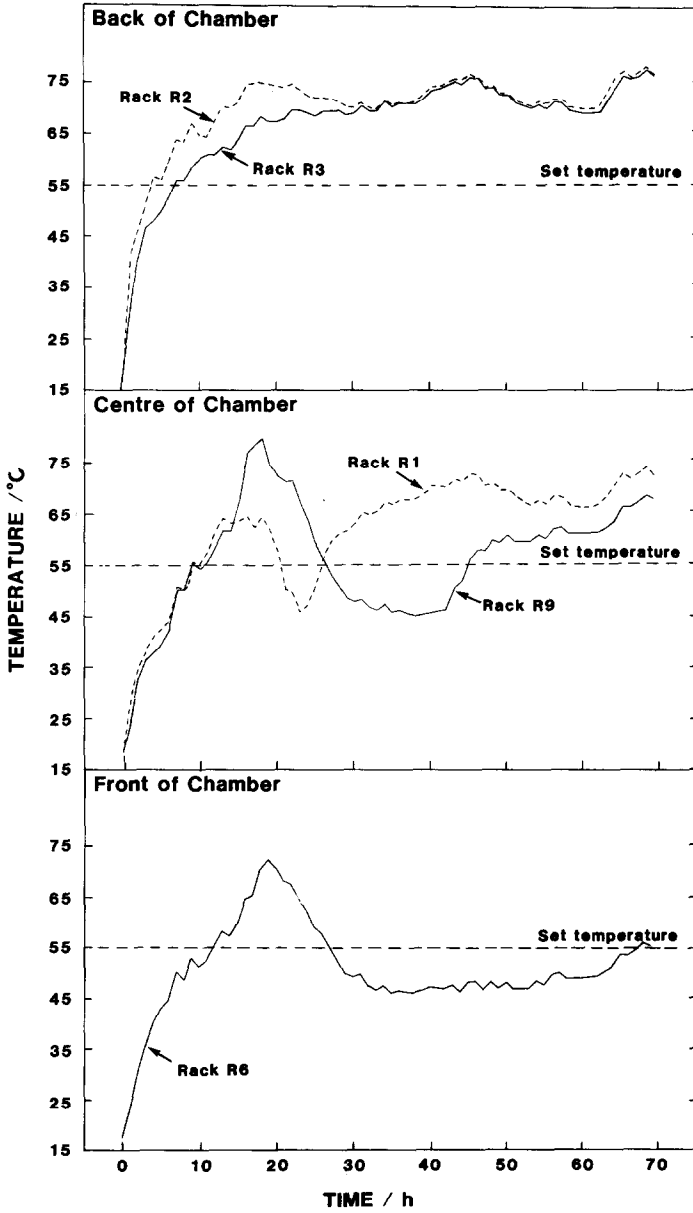


Fig. 5. Temperature profiles of plates at different locations within the curing chamber.

R3 than in other regions of the chamber (Table 2). It is interesting to note that the transformation  $\alpha\text{-PbO} \rightarrow \beta\text{-PbO}$  has been observed in pastes prepared at both 35 and 80 °C [17]. The higher free-lead content of racks R2 and R3 provides further evidence that the curing process has been stalled or changed by the high temperature conditions at the back of the chamber.

Similar trends are exhibited by plates in the front position, though the effects are not so marked; the nett result is that the 3BS is replaced by a similar proportion of 4BS. Finally, there is an appreciable reduction in the red lead content of plates cured in the centre of the chamber and which reported the highest quantities of 4BS (Table 2). This observation contradicts the generally held view that red lead is inert during the curing procedure.

From the above observations, it is clear that the phase composition of cured material is very sensitive to the moisture (or humidity) level as well as to the rate of temperature rise and its variation during the process. Further experimental work is required to determine, in detail, the influence of these parameters on curing reactions. In the meantime, attention should be given to establishing the correct placement of a curing chamber's thermocouple so that the set temperature is maintained throughout the curing process. In the present study, for example, the temperature of the plates in the centre and the front of the chamber fell well below the selected value (55 °C, Fig. 5) at various stages of curing.

## Conclusions

The above investigation illustrates the difficulties faced by battery manufacturers in seeking means to prepare cured plates with uniform and/or desired phase compositions, particularly when a high content of 4BS is required. The latter requires a delicate balance to be maintained between plate moisture content (or humidity) and temperature. This, in turn, necessitates the development of improved methods for controlling the atmosphere within curing chambers. Progress towards this objective is assisted by the use of PEAKS®. With the latter providing a quantitative measure of the effect on phase composition, the major parameters of the curing process (*i.e.*, temperature, humidity and time) can be fine-tuned to obtain finished plates of consistent quality and required composition.

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