

Valve-regulated lead-acid batteries for heavy-duty cycling applications

L. Narasimhan ^{*}, P. Raj, Z. Hussain

HBL Ltd., Hyderabad, India

Received 14 September 1998; accepted 27 November 1998

Abstract

The influence of various parameters on the cycle-life of valve-regulated lead-acid (VRLA) batteries has been investigated. Experiments are performed to arrive at optimum design parameters for a specific application, namely, train lighting for passenger rail-cars. A combination of parameters which relate to paste mixing is investigated in order to maximize plate strength. Factors which relate to curing, inter-electrode spacing and compression ratio are also studied with a view to maximizing life. Accelerated life tests are carried out at 50°C and the results indicate that the optimized parameters yield a life in excess of 500 cycles. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Cycle-life; Plate strength; Separator compression; Train lighting; Valve-regulated lead-acid batteries

1. Introduction

Valve-regulated lead-acid (VRLA) batteries have emerged as the best option for stationary applications. By contrast, questions are still being raised about their suitability for non-stationary cycling applications. Research on new grid alloys and improved paste/active-material structure has encouraged industries to produce versatile VRLA batteries for such applications. This study examines the importance of paste mixing, curing and stack compression in the design of a deep-cycling VRLA battery.

2. Experimental

Mechanical integrity is a prime requirement for a positive pasted plate for non-stationary cycling applications. Based on experience and the literature available on the subject, plate strength is considered to be influenced principally by six parameters during the mixing and the curing stages. Table 1 lists these parameters. In this work, two levels have been selected for each parameter. The experimental plan is given in Table 2. It can be seen that eight types of paste mixes were made and tested.

100 kg of oxide was used for each batch. Depending on whether red lead is used or not and depending on the

quantity of acid used, the acid-to-oxide ratio for the mixes varied from 4 to 4.8%. A curing temperature of 75°C or above was selected in order to produce tetrabasic lead sulfate (4BS). Formation of 4BS during the mixing stage was not attempted in order to avoid the use of complicated mixing equipment.

A sigma mixer with an acrylic cover and tubing was used to dispense the acid uniformly. Water was circulated through an outer jacket and a small blower was used to control the temperature of the mix. A sensor was suitably located in the mixer to record the temperature of the fresh paste during each revolution of the kneader. An automatic acid-dispensing system was used. This ensured the start of acid addition after a preset time from commencing the mixing. The arrangement also regulated acid flow to keep the temperature below a preset peak value and to ensure that attainment of the peak temperature coincided with the completion of acid addition.

The mixing sequence comprised: (i) adding oxide, SCMC and DF and dry mixing for 3 min; (ii) adding water and mixing for 4 min; (iii) adding acid for about 10 to 15 min; (iv) cooling the mix to 45°C before dumping. A typical mixing curve is presented in Fig. 1. A final paste density of $4.2 \pm 0.1 \text{ gm cm}^{-3}$ was maintained.

Improved lead-calcium alloy grids were cast on a Wirtz 40 C machine and used to produce plates by machine

^{*} Corresponding author. Fax: +91-40-309-7022; E-mail: rk4ces@hd1.vsnl.net.in

Table 1
Experimental parameters and levels

Parameter	Level 1	Level 2
Type of oxide	Barton pot	Ball mill
Red lead quantity (wt.%) ^a	0	6
Binder	None	SCMC
Acid quantity (1.4 rel. dens.)	6 l/100 kg oxide	6.9 l/100 kg oxide
Peak mixing temperature (°C)	55	65
Curing temperature (°C)	75	85

^aWith respect to oxide.

paste. The plate weight was maintained within ± 10 g. The plates were pickled for 24 h in dilute sulfuric acid before curing, followed by drying at 50°C for 8 h.

3. Plate strength assessment

A drop test was standardized to assess qualitatively the plate strength. The plates were dropped to fall flat on the floor from a height of 50 cm for 10 times. The initial weight of the plate and the weight of material shed after 10 drops were noted and the percentage of active material

Table 2
Experimental plan for paste mixing. Parameters in different trials

Trial no.	Type of oxide	Red lead quantity (kg)	Binder	Acid quantity (l)	Peak mixing temperature (°C)	Curing temperature (°C)
1	Barton	Nil	None	6	55	75
2	Mill	Nil	None	6.9	65	85
3	Barton	6.0	SCMC	6	55	85
4	Mill	6.0	SCMC	6.9	65	75
5	Mill	Nil	SCMC	6	65	85
6	Mill	Nil	SCMC	6.9	55	75
7	Mill	6.0	None	6.0	65	75
8	Mill	6.0	Nil	6.9	55	85

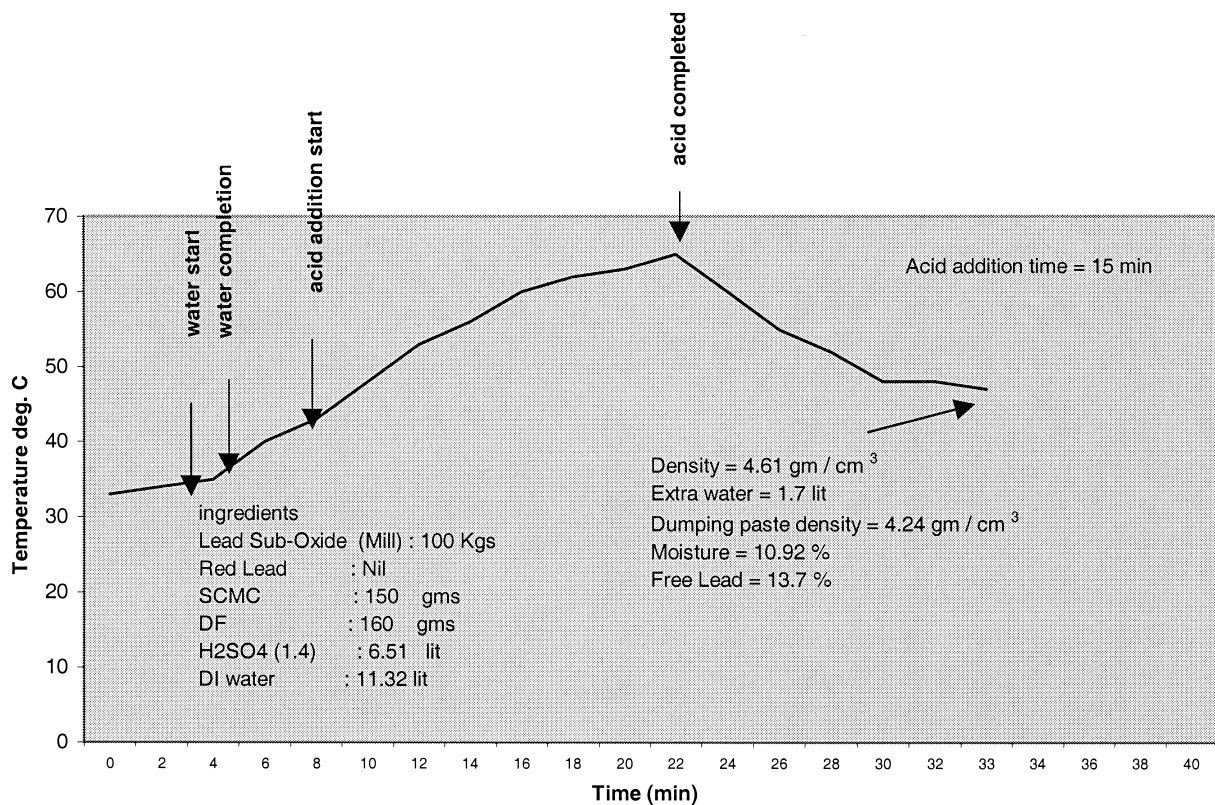


Fig. 1. Typical paste-mixing curve.

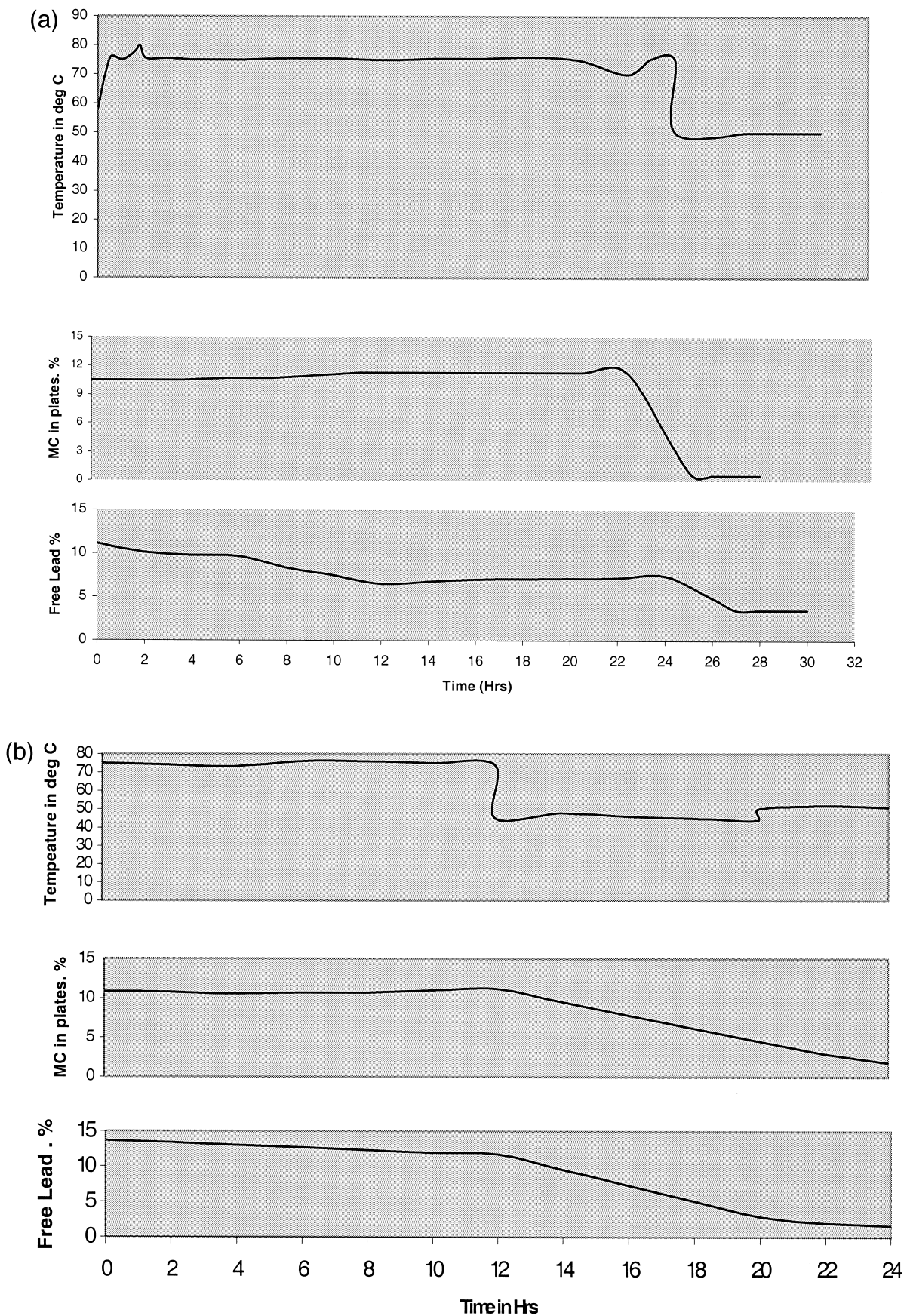


Fig. 2. Moisture (MC) and free-lead contents during curing: (a) Regime 1; (b) Regime 2.

Table 3
Drop test results

Trial no.	Percentage of material shed after 10 drops
1	77
2	34.4
3	30.2
4	8.1
5	48.5
6	29
7	20
8	43

shed (with respect to the total active material in the plate) was calculated. Plates from all eight trials (Table 2) were subjected to the drop test.

The percentage of material shed from plates in each trial is given in Table 3. The parameters of Trial 4 yield the best plate strength. For the best two plates (Trials 4 and 7), mill oxide was used and curing was performed at 75°C. The parameters of Trial 4 were adopted and the plates were assembled into cells.

4. Optimizing curing conditions

Though a 24-h regime of curing was used in earlier trials, it was decided to study the changes in the moisture and the free-lead contents during curing to optimize this process. Accordingly, two curing regimes were followed:

Regime 1: 75°C and 100% relative humidity (r.h.) for 24 h.

Regime 2: 75°C and 100% r.h. for 12 h +45°C and 50% r.h. for 12 h.

In both cases, drying was conducted at 50°C for 8 h.

The cured plates were kept in racks at a spacing of about one plate thickness. The moisture and free-lead contents were determined at 3-h intervals throughout both the curing and the drying periods.

The curing and drying regimes with the corresponding levels of moisture and free-lead in the plates are shown in Fig. 2. With Regime 1 (Fig. 2(a)), the initial moisture content of about 9.5% remains at the same level throughout curing at 75°C, even after 12 h. During this period, the conversion of free-lead proceeds at a slow rate, i.e., from an initial 11 wt.% to 7.4 wt.%. This is to be expected because of the retention of high moisture until the end of curing. As the moisture drops to less than 1 wt.% during drying, the free-lead content falls to around 4 wt.%. With Regime 2 (Fig. 2(b)), the 75°C–100% r.h. curing was limited to 12 h and then continued at 45°C at a lower r.h. for a further 12 h. During the first stage, the variations in moisture and free-lead proceed in a similar way to that in Regime 1. During the second phase, however, the moisture falls to 4.5 wt.% in 9 h and there is a corresponding rapid oxidation of the free-lead. In fact, the free-lead content is lowered to less than 1 wt.% in 8 h.

Drop tests revealed that both types of plates had similar strength, which means that the crystal growth phase at 75°C is completed in 12 h and, therefore, longer periods are not necessary. After this, the only requirement is oxidation of the free-lead, which is seen to reduce to 0.6 wt.% at a rapid rate within 6 h. Thus, extending this period further is not necessary. At this stage, the plates can be dried and stored. As seen from the moisture graph, 3 h is sufficient for drying at 50°C. Hence, in all further trials, a regime consisting of the following was adopted: (i) 75°C

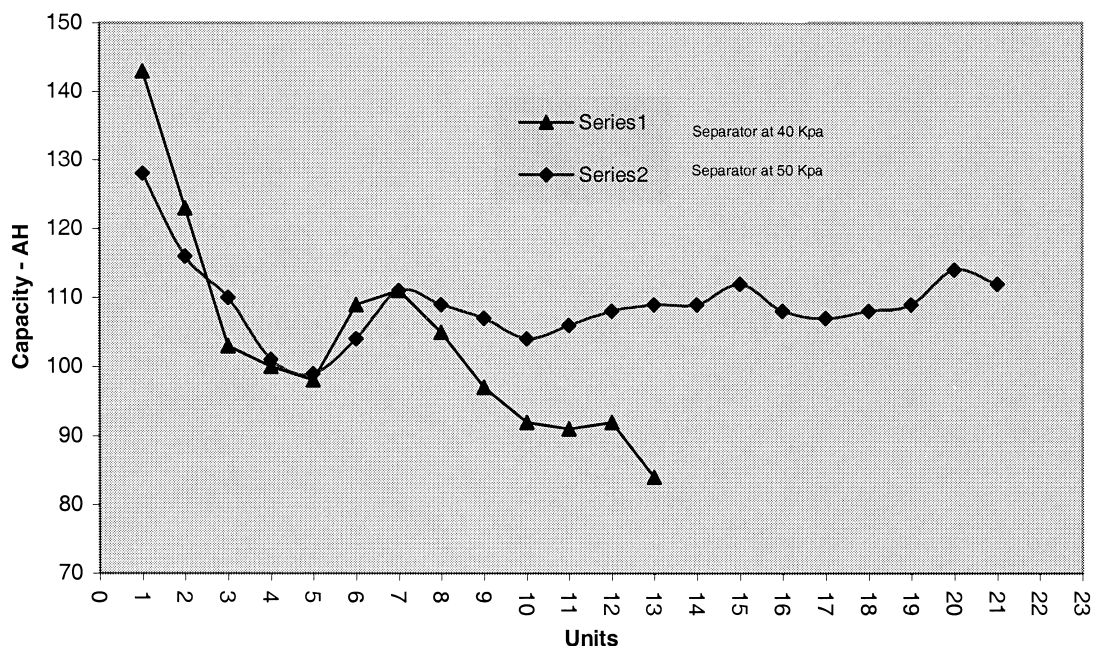


Fig. 3. Effect of separator compression of cycle-life.

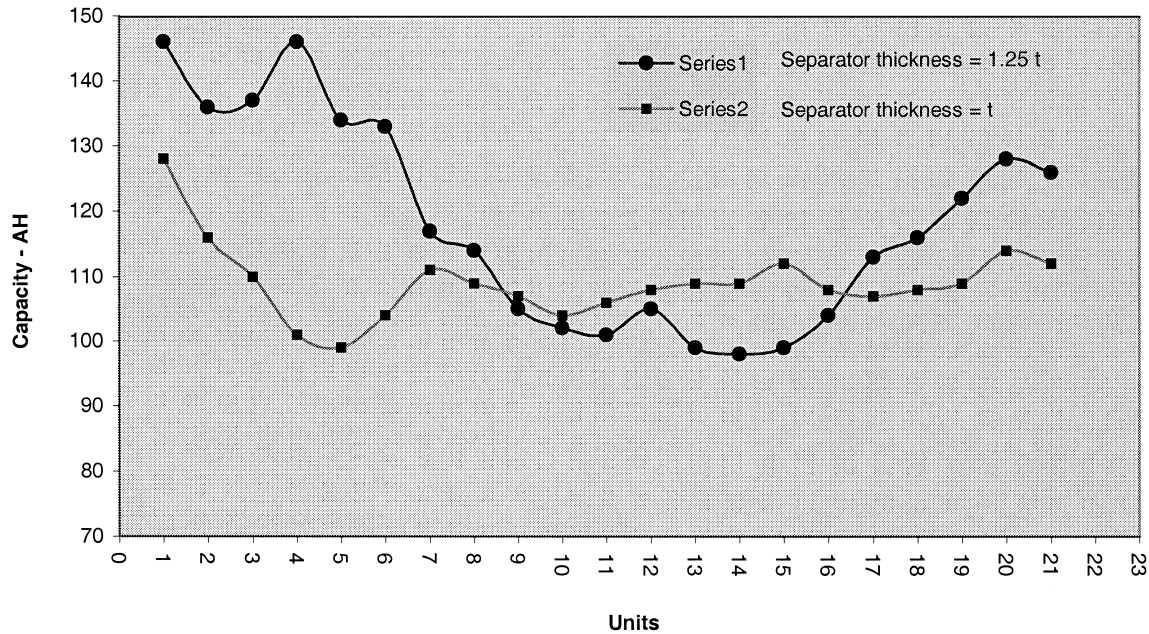


Fig. 4. Effect of separator thickness on cycle-life.

and 100% r.h. for 12 h; (ii) 45°C and 50% r.h. for 6 h; (iii) drying at 50°C for 3 h.

5. Cell parameters

Parallel work was performed to study two cell parameters, namely: (i) inter-electrode spacing, i.e., thicker separators for larger spacing; (ii) separator compression.

Two plate pitches were selected and 120-Ah cells were assembled with separator (absorptive glass-mat, AGM) compression at 40 or 50 kPa. The plates used for these cells are not those employed in studies on mixing and curing, but of a different formulation. This is to facilitate parallel studies to be undertaken on plates and cells.

The assembled cells were subjected to an accelerated life-cycle test at 50°C that followed the specifications of

the Research, Design and Standard Organization (RDSO) of the Indian Railways. The test involved the following:

- (i) initial charge and discharge at the 0.1 C rate;
- (ii) charge at 2.3 V/cell, with a current limit of 40% of the rated capacity, for 21 h; discharge at 0.25 C for 3 h or to a cut-off voltage of 1.75 V/cell, whichever is earlier; the repetition of 5 such cycles is termed 'one unit';
- (iii) capacity measurement at the 0.1 C rate;
- (iv) repeat steps (ii) and (iii) until the capacity falls to 80% of the initial capacity.

The performance of two designs of cell, one with a separator compression of 40 kPa, the other with 50 kPa, is given in Fig. 3. Though there is a fall in capacity during the first 3 or 4 units in both cases, cells with the higher separator compression recover and stabilize in capacity. By contrast, cells with lower compression continue to decline

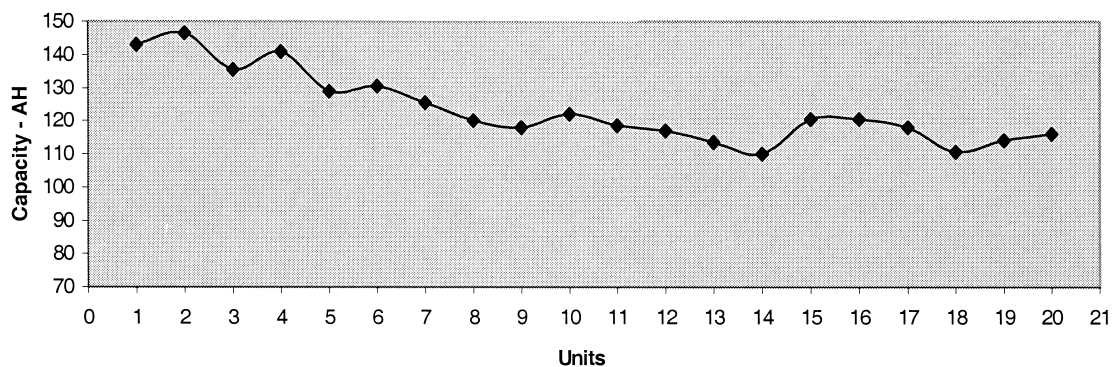


Fig. 5. Cycle-life performance of test cells at 50°C.

in capacity and there is no recovery. The test was stopped after 13 units.

The cycle-life performance of two cell designs is shown in Fig. 4. The separator thickness at 20 kPa is 15% more in one than in the other, but the compression is same in both cases. It appears that a larger separator thickness is better in that it ‘postpones’ the initial decline in capacity. Earlier work has shown that a thickness of 0.85 t could give only 15 units and the cells do not recover after falling to a low capacity. It appears that there is a critical thickness at which cycle-life is improved and, thereafter, the benefit is not significant, particularly when the additional cost is considered. Thickness t (Fig. 4) was retained in the final design.

Cells were assembled from experimental plates with each parameter at its optimum value, and were subjected to the same cycle-life test. The results are given in Fig. 5. To date, 20 units have been completed and the test is still

continuing. A life of 20 units under the accelerated test regime (50°C) is equal to 500 cycles at 27°C under normal cycling.

6. Conclusions

It has been found that good battery cycle-life can be obtained by providing sufficient acid through a larger inter-electrode spacing and by maintaining a separator/stack compression of 50 kPa or more. It has also been shown that a shortened curing cycle can yield good plate strength. In general, plate strength is not good in the absence of a binder. Red lead is not harmful to plate strength. Work is in progress to investigate further the effect of curing conditions and to fine-tune plate processing.