

Advanced separator construction for long life valve-regulated lead-acid batteries

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Abstract

The performance of absorptive glass mat separators in valve-regulated lead-acid (VRLA) batteries is strongly influenced by the diameter of the fibres from which they are made. Coarser diameter fibres are beneficial for the compressive properties of separators while finer fibres maintain the uniform distribution of the electrolyte. Studies of cell compression and electrolyte stratification are reported using separators manufactured with segregated layers of fine and coarse fibres incorporated into a single sheet. This construction locates the different classes of fibre at their location of maximum effectiveness. Improvements in battery life in both cyclic and float charge applications are recorded, and compared with single layer separators.

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1. Introduction

The performance of valve-regulated lead-acid (VRLA) batteries is fundamentally affected by the structure of the material used to separate the electrode plates and immobilise the sulphuric acid electrolyte in the space between them [1]. Where the separator is manufactured from glass micro-fibres, the main factor determining its structure and properties is the diameter of these fibres [2]. The necessary properties of separators continue to be elucidated during the evolution of VRLA technology [3].

A number of conflicting effects have been identified, which makes it impossible to select a single fibre diameter that provides optimal performance with respect to all properties. For example, a taller column of electrolyte can be supported in a fine fibre separator, where the capillary action of its small diameter pores is stronger than that of a coarser fibre material. The rate of absorption of acid by the fine fibre material however is much slower. Production rates can be severely limited, where very fine fibres are used for larger capacity plates, and in the worse case, dry patches can remain in the separator.

As well as technical conflicts, there are significant commercial pressures in the choice of fibres, because their cost increases almost exponentially as their diameter decreases.

Much work has been done to reduce these conflicting effects by blending fibres of different diameters to yield benefits from each end of the fibre spectrum [4]. An alter-

native approach treated in this paper is to manufacture separator with two or more layers as illustrated in Fig. 1 [5]. These layers are intimately linked as a single sheet of separator, but they are derived from separate stocks of fibres laid down sequentially in the paper making process. This paper shows that by selecting fine fibres for the layer adjacent to the electrodes and coarser fibre in the centre of the separator it is possible to optimise separator performance with fewer compromises than the blended fibre method.

2. Experimental

2.1. Measurement of dry compressibility

The equipment used to evaluate the relationship between separator thickness and compression force is similar to that described previously by Nakayama et al. [4]. Samples of separator were cut into rectangles of dimension 50 mm × 100 mm. Ten pieces of separator were stacked together and placed into a compression jig illustrated schematically in Fig. 2.

The apparatus was clamped to a fixed distance determined by interchangeable spacer tubes. The resulting force, applied by the separator on the load cell contained between the end plates, was measured after a period of 15 min to allow stabilisation of the reading.

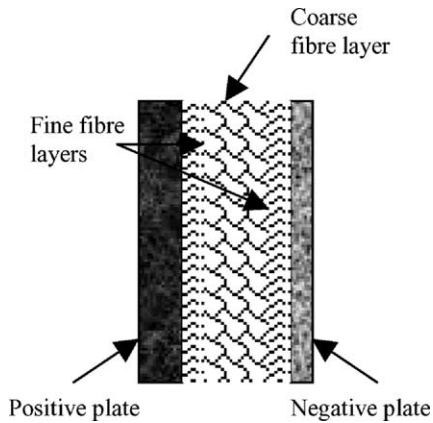


Fig. 1. Multi-layer separator construction.

Two tests were made at each thickness and a fresh set of sheets was used for every test.

2.2. Measurement of wet compressibility

The change in compression force as separator was wetted was measured using the same equipment. It has been shown that the force changes that occur when water is added to glass separator are very similar in value to the changes caused by the addition of sulphuric acid electrolyte [4]. For convenience, water was used to compare the changes in separator made with differing amounts of coarse and fine fibre material.

Ten sheets of separators were cut to 50 mm × 100 mm and weighed (W_s). The sheets were stacked in the test jig and spacer tubes were selected to allow the separator to be compressed to a thickness that provides a 50 kPa pressure in the dry condition. This spacer length was calculated from the results of the previous dry compression tests.

The pore volume within the separator stack in this compressed condition was calculated from the measured volume of the stack and the density of the glass (D_g), used to make the micro-fibre.

$$\text{Pore volume (cm}^3\text{)} = 50 \text{ (mm)} \times 100 \text{ (mm)} \\ \times \frac{T \text{ (mm)}}{10^3} - \frac{W_s \text{ (g)}}{D_g \text{ (g cm}^{-3}\text{)}}$$

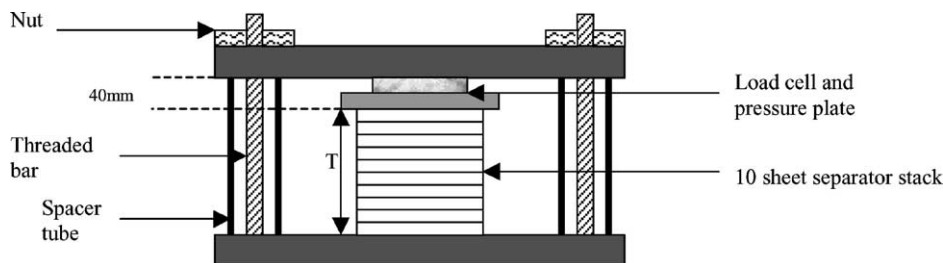


Fig. 2. Diagram of compressibility measurement equipment.

The density of the glass used in these tests was 2.52 g cm^{-3} , based on manufacturer's specification.

Water was added to the separator stack in 2 cm^3 increments from a pipette. One cubic centimetre of water was added at each end of the stack and allowed to soak into the separator. The force on the load cell was measured after a 5 min standing period, when the force reading had stabilised. Water additions continued until water ceased to be absorbed into the separator stack.

2.3. Measurement of electrolyte convection velocity

The rate of displacement of water from a vertically mounted separator by a denser electrolyte solution added to the top of the strip was measured in the equipment depicted in Fig. 3.

A strip of separator was cut to dimension $250 \text{ mm} \times 50 \text{ mm}$ and placed flat on one of the Perspex clamping sheets. This separator was soaked in de-ionised water for 2 min then compressible sealing strips were mounted on either side of the strip and stainless steel spacers located at the edge of the Perspex. A second Perspex sheet was clamped to the open surface of the separator. The spacer blocks were selected with a thickness that would produce a pressure of 20 kPa if a dry piece of separator were used. The spacer thickness calculation was based on the results of dry compression testing. The clamp apparatus was then placed in the test apparatus base in a vertical orientation. Sulphuric acid solution of density 1.3 g cm^{-3} , containing methyl red indicator, was transferred by pipette into a reservoir at the top of the apparatus and timing started simultaneously.

The head of electrolyte was maintained continuously and the distance penetrated by the electrolyte solution down the separator was measured every 5 min until the bottom of the separator was reached.

2.4. Measurement of electrolyte stratification during cycling of VRLA batteries

Test batteries were prepared using normal production techniques for the Yuasa NPC range of VRLA batteries. The NPC17-12 model was selected for this purpose as it has the largest ratio of plate height to width (2.1:1). This magnifies the effects of electrolyte stratification.

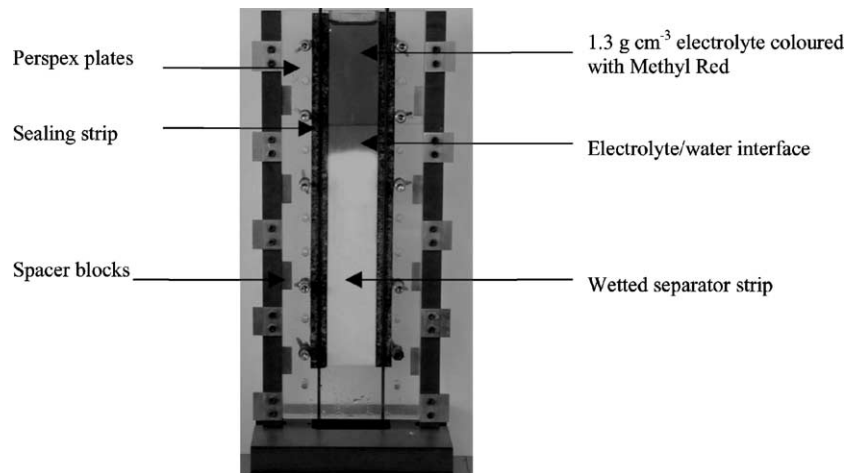


Fig. 3. Apparatus for measuring rate of penetration of acid into wetted separator.

A range of separators was used with different fibre compositions. The thickness of each was selected to provide a dry compression of approximately 55 kPa within the cells.

Completed batteries were discharged for 3 h with a constant current of 0.25 °C A to give a 75% depth of discharge. They were then recharged for 9 h with a constant voltage charger set at 2.45 V per cell and a current limit of 0.25 °C A. This cycle was performed 20 times.

Within 1 h of the completion of the final charging stage, batteries were dismantled and the separator isolated from the plate groups. Each battery contained six cells, of which cells 1, 3 and 5 counting from the positive terminal end were analysed. Sections were cut from the top and bottom 10% of the separator. Electrolyte was squeezed from the separator and the concentration measured by titration with sodium hydroxide solution.

2.5. Cycle life test measurements

Further samples of NPC17-12 VRLA batteries were prepared with a range of single and multi-layer separators. These batteries were discharged with a constant resistance load of 0.6 ohm to an end point at 9.0 V. The initial discharge time for the test batteries was approximately 35 min, which gave a depth of discharge of approximately 60% of the C_{20} capacity.

Within 1 h of the end of discharge the batteries were connected to commercial charging equipment designed for cyclic applications. The chargers provided a current of 4 A until a voltage of 14.8 V was reached. The charging control circuit monitored the time elapsed between the start of charge and the point where the charging current fell to 1.2 A. The charging of voltage of 14.8 V was maintained for a further period equal to half the time taken to reach the 1.2 A threshold. At this point the charging voltage limit was reduced to 13.8 V and maintained until the battery was disconnected.

Batteries were discharged daily for 5 days per week and maintained on floating charge over weekend and holiday periods. The tests were terminated when discharge times of less than 25 min were recorded. Batteries were dismantled at the end of life and the cause of failure determined.

2.6. Accelerated float charge life test measurements

The 100 Ah, 6 V monoblocs with a design life of 10+ years were prepared using separator consisting of either single layers of 100% fine fibre glass or double layers of fine fibre glass at 20% by weight attached to layers of coarse fibre at 80% by weight.

The batteries were tested according to the method of British Standard 6290, Part 4 (1997). The batteries were float charged at 2.28 V/cell at a temperature of 55 °C for a period of 42 days. After cooling to room temperature they were discharged tested at the 8 h rate, recharged and tested at the 1 h rate. This regime continued until the 8 h rate test yielded less than 80% of nominal capacity.

3. Results

3.1. Dry separator compressibility

The change in pressure as separator is compressed in the dry state is shown in Fig. 4. To make comparison of thickness changes easier, for different separator samples, the thickness is expressed as a proportion of the thickness of each material measured at a standard pressure of 20 kPa.

The material identified as coarse fibre layers in this paper is produced from fibres with a range of diameters centred on 4.1 µm with a specific surface area of 0.6 m² g⁻¹ mixed with small quantities of 20 µm diameter, “chop pack” fibre. The fine fibre layers are produced from fibres with a range of diameters centred on 0.8 µm and a specific surface area of 1.7 m² g⁻¹.

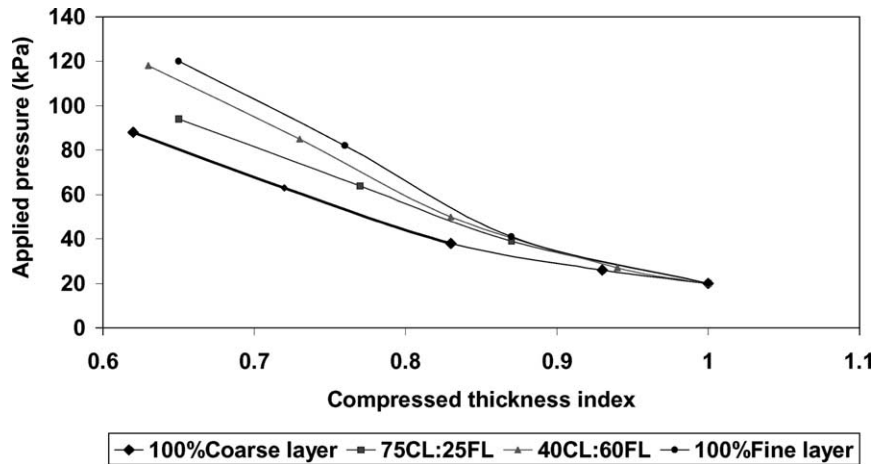


Fig. 4. Relationship of dry separator thickness to applied pressure.

3.2. Compression relaxation in wet state

As the separator is wetted a progressive reduction in compression occurs until close to the point of saturation, when a partial recovery occurs. This is shown in Fig. 5, for separators with different ratios of fine and coarse fibre. The drop in pressure and the height of the recovery at saturation increase as the proportion of fine fibres in the separator increases.

3.3. Electrolyte convection velocity

The penetration of electrolyte through water saturated separator strips is shown in Fig. 6. Results are shown for coarse fibre and fine fibre separator as defined in Section 3.1. The steeper slope of the coarse fibre plot indicates a much greater penetration rate, due to the larger pore sizes of this material.

This method was only applicable to separators with homogeneous fibre structure, because the differential flow rates and exchange of acid, between different layers of multi-layer separator produced very distorted flow patterns.

3.4. Electrolyte stratification

The strength of electrolyte, extracted from cycled cells, was measured and the difference between samples from bottom and top levels calculated. In each case, the acid concentration was higher at the bottom of the cycled cells. The difference in strength for cells made with different ratios of coarse and fine fibre separator is shown in Fig. 7.

Most of the reduction in stratification caused by the fine fibre material was achieved using a layer making up 25% by weight of the total separator. The sg values for the cells made with single layer separators are shown in Table 1.

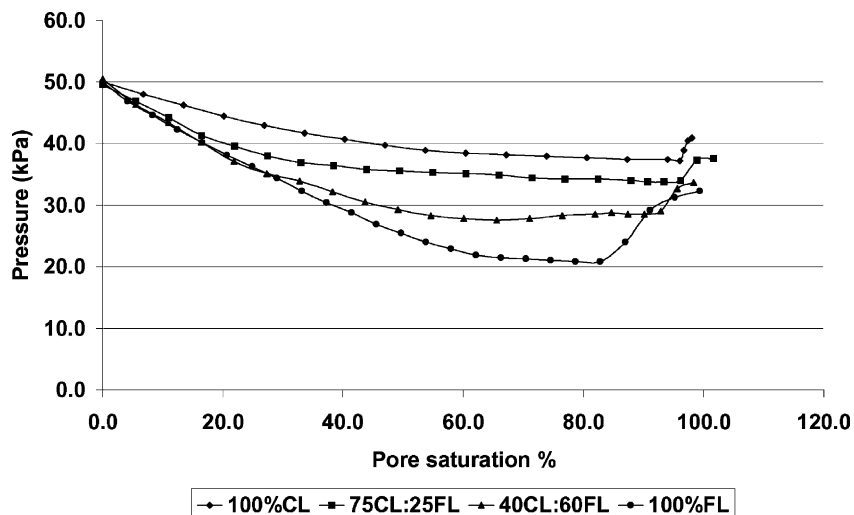


Fig. 5. Separator compression change with increasing pore saturation.

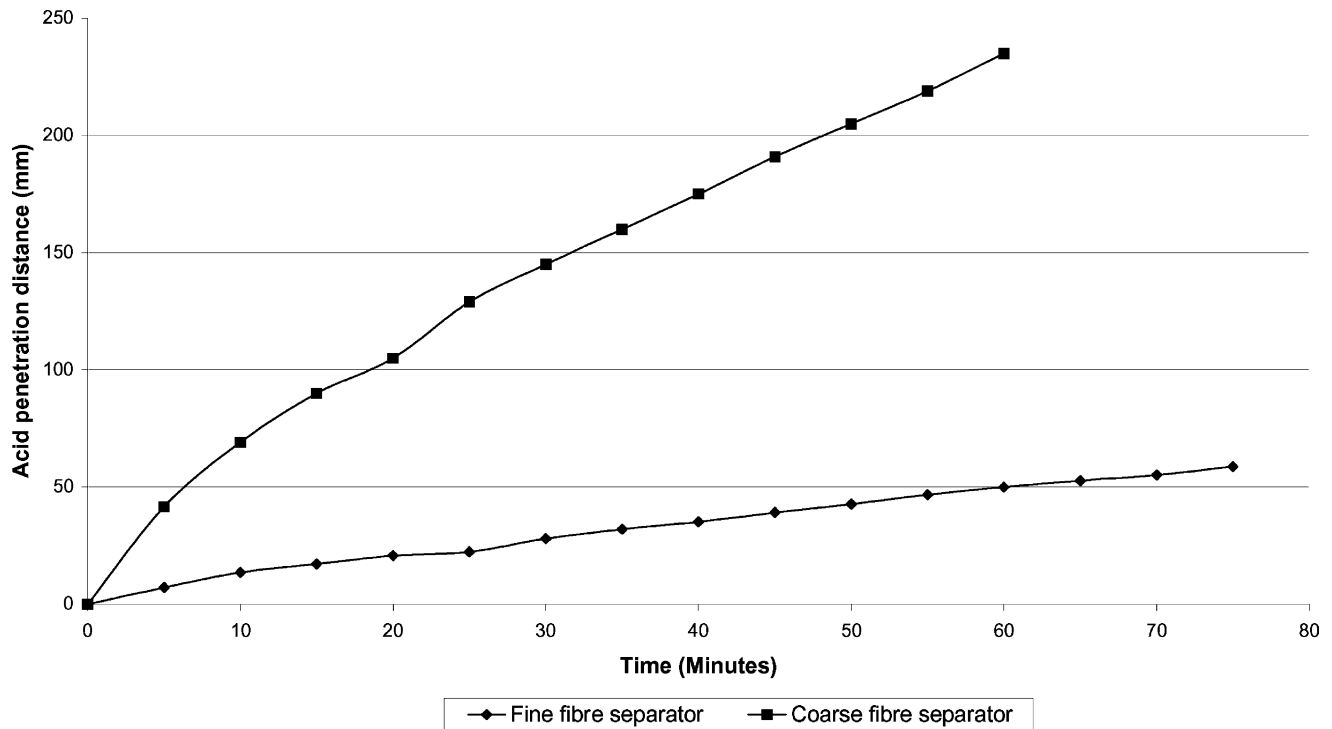


Fig. 6. Electrolyte penetration distance into wetted separator vs. time.

The batteries were dismantled soon after the end of charge to accentuate any differences in stratification between batteries of different types. This would have prevented full equalisation of acid strength between electrolyte in the separator and electrolyte in the plate pores. The overall separator electrolyte strength can be expected to rise after longer standing times.

It was also noted that the amount of variation in the results between different cells of the same test battery was significantly lower for multi-layer separator than for single layer separator.

Table 1
Electrolyte strength after cycle testing

Separator type	Cell number	Sg at top of cell (g cm ⁻³)	Sg at bottom of cell (g cm ⁻³)
Coarse fibre	1	1.234	1.364
	3	1.171	1.377
	5	1.156	1.380
Fine fibre	1	1.239	1.345
	3	1.288	1.316
	5	1.275	1.326

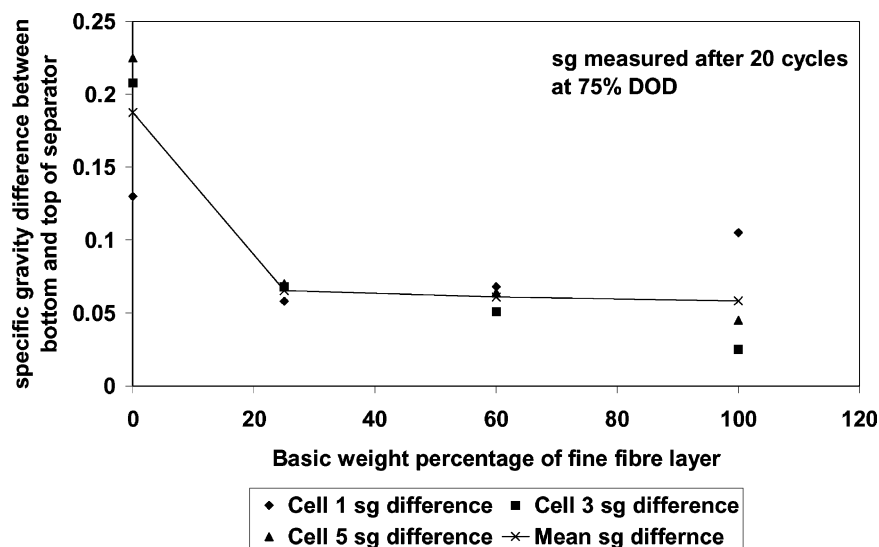


Fig. 7. Electrolyte stratification with separators of different fine fibre layer proportions.

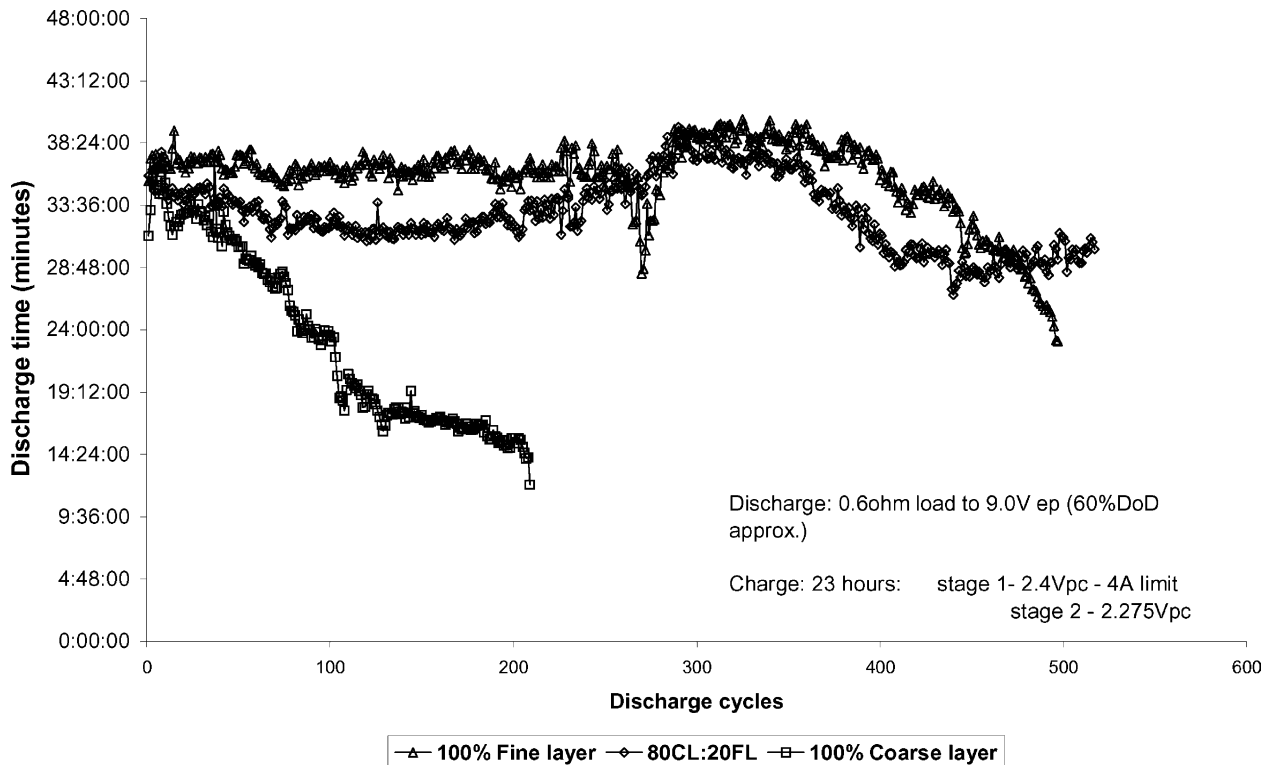


Fig. 8. Cycle life results for NPC17-12 with various separator constructions.

3.5. Cycle life duration

Batteries were constructed with each of three types of separator: single layer coarse fibre, single layer fine fibre and multi-layer coarse/fine material. The capacity changes are plotted in Fig. 8.

The coarse fibre material resulted in a steady walk down of capacity leading to failure after 80 cycles. The battery was allowed to continue cycling to see if any stabilisation point was reached. This did not occur and the battery demonstrated electrolyte stratification when it was analysed. The concentration values were similar to those seen in Section 3.4.

The battery made with single layer, fine fibre separator continued for 495 cycles. It showed a number of fluctuations in performance during the test, with a final steep reduction in capacity at the end of life. Internal analysis of the battery showed the separator to be very dry making it difficult to extract enough electrolyte for stratification tests. The positive grids were heavily corroded with less than 20% of the lead alloy remaining after PbO_2 was dissolved from the surface. The growth in length and width of the plates was relatively small at less than 3% of the original size at the maximum point of growth. The overall cause of failure appeared to be loss of conductivity within the separator and positive grid components.

The battery made with multi-layer separator has performed more than 520 cycles and the test is continuing. The capacity of this battery has exhibited a number of broad

fluctuations during the test. This does not appear to be related to changes in test conditions as the same equipment has been used throughout and the battery has remained in a temperature controlled room at $20 \pm 2^\circ\text{C}$.

3.6. Accelerated float charge results

The performance of three pieces each of batteries made with either single layer fine fibre or multi-layer separator was compared. The capacity changes at the 8 and 1 h rates of discharge are shown in Figs. 9 and 10, respectively.

Both sets of batteries exhibited similar capacity profiles at the 8 h rate although two pieces with single layer separator separated from the rest at the fourth cycle and consequently passed just below the 80% capacity threshold earlier than the multi-layer samples. The single layer sample performed an average of 8 cycles while the multi-layer sample performed an average of 10.1 cycles.

If the method for estimation of life based on a doubling for each 10°C drop in average temperature is applied this predicts a life of 10.3 years for the single layer separator and 13 years for multi-layer separator.

Internal analysis of both sets of batteries at the end of the tests showed extensive corrosion and growth of the positive grids. The separators were significantly drier than the as-manufactured condition but the electrolyte could still be expelled from them with ease.

The separation between the capacity profiles for the two samples is much more pronounced at the 1 h rate of

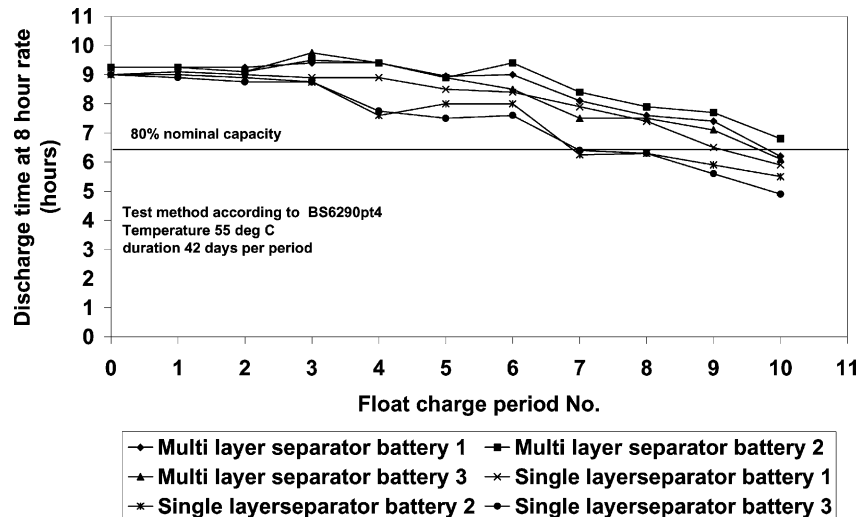


Fig. 9. Accelerated float charge life test on 100 Ah 6 V monoblocs at the 8 h discharge rate.

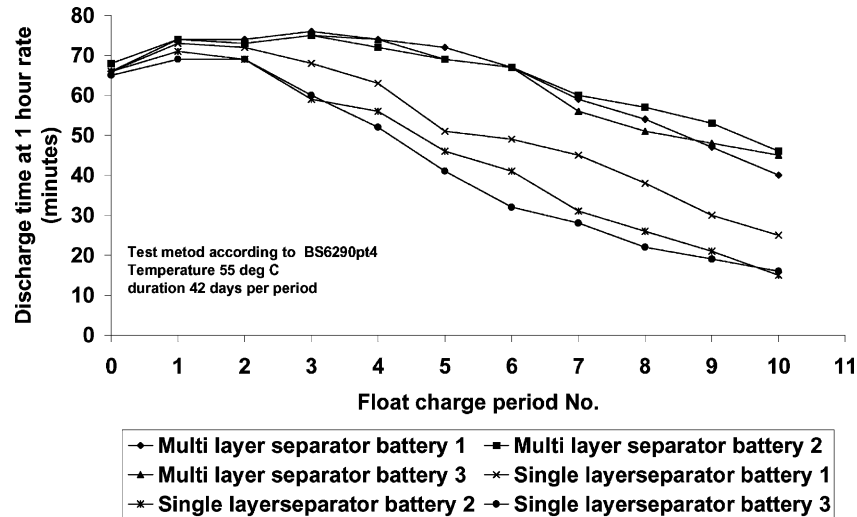


Fig. 10. Accelerated float charge life test on 100 Ah 6 V monoblocs at the 1 h discharge rate.

discharge. The multi-layer sample also shows a much smaller variation in performance than the single layer sample.

4. Discussion

4.1. Compression effects

Given the importance that has been established for maintaining high compression within a VRLA cell [3], it follows that uniformity of pressure between cells will contribute to consistent product performance. This pressure is first generated when the glass mat separator is inserted with the electrode plates into the cell container. The value of this pressure is dependent on the free space available when the thickness of the electrode plates is subtracted from the length of the cell container.

Because there is a significant manufacturing tolerance in the thickness of plates, the separator pressure will never be uniform for all cells. Another source of free space variation is the draft angle applied to the container moulding tool, to allow the release of the component. This means that there is less free space at the bottom of the cell, giving higher compression there.

This variability in the space available for the separator means that the slope of the curves in Fig. 4 will determine the amount of variation in pressure between cells in production conditions. A steeper slope will give greater product variability. Fig. 4 shows that the slopes increase steadily as more fine fibre is used in the separator. For example, the change in pressure caused by moving from the compression index of 0.9–0.8 in Fig. 4 is listed in Table 2.

This relationship shows that a high proportion of coarser fibres can be useful to provide uniform compression.

Table 2
Effect of thickness change on separator compression

Fine fibre content as percentage of basic weight	Pressure at 0.9 CI (kPa)	Pressure at 0.8 CI (kPa)	Pressure difference (kPa)
0	30	44	14
25	35	56	21
60	35	60	25
100	35	67	32

Another property that is improved by using high proportions of coarse fibres is the maintenance of high compression levels within cells after acid filling. The results shown in Fig. 5 demonstrate that fine fibre separators exhibit greater compression loss, as they become wetted, than coarse fibre separators. A model for this loss of compression has been proposed [4]. This suggests there are two major causes for relaxation of pressure within the separator. One is the dissolution of bonds at intersection points between glass fibres. This is an irreversible effect, allowing fibres to slide into tighter packed configurations.

The second effect is based on the drop in pressure within the pores of the separator as they fill with acid. The drop in pressure across the curved meniscus formed at the gas/liquid interface within a partially filled tube is quantified by the equation of Young and Laplace:

$$\Delta P = \frac{2\gamma}{r}$$

ΔP is the pressure drop from the convex to the concave side of the meniscus (Pa), γ the surface tension of the electrolyte (N m^{-1}), r the radius of the capillary tube (m).

Some of this drop in the pressure, within the separator pores, will be transmitted to the plates touching the separator surface.

The separator structure is not a uniform collection of capillary tubes and it is difficult to make quantitative calculations of these effects. In principle however, it can be seen that as the mean pore size decreases the pressure drop within the separator, caused by wetting, will increase. It is a common feature of separator manufacture that finer fibres yield smaller pore sizes.

This compression loss feature is reversible, because the capillary pressure drop disappears once the separator is fully saturated, when the glass-acid-air interfaces are eliminated. This can be seen in Fig. 5 as the separators approach saturation point. Because VRLA batteries are designed to operate in a partially saturated condition they start life at the lower part of the curve and as they dry out, during operation, the compression continues to drop further [4].

The magnitude of the recovery of pressure, as the separator reaches saturation, can be used as an indication of the capillary pressure. The relationship of this pressure to fibre content is shown in Fig. 11. It can be seen that relationship is quite linear, with an increase in capillary pressure as the fine fibre component increases.

4.2. Electrolyte distribution effects

The ability of micro-fibre glass separator to prevent electrolyte stratification is also related to pore size. In this case however, small pore sizes are desirable, to interrupt the connective flow of electrolyte at the plate-separator interface during charging.

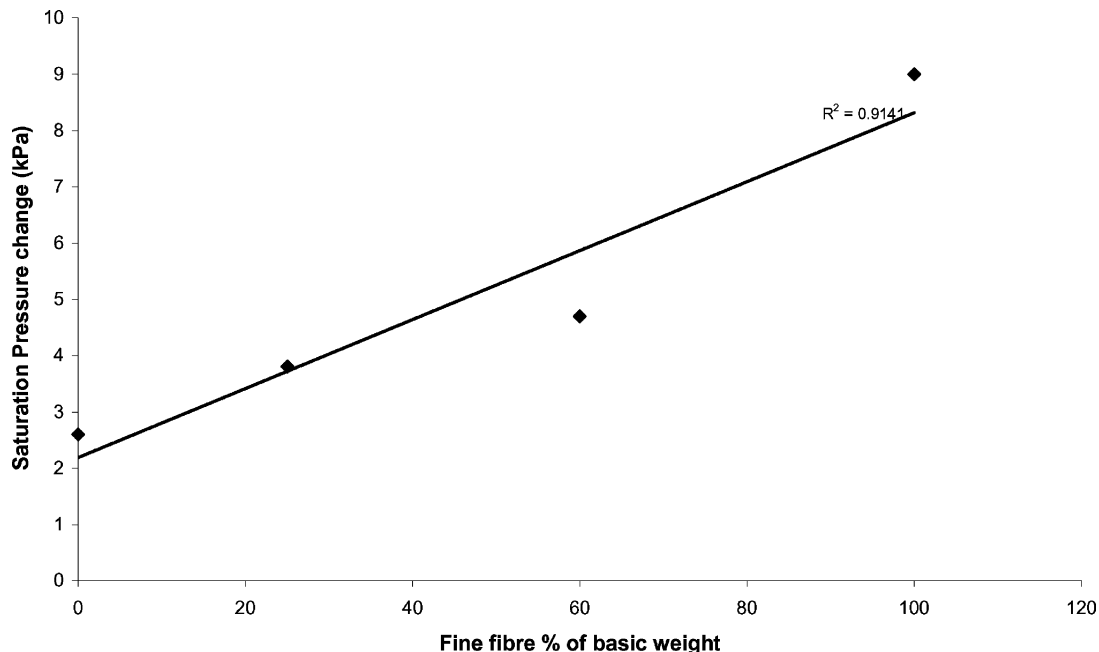


Fig. 11. Relationship of capillary pressure drop to fine fibre content of separator.

The convection effect is greatest at the surface of the plates because acid is generated within them and moves into the separator by diffusion along a concentration gradient. The concentration and therefore density of the electrolyte is greatest at the plate surfaces. If the fine fibre layer of the separator is placed adjacent to the plate surface it will contribute most effectively to stratification inhibition. This is confirmed by the result shown in Fig. 7.

Significantly, this result shows that the degree of stratification is not a linear function of the thickness of the fine fibre layer. This contrasts with the pressure related features of separator, which do exhibit linear relationships to the fine fibre ratio. The difference arises because pressure effects are transmitted through the whole cell, while convection is concentrated at plate surfaces. This is one reason why the contribution of different fibre groups will be more effective if they are introduced as separate layers rather than blended homogeneously.

The effectiveness of multi-layer separators in actual battery applications is confirmed in the cycle and float charge life tests. In each case, the choice of separator has had no measurable effect on the initial performance of the test batteries, which were equal to the controls. The benefits for the cyclic application are mainly economic because they show that stratification can be inhibited with much less of the fine fibre material than has been used previously.

The performance differences that appear after a few cycles of the accelerated life test are probably related to electrolyte distribution, but in a different way to stratification. The volume of water in the electrolyte diminishes throughout life of a VRLA battery for a number of reasons [6]. This leads to decreasing saturation of the separator. When a multi-layer separator is used, the coarse fibre layer will drain first because the pressure of the liquid in its large pores will be higher than the fine fibre pores. The effect will be to maintain a high level of saturation at the separator to plate interface. This may help to support conductivity and exchange of the sulphuric acid active material necessary for good discharge performance.

Alternatively, the performance effects may simply be due to improved pressure maintenance within multi-layer separators as dry out proceeds. Further work is planned to try to distinguish between these effects.

5. Conclusions

1. It is not possible to identify a single diameter of glass micro-fibre that gives the best performance with respect to all the requirements of a VRLA separator.
2. Coarser fibres produce better compression properties, yielding higher and more uniform values in acid filled cells. These effects are transmitted throughout the cell structure.
3. Finer fibres improve electrolyte distribution within the cell, both in concentration and volume terms. These effects are most important at the interface between plate and separator.
4. Multi-layer separators focus the beneficial properties of each class of fibre at the optimum location. This produces a synergistic effect; enhancing battery life in a more cost effective manner than the mixing of fine and coarse fibres homogeneously.

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