

# Techniques for jar formation of valve-regulated lead–acid batteries

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## Abstract

The market for valve-regulated lead–acid (VRLA) batteries is growing steadily and will be given a further boost as the market for 36-V batteries for the 42-V PowerNet develops over the next few years. The manufacture of VRLA batteries poses, however, a number of complex technical problems that are not experienced in the manufacture of conventional flooded batteries. For the large-scale manufacture of automotive batteries or other small VRLA batteries of 100 Ah or less, jar formation rather than plate formation and dry charge would seem to be a logical and economically sound decision. For this to be successful, however, a number of key issues need to be reviewed, starting with a detailed consideration of battery design. This paper reviews issues associated with the jar formation of VRLA batteries. Guidance is given concerning filling techniques (gravity or vacuum fill), the formation process, charging techniques, and formation algorithms. Battery design and separator optimisation is discussed. The properties of the separator, e.g. wicking rate, fibre composition, surface area and compression, may have a critical impact on acid filling and jar formation, and may partially determine the filling and formation conditions to be used. The control of temperature during formation is particularly important. Formation algorithms and temperature data are presented. Attention is drawn to the possible loss of plate-group compression during the formation process, and how this may be avoided.

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## 1. Introduction

The market for small valve-regulated lead–acid (VRLA) batteries is expected to increase, particularly for automotive applications with the move to 36-V batteries and hybrid electric vehicles. Major automotive battery manufacturers employ jar formation for conventional flooded batteries and will want to continue to use this procedure for the new generation of advanced VRLA automotive batteries. The VRLA battery does, however, pose particular problems in jar formation, and the ease or otherwise of jar formation is heavily influenced by the detailed battery design. Therefore, the battery design must take into account the requirements of jar formation.

Jar formation of VRLA batteries becomes more difficult and less appropriate the larger the battery. This study concentrates on batteries with a maximum capacity of 100 Ah. This is rather an arbitrary cut-off but, in general, a VRLA

battery of higher capacity than this will need to be prepared using plate formation and dry charge.

By way of general guidance, jar formation can be considered in the following circumstances:

- cylindrical battery design;
- thin-plate, prismatic battery design;
- battery with a low height ( $L$ ):plate-spacing ( $d$ ) ratio, viz.  $L:d < 100$ ;
- large separator fringe area;
- high separator grammage ( $>2 \text{ g Ah}^{-1}$ );
- high surface-area separator.

Conversely, jar formation is probably not suitable and plate formation needs to be considered for:

- tall batteries;
- large, high-capacity batteries;
- long-life batteries (deep cycling);
- batteries with high  $L:d$  ratios ( $>100$ ).

In principle, all VRLA batteries could use plates that are prepared by means of plate formation/dry charge, but not all VRLA batteries can be successfully jar-formed. This study

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gives guidance concerning techniques for the successful jar formation of VRLA batteries.

## 2. Jar formation of VRLA batteries

### 2.1. Filling process

The formation process for VRLA cells and batteries begins with the filling process. Several different approaches can be used, namely:

- gravity top fill, single- or multi-step;
- gravity bottom-up fill;
- ‘push’ fill where electrolyte is pumped into the cell or battery, usually from the bottom-up (usable only with spiral-wound products);
- soft-vacuum fill ( $\geq 20$  mm Hg), single- or multi-step, possibly with a ‘push–pull’ step to distribute electrolyte more evenly;
- hard-vacuum fill ( $\leq 10$  mm Hg).

Gravity top fill is the simplest approach; it can be used for any cell or battery and involves pouring electrolyte into the headspace at a rate that the battery can accommodate. This can be done slowly with a single addition or in several measured amounts. Fill times are around 10–40 min, but heat is generated slowly and there is only a limited effect from carbon dioxide released from carbonated paste surfaces. Incomplete wetting is possible due to trapped gas pockets. Heat generation in larger batteries can be counteracted by chilling the electrolyte (0 to  $-10$  °C) and/or the unfilled elements and, if necessary, putting the filled battery into a chilled water bath. For small products (1.2–10 Ah), simple bath cooling after fill is sufficient. For larger sizes (10–100 Ah), chilled electrolyte and bath cooling may be mandatory.

Gravity bottom-up, or ‘dunk’, filling involves dipping a cell or battery into a bath of electrolyte (the case has a hole or holes in the bottom to allow ingress of acid) until wicking has resulted in complete filling of the separator and plate pores. This is also a slow process (several minutes), and has the advantages and drawbacks listed above for gravity top fill. An added disadvantage is that the filling hole has to be sealed before the battery goes into formation. Allowing the battery to take as much acid as it wants is actually very reproducible in terms of fill weight and the final saturation level is typically  $\sim 95\%$  (i.e. the plate stack does not saturate completely).

‘Push’ fill is a specialised technique for spiral-wound products where electrolyte is forced up through the wound element, either from the bottom or using a probe in the wound-element mandrel space. This is faster than the gravity-fill techniques (around 30–60 s) and requires more care in thermal management.

Soft-vacuum filling involves drawing a moderate vacuum level and allowing the element to ‘suck in’ electrolyte at its own rate. As this approach does not usually result in uniform

electrolyte distribution, there is often a ‘push–pull’ (pressure–vacuum) finishing step to move electrolyte around physically in order to help diffusion. The filling rate is moderate (30–60 s) so thermal management is mandatory, along the lines of that given above for the gravity-fill approach.

At first sight, hard-vacuum filling is very attractive for high-volume manufacturing as it is a very rapid technique (1–10 s for sizes 1.2–25 Ah). It also requires extreme care, both during filling and for processes prior to filling. In addition to speed, hard-vacuum filling can result in uniform electrolyte distribution due to the almost total absence of air displacement. The absence of air, however, also means that the paste is very reactive and the rapid introduction of electrolyte results in very high heat generation over a short period of time. Thus, careful thermal management is required. The rapid heat generation restricts this technique to small batteries ( $< 50$  Ah). Poor thermal management can result in staining of the AGM separator by dislodged paste, plate deformation and case bulging. Hydration shorts (lead sulphate in the separator) are also possible due to the high temperatures and low acidity conditions that can be generated. Plate carbonation during processing is also a problem because the rapid introduction of electrolyte can result in a ‘burst’ of liberated carbon dioxide, which can help to defeat the vacuum created and result in low fill weights. Further liberation of  $\text{CO}_2$  can cause regurgitation of electrolyte in extreme cases. Separator damage can also result from the hydraulic action of the electrolyte if it is added too quickly. This, in turn, can promote plate-to-plate shorting due to the removal of overlapping separator between adjacent plates.

Commercially available equipment for vacuum filling typically enables a preselected volume of acid to be metered into each cell. It also permits pulse filling, in which the operating conditions alternate between vacuum and atmospheric pressure to ensure that the full preselected volume is metered into the cells.

### 2.2. ‘Fill-to-form’ time

The time gap between electrolyte filling and the initiation of the formation process must be considered very carefully. If batteries are put into formation immediately after filling, a significant amount of acid may remain unreacted. Obviously, the longer the delay between filling and the start of formation, the more the lead sulphate that is formed. This facilitates the formation process, but it also increases the resistance of the unformed plates (particularly the positive), since lead sulphate is an insulator. The filling reaction is exothermic, so to avoid excessive formation temperatures it may be beneficial to allow this reaction to go to completion and the battery to cool before starting the formation charge. Nevertheless, a long stand-time after filling can also aggravate the conditions that can initiate hydration shorts by allowing lead sulphate to slowly dissolve and diffuse into the separator. With a good filling process this is not a problem, as even a

mildly acidic condition will suppress the solubility of lead sulphate, particularly if sodium sulphate is used as an additive in the fill electrolyte. Alternatively, if batteries are put on to formation as quickly as possible after filling, areas of the plate stack can exist where hot electrolyte is depleted of acid, and there is the danger of the battery overheating.

In order to allow the filling reaction to go to completion and allow the battery to cool adequately, a fill-to-form time of between 2 and 4 h is recommended. The inclusion of 10–25% red lead ( $\text{Pb}_3\text{O}_4$ ) in the positive paste will also help the initial stages of the formation process.

### 2.3. Battery preparation for formation

The most commonly used technique is ‘open’ formation in which the vent valve has not been put in place. The battery headspace may also be open to the air (lid not fitted until after formation). In either case, batteries are usually flooded, or close to it, and have the capability of removal or addition of acid during processing. Open formations are useful in that plate processing is not as critical (in terms of carbonation), heat dissipation due to gassing is greater by about an order of magnitude than in sealed formation (because the battery is formed in the flooded state), and adjustments in saturation levels are possible at any time.

In the so-called ‘fill and spill’ formation, batteries are formed saturated and then the electrolyte level is adjusted at the end of formation by simply pouring off excess electrolyte. This results in a near-saturated condition following formation (trapped gas in the plate pores ensures that some electrolyte is absorbed and, thus, there is a small amount of void space in the formed battery), which may result in higher-than-usual overcharge gassing and weight losses early in life and, possibly, acid leakage during heavy overcharge. This approach has been promoted by Hollingsworth and Vose for use with their Hovosorb II organic fibre-glass separator [1], and is particularly well suited to manufacturing processes with high manual labour inputs, as well as those where precise control over finished battery quality is not required. The saturation levels in the cells are not precisely known and significant cell-to-cell variations could exist. Heavy hydrogen gassing during formation must be tolerated, but the high levels of gas generation help with heat dissipation.

The main alternative is ‘saturation/electrolysis’ formation, which enables an accurately known saturation level in the region of 95% after formation. A standard open formation is carried out, followed by over-saturation and pouring off of excess electrolyte (much like ‘fill and spill’ above). The fully saturated, formed battery (still open) is then subjected to a period of electrolysis at a known current level to drive off an accurately known amount of water, which thus brings the battery to the desired saturation percentage. Battery weight measurement before and after formation may be used to ensure that the saturation level is correct.

## 3. Formation algorithms

Most VRLA battery manufacturers have developed their own formation algorithms, which are commercially confidential. Therefore, this section can only give general guidance. Each company will need to carry out tests to establish the best algorithm for its specific manufacturing process and battery application.

### 3.1. Initiation of current flow

Three possible techniques for the initiation of the formation charge are illustrated in Fig. 1.

#### 3.1.1. Low-current initiation

A low initial current will minimise the temperature rise at the start of formation. There may be a continuation of the heat production from the oxide/acid filling reaction. There may also be a variable fill-to-form hold time due to the time lag in filling a formation circuit queue. The low initial current will also compensate for possible high battery resistances (e.g. if the plates have become heavily sulphated due to a prolonged time lag after filling). The low-current charge should be continued until the battery temperatures have fallen below 50 °C. Typically, a short initiation charge period of 0.5–1 h can be beneficial.

#### 3.1.2. Ramp-current initiation

Alternatively, the current can be ramped up slowly over an hour or so before the main current is applied.

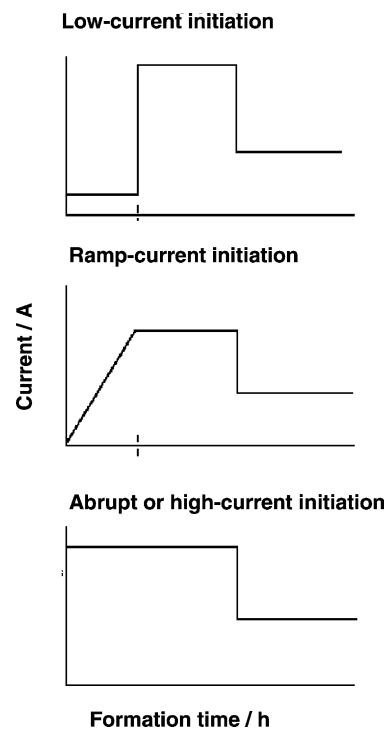


Fig. 1. Techniques for the initiation of formation charge.

### 3.1.3. Abrupt or high-current initiation

This can assist in reducing the total formation time. The method does, however, result in a high initial voltage and the initial rise in temperature may be excessive. In general, low-current or ramp-current initiation is preferred over high-current initiation.

Initial resistance to proper current flow can be detected either by an immediate rise in charge voltage to very high levels (or to the voltage limit if constant-voltage charging is used), or by a relatively sharp temperature increase. Unless the battery plates are very heavily sulphated, the voltage and temperature will, after a short period, drop to normal levels, i.e. to temperatures below  $\sim 50^\circ\text{C}$  and voltages of  $\sim 1.8$ – $1.9\text{ V}$  per cell. There will then be a gradual rise in both temperature and voltage, but because almost all of the formation current is going into the conversion of lead sulphate, these increases will be very gradual.

### 3.2. Constant-voltage charging

The primary drawback of constant-voltage (CV) charging is that the current taper toward the end of formation results in relatively long charge times. In order to minimise this and speed up formation times, multi-step CV algorithms can be used, by programming for current-limit reductions when the voltage limit is reached. This, then, becomes a stepped constant-current (CC) formation, but with a voltage limit (usually  $\sim 16\text{ V}$  for a 12-V battery) to minimise gassing and grid corrosion. Typical examples of single-step CV and stepped CV/CC algorithms are shown in Fig. 2. The last step usually allows for a current taper when the voltage limit is reached, the duration depends upon the desired formation time.

For the jar formation of VRLA batteries, the disadvantages of CV charging probably outweigh the advantages. Overcharge is minimised due to the current taper during the

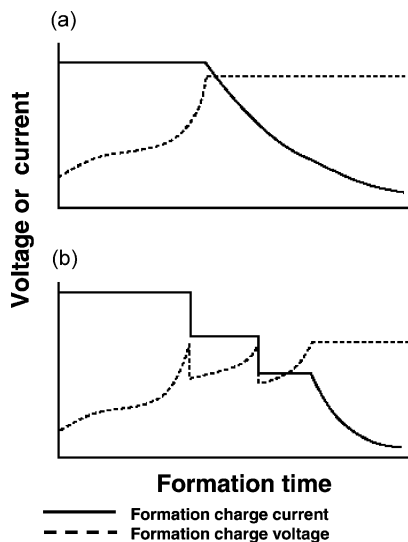


Fig. 2. (a) Single-step, current-limited, constant-voltage formation profile. (b) Multi-step, current-limited, constant-voltage formation profile.

finish of formation, and so the charge efficiency is relatively high and concerns about gas monitoring and ventilation are less important. As the battery spends a significant time in the current-taper mode, the total Ah input must be integrated electronically. In the single-step CV procedure, the long charge ‘tail’ lengthens the formation time significantly.

Actual charge voltages for each cell can be highly variable, because in the production situation, voltage is applied to long strings or series-parallel arrays as a multiple of a given volts per cell. More seriously, paralleled strings can draw different currents based upon their cumulative dc resistances. This can have the effect of routing high currents through individual strings early in formation, which can cause large imbalances of total Ah passed through different strings. In the extreme, this can result in strings with low initial dc resistance going into thermal runaway, particularly for large batteries with poor heat-dissipation capabilities.

If strict voltage control is desired, temperature-compensated charging must be used, which further increases cost.

### 3.3. Constant-current charging

The major advantages of CC charging are that it is easily programmable, it is relatively rapid and the total Ah input can be determined easily. In addition, the current level is controlled. Thus, even in series-parallel arrays, battery damage due to high charge currents, as noted above for CV formation, is largely avoided. Nevertheless, there are several drawbacks, namely:

- single-step CC formation is either very lengthy (low current) or very overcharge-intensive (high current);

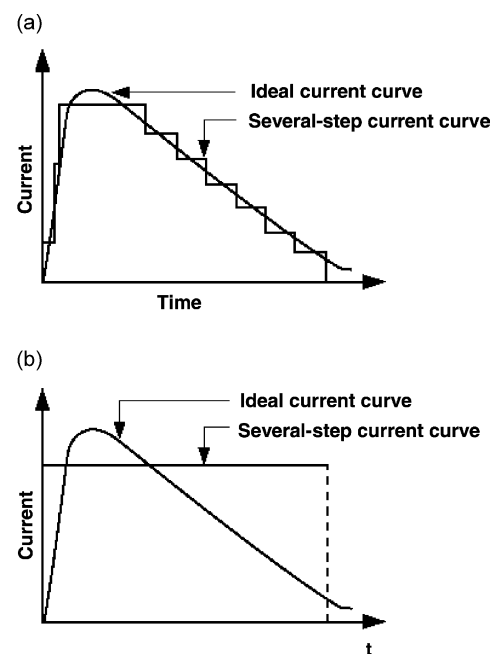


Fig. 3. (a) Stepped constant-current formation. (b) Conventional constant-current formation.

- heavy overcharge results in high heat production, grid corrosion, and gassing;
- voltage regulation on charge is not possible, except for the high upper limits used (2.8–3.0 V per cell, or more).

More innovative, multi-step algorithms are now in use where relatively high currents are used early in formation and lower finishing currents are then applied, either as a two-step or a multi-step algorithm. Dramatic gains in charging efficiency can be realised, as shown conceptually in Fig. 3 [2]. In some cases, this is done as a fixed, programmed algorithm with defined current levels for pre-set time intervals. Other approaches involve monitoring of battery parameters in order to apply optimal current levels for as long as possible. One example of this is shown in Fig. 4 [3], where battery temperature is used as the control variable. As can be seen, this allows for an initial high CC level, followed by

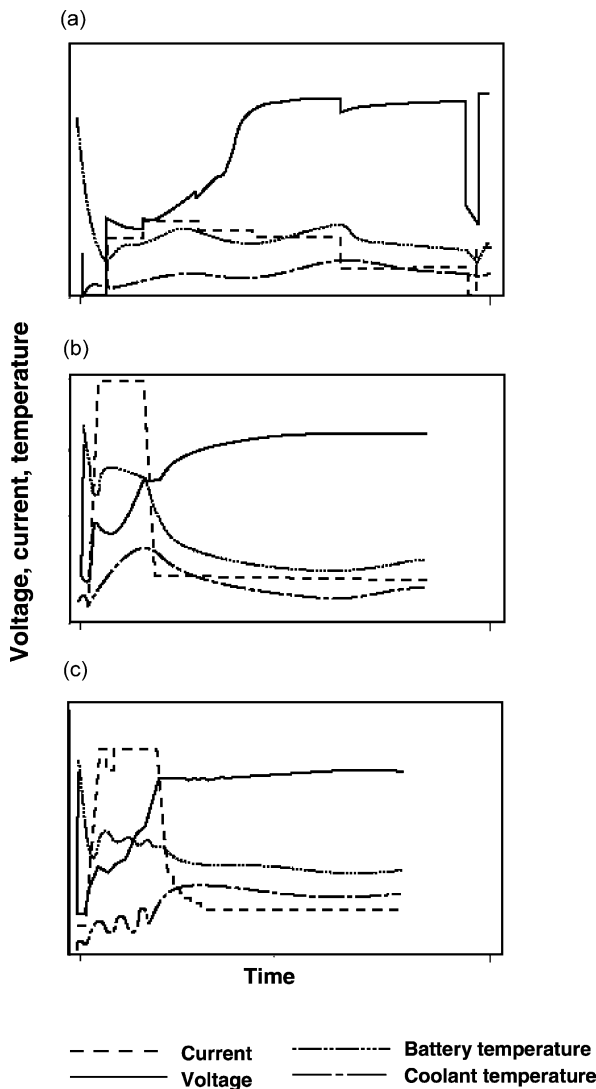


Fig. 4. (a) Normal formation; battery placed in non-flowing water pool. (b) Formation in flowing coolant with maximum initial current; limit set on voltage but not on temperature. (c) Formation with initial maximum current limit, followed by temperature and voltage limits.

step-downs to lower currents at values that are based upon battery temperatures.

On balance, CC charging is the simplest approach to formation and is the most commonly used, particularly in multi-step algorithms. It is also possible to combine the CC and CV approaches, in which CC steps are used for the bulk formation charge, with one or more CV steps in the final stages of charge.

### 3.4. Taper-current charging

This is not a common method, but taper-current (TC) charging for formation combines some of the best aspects of the CV and the CC approaches, and is probably the least expensive of the three options. A typical circuit for TC charging, along with a typical charging curve, is shown in Fig. 5. A power supply is wired in series with a load resistor and the battery string (or strings) that is to be formed. If desired, some form of sensing of battery parameters (voltage, temperature, etc.) can be included to provide feedback control. When formation is initiated, current flows according to the rating of the load resistor and the difference ( $\Delta V$ ) between the voltage setting of the power supply (typically a high value of 2.6–2.8 V per cell) and the voltage of the battery array (which, initially, will be at a very low value). At the beginning of formation, the voltage difference is large, i.e. of the order of  $\sim 1$  V per cell, and the inrush current is relatively high, as in CV charging. As the cumulative voltage of the battery array climbs, the formation current decreases because of the decreasing value of  $\Delta V$ . Unlike CC charging, when the voltage of the battery array climbs into the gassing region, the charge current begins to taper. The current does

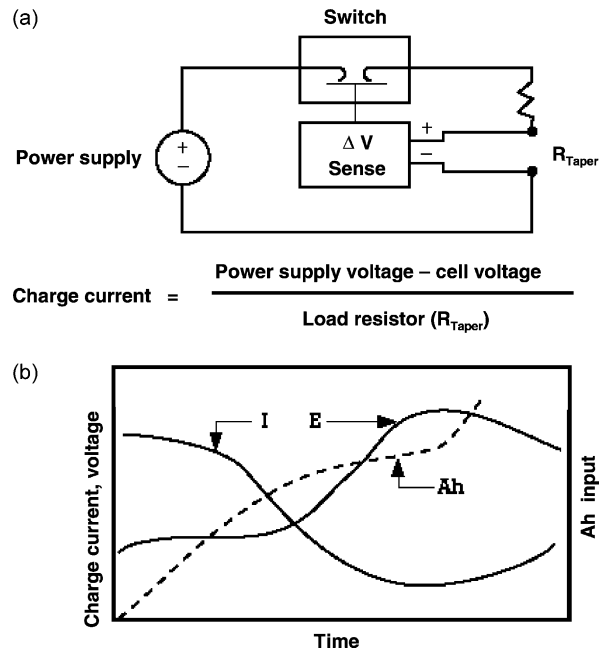


Fig. 5. Taper charge formation: (a) typical circuit; (b) typical charging curve.

$$\text{Charge current} = \frac{\text{Power supply voltage} - \text{cell voltage}}{\text{Load resistor } (R_{\text{Taper}})}$$

not, however, taper off as sharply as with CV charging because of the higher voltage setting. Initial and final currents are roughly set by the choice of power-supply settings and resistor values. These yield an approximate formation voltage–time profile, but the exact shape of the curve will vary considerably as dictated by the charge-acceptance properties of the battery array. This can be viewed as both a strength and a weakness of the approach. Nevertheless, it is well suited to the formation of VRLA batteries, as many products do not require precise voltage control.

This approach does have some drawbacks, namely:

- because the current tapers, Ah input must be determined by electronic integration;
- the amount of overcharge is high relative to CV or multi-step CC charging;
- voltage and current are not controlled, so the formation profile and total Ah input may vary significantly from batch-to-batch;
- the use of unregulated power supplies can result in shortened lifetimes in service.

### 3.5. Pulsed-current charging

Pulsed-charge algorithms can be applied to the formation of VRLA batteries; typical algorithms are shown in Fig. 6. Profiles analogous to CV or TC charging, as well as pulsed CC, can be used. In the ‘off’ periods, rests or partial/complete discharges can be applied. The discharges are thought to be beneficial in eliminating surface charge from the plates, which can result in lower gassing levels; it has not been unequivocally established if this is indeed the case. Much work has been undertaken on pulsed methods, but it remains unclear whether gains in product quality can be realised. There are clear advantages in enhanced heat dissipation while allowing the use of relatively high currents (even late in formation), as well as in reduced gassing due to reductions in coulombic input per pulse as the gassing region is approached late in formation. While most battery companies have investigated this for the above reasons, it is not commonly used.

### 3.6. Rests and discharges

One of the major electrochemical problems in using any of the above formation regimes (with the exception of pulsed charging) is that gas generation can severely impede the efficiency of the formation process by retarding the diffusion of acid and water within the plate pores. The charge efficiency of the positive electrode is relatively low even when completely formed, but in formation itself, the efficiency is so poor that gassing of oxygen can begin after only a few hours, or even less. Later, the negative plate will also begin gassing. For both plate polarities, gassing hampers proper conversion of unreacted lead oxides deep in the plates to lead sulphate, and then subsequent reaction of the sulphate to the active materials. The first reaction requires acid to be generated at the plate surfaces early in formation in order to penetrate into the plate interiors. The second reaction requires water to produce  $\text{PbO}_2$  and sponge lead. When either or both of the plate polarities goes into gassing, liquid will be forced out of the plate pores and into the glass-mat separator. Eventually, with heavy gassing, much of the electrolyte will be forced into the head space, or even out of the battery as regurgitated acid or acid spray.

These conditions can be avoided by inserting one or more rest periods or discharges into the formation algorithm. When the charge voltage is removed, gassing ceases and time is allowed for water and acid to diffuse into the interiors of the plates. This allows acid to react with any remaining lead oxide in the plates. When formation is re-initiated, more lead sulphate has been generated and water is present as a part of the filling reaction. When formation is continuous, gassing seriously impedes these processes. Use of significant ‘off’ times can actually result in faster, more complete, formation processes. Rests or discharges can be applied at fixed points in formation, or they can be initiated when a ‘trigger’ voltage is reached. These considerations probably apply more to products with thick plates (2.0 mm or more) rather than to those with thin plates (where diffusion paths are shorter and plate wetting is more efficient due to the higher surface areas).

Little documentation is available on the relative effects of rest periods and discharges. Thus, the technologist is left to

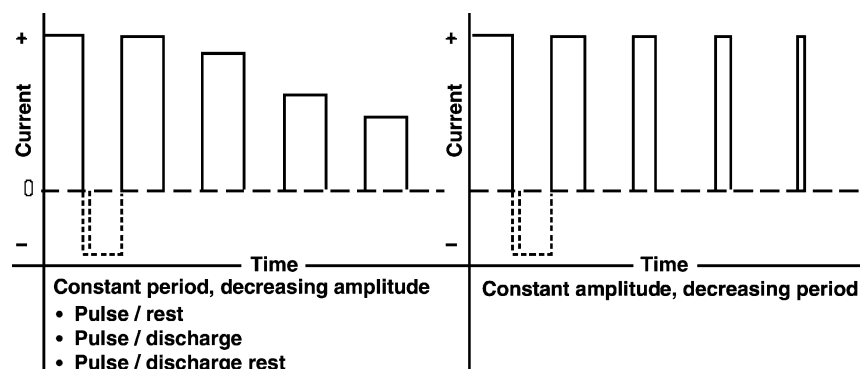


Fig. 6. Pulsed-charge formation algorithms. In all cases, coulombic output decreases as top-of-charge is approached.

weigh the possible benefits given above against the significantly higher costs of the discharge equipment. Discharges are clearly more complex in terms of capital equipment and they will lengthen formation time relative to rests due to the requirement for replacing charge taken out during the discharge. Discharges are thought to be beneficial because, in principle, they should increase the porosities of the plates and further aid acid and water penetration, as well as improve post-formation discharge capacities. Both approaches are clearly beneficial in reducing formation weight losses and in improving finished-product quality.

#### 4. Formation algorithms and profiles

##### 4.1. Simple algorithm

Examples will now be given of sample formation profiles that might be recommended for a typical 12-V/20-Ah VRLA product. The simplest approach would be a single-stage CC formation over, for example, 36 h with a total Ah input of four times the rated capacity, i.e. 80 Ah. Over a 36-h period, this would be a CC level of  $\sim 2.2$  A, as shown in Fig. 7a. This approach results in relatively high temperatures towards the end of formation and large overcharge amounts and gassing levels, but it will form the battery successfully. Since the pore structure may not be optimal due to the low initial current, a modification would be to use a two-step CC algorithm with, say, 2 h at 8 A (16 Ah) followed by 34 h at 1.88 A. (Fig. 7b). For a CV formation, somewhat more

time may be required or a high-inrush current may be needed, accepting a somewhat lower charge input at 36 h, as shown in Fig. 8a. In order to increase the charge input towards the end of formation, a TC algorithm may be used, as shown in Fig. 8b. This has a high-inrush current as is used with CV formation, but the current only tapers to  $\sim 30\%$  of its initial value. This results in a higher Ah input, but also higher temperatures and more gassing (weight loss) in the final 12 h or so.

An intermediate level of complexity can be applied by introducing two rest periods into a 36-h CC formation. The rest periods can be shifted towards the end of formation as there is, initially, a great deal of lead sulphate produced by the filling process and it will take some time to consume this material. In the example shown in Fig. 9a, the voltage is monitored and ‘trigger’ levels are used to start the two rest periods. A total of 4 h has been allocated for rest periods; this could be divided into one or two rests, but it is more practical to use two. More rest periods and longer total rest times may also be suitable for some VRLA thick-plate products.

To achieve a relatively fine pore structure in the positive active-material, a short period of high-inrush current has been used to provide smaller, more numerous,  $\text{PbO}_2$  seed crystals upon which to build during the rest of the formation. After this, a fixed CC level can be used in combination with the two rest periods, as shown in Fig. 9a. The rest periods are beneficial not only in providing time for electrolyte penetration, but also in keeping the temperature down compared with a continuous one- or two-step CC algorithm. Because the time spent in overcharge and resultant gassing is lower

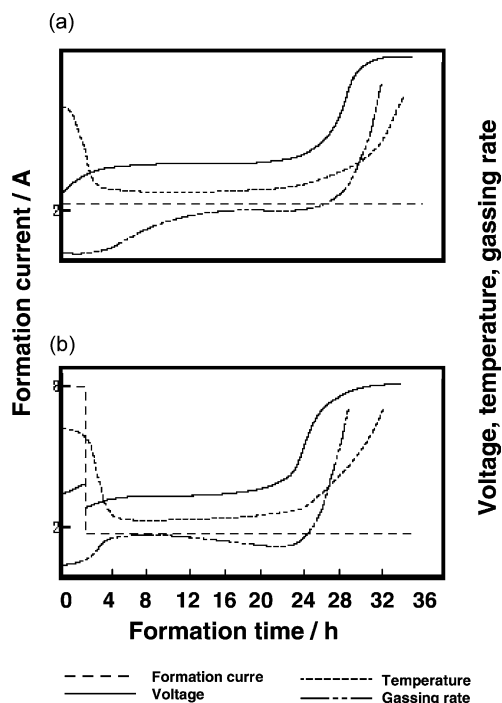


Fig. 7. Voltage, temperature and gassing curves for: (a) one-step CC formation; (b) high-inrush, two-step CC formation.

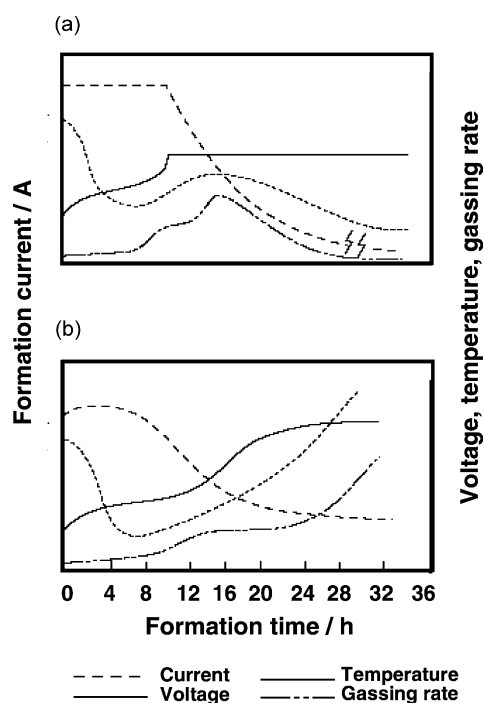


Fig. 8. Voltage, temperature and gassing curves for: (a) one-step CV formation; (b) one-step TC formation.

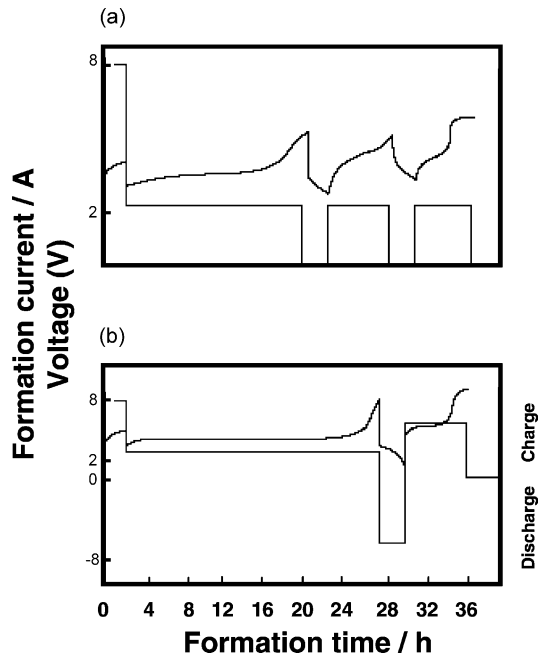


Fig. 9. Current and voltage curves for: (a) CC-rest formation; (b) CC-discharge-recharge formation.

overall with rest periods (even though the charging current is higher to compensate for the 4-h off time), weight losses are also reduced.

If a discharge were to be used instead of the two rest periods, it would be most beneficial to apply it near the end of the formation, as shown in Fig. 9b. Only a partial discharge is carried out; a complete discharge would obviously be more effective in promoting pore formation and electrolyte penetration, but it would also require substantially more time for the full discharge and subsequent recharge. If this were undertaken within the 36-h schedule time, it would require much higher levels of charge current. There is no clear evidence, however, that a discharge is more effective than rest periods. One advantage with a discharge is that it could be used as a matching tool for building battery modules into high-voltage packages, i.e. through the use of discharge capacity and top-of-recharge data recorded during formation. This would, of course, require that all batteries be monitored and that the data be collected and processed. Equipment to carry out the discharges would, of course, increase costs. In addition, if the formation time was extended, this would reduce the battery throughput level and would require more formation stations to process the same number of batteries. Despite these issues, finished battery quality and uniformity would be improved significantly.

#### 4.2. Development of a suitable formation algorithm

The battery manufacturer will need some experimentation to determine the most effective formation algorithm for a specific product. The following steps can be used to define a suitable algorithm.

- Take at least 12 filled modules and monitor temperature between fill and formation; note the battery temperatures at the initiation of formation.
- Weigh the batteries prior to formation, but at the end of the fill-to-form period. It should not be assumed that the electrolyte fill weight can be added to the pre-fill battery weight in order to get the pre-formation weight; all batteries, especially large ones, that are processed whilst open to the atmosphere, will lose weight between filling and formation due to evaporation and, in some cases, acid spraying or regurgitation.
- Batteries should be configured as close as possible to their ultimate layout in the manufacturing process. In addition, thermal conditions should be close to those that will be seen by the batteries in manufacturing. Initial formation studies can be conducted on small numbers of batteries, but it should not be assumed that product quality would be the same as in full-scale manufacturing.
- Wire up the test batteries so that the following parameters can be monitored: voltage, time, current, Ah input and internal pressure (if batteries are formed sealed). Reference-electrode measurements should also be taken and, at some point, gas collection and analysis should be performed on several batteries during formation.
- An initial run should be done using a very simple one-step CC, CV and/or TC charge, in order to determine how the battery reacts to these 'baseline' conditions. Then, several preferred algorithms should be applied. These should cover a range of times and currents and should use rest periods and, possibly, discharges.
- After formation, batteries should be weighed and inspected carefully for cosmetic and product defects (acid spray or leakage at lid/box seals or terminal posts, label damage, etc.). Tear-downs should be undertaken to allow examination of the plates in detail, i.e. (visual inspection for white sulphate, colour, hardness (positive active-material) or softness (negative active-material), distortion, massive grid corrosion or growth. The separator should be inspected for holes/tears, damage from filling, staining by expander or paste, and the possible presence of lead sulphate (hydration shorts). The presence of lead in the separator can be determined by spraying a sodium iodide solution on the separator; insoluble lead dioxide shows up as a bright yellow precipitate. Electrolyte should also be squeezed out of the separator at several points to allow measurements of relative density to be taken.
- Negative plates should be dried and prepared for scanning electron microscopic, BET surface area and porosimetry analysis; other tests may also be conducted. Positive active-material should be treated similarly. In addition, several positive plates should be stripped of active material and the grids should be inspected and weighed for assessment of general or localised corrosion during formation. Wet-chemical analysis of the negative active-material (free-lead, sulphate) and the positive active-material (PbO<sub>2</sub>, sulphate, unformed PbO) should also



be undertaken. X-ray diffraction phase analysis should be applied, if available, to determine the amounts of  $\alpha$ -PbO<sub>2</sub> and  $\beta$ -PbO<sub>2</sub> generated at different locations in the positive plates.

- Taking all of the data above, several iterations of formation algorithms should be applied to ensure that the most effective procedure has been developed.
- As a final step, a pre-production run should be carried out under actual manufacturing conditions to confirm that the development work performed on a limited number of batteries (particularly the thermal conditions and the series–parallel configurations) is relevant to full-scale production.
- In addition to the above analytical work, full electrochemical characterisation of the formed batteries is necessary to ensure that nominal quality levels and the desired uniformity have been achieved using the selected formation algorithm. Self-discharge (shelf-life) measurements should also be taken to ensure that the degree of formation of the positive plate and the remaining amount of unformed oxide are acceptable.

## 5. Temperature limits for VRLA jar formation

For jar formation of conventional flooded batteries, a maximum formation temperature of up to 65 °C may be permitted with no apparent harmful effects on battery performance. This is certainly the case for automotive batteries. Industrial battery designs may have significantly longer formation times and lower recommended maximum formation temperatures (e.g. 50 °C).

The temperature during all stages of the filling and formation process is much more critical for VRLA jar formation. The control of temperature is necessary from the initiation of formation until its completion. Sometimes, it involves active control and at other times it dictates passive processing conditions. The latter is true going into formation, where the battery has been filled with electrolyte and allowed to stand for some time before being placed in the formation environment.

With VRLA batteries, high formation temperatures may result in the formation of lead dendrites and/or hydration shorts. Therefore, the maximum formation temperature should be kept below 40 °C. Normally, this will require water cooling or forced-air cooling. The formation regime may also include brief rest periods. Some VRLA battery manufacturers may specify a maximum temperature of 50 °C, or even 60 °C, but there are risks associated with this approach. By comparing formation at 60 °C with that at 40 °C, it has been found that the PbO<sub>2</sub> content is higher at 60 °C, and the  $\alpha$ -PbO<sub>2</sub>: $\beta$ -PbO<sub>2</sub> ratio is lower. The higher temperature has, however, an adverse effect on the negative plates, and results in a decrease in battery capacity at high discharge rates. The surface area of the negative plates is decreased if formation is carried out at high temperature, possibly because of deterioration of the negative-plate

expander [4]. It is important to note that if the measured temperature at the top of the cell is 60 °C, the maximum internal temperature inside the cell may be significantly higher, i.e. 70 °C or even as high as 80 °C. This has implications with respect to the stability of the negative-plate expander, and it has been found that the surface area of the negative plates is significantly reduced. Localised overheating may also result in grid corrosion and/or increased risk of lead dendrite formation.

In practice, there must be sufficient time after filling and before the start of formation to allow the heat generated during the filling process to have passed its peak. Thermal management during the filling process should not be too efficient or the exothermic acid-oxide reaction may ‘shut down’ if the battery is too cold, and start up again—generating excessive heat—when the formation process is started. The degree of cooling (or even heating) during formation is dependent upon a number of factors that include: product size, temperature at start of formation, cooling technique, plant temperature, and sealed or open formation.

## 6. Battery design

Battery design has a critical influence on the filling and formation of VRLA batteries. Some of the potential problems with VRLA battery filling and formation can be minimised, or eliminated, by careful battery design. Unfortunately, some of the design strategies to improve filling and formation may have an adverse effect on battery performance and life, so some compromise may be necessary.

The battery design parameters which may influence VRLA cell/battery filling and formation include:

- battery height, tall batteries are harder to fill than short ones;
- battery width, short, wide batteries are more difficult to fill from a single port;
- plate thickness and inter-plate spacing;
- plate height and plate-height:plate-spacing ratio ( $L:d$ );
- position of filling port;
- battery case draft;
- active-material additives (expander/reinforcing fibres);
- gravity, liquid will only wick so high before being defeated by gravity (this is not a concern in gravity filling from top to bottom);
- separator properties:
  - volume porosity and pore structure (mean pore size); finer pores wick more slowly but to greater final heights;
  - saturation;
  - compression, this results in a finer pore structure with high tortuosity, and therefore slower wicking, e.g. 15% compression will double wicking time to a given height;
  - calliper (thickness at defined pressure);
  - grammage ( $\text{g m}^{-2}$ );
  - surface area and diameter of fibres, finer fibres (higher surface area) result in finer pores, hence slower wicking;

- wettability;
- fibre structure (coarse/fine fibres, inclusion of synthetic fibres), organic fibres inhibit wicking (not wetted by sulphuric acid), and also promote faster drainage;
- fringe area of separator (area of separator not covered by plates).

It can be seen that the separator properties are critical, and these are discussed in more detail in Section 7. The other critical battery design parameters are discussed below.

### 6.1. Plate-height:plate-spacing ratio ( $L:d$ )

The ratio of plate height to plate spacing ( $L:d$ ) can be used as a rough measure of the difficulties that are encountered in filling. For a  $L:d$  ratio  $\leq 50$ , easy filling results. If the ratio is between 50 and 100, care should be taken to avoid potential problems. Filling becomes more difficult when the ratio is between 100 and 200, and is almost impossible at ratios above 200 [6]. These characteristics show that the worst situation is a tall battery with a close plate spacing, and the best situation is a short, narrow battery with a wide plate spacing.

### 6.2. Battery case draft

Battery case draft can result in a 10% change in compression from the top to the bottom of the plate. For example, with a target compression of 25%, the compression may actually vary from 20 to 30% between the top and bottom of the plate. The effect of this on the performance and life of the battery may be highly significant, and should not be ignored in the formation process as well. The separator at the bottom of the cell will be subject to a higher compression and this will result in a smaller pore structure which, in turn, will influence the speed at which the acid fills the separator during the acid-filling process. There will be a slower drip speed as the acid approaches the bottom of the plate. Because smaller pores have a greater force to pull liquid, this may also increase stratification [7,8].

### 6.3. Active-material additives

Additives in the active material can also affect the filling operation. The expander or reinforcing fibres in the paste may interact and result in excessive gassing during acid addition. This will result in a longer fill time or even in an unacceptable product. Care needs to be taken when any new material is used since the VRLA battery should be considered as a system and all the ingredients interact.

### 6.4. Electrolyte additives

Most VRLA battery manufacturers use sodium sulphate as an additive to the electrolyte. It is added to the electrolyte in powder form, at about 1% by weight. Sodium sulphate

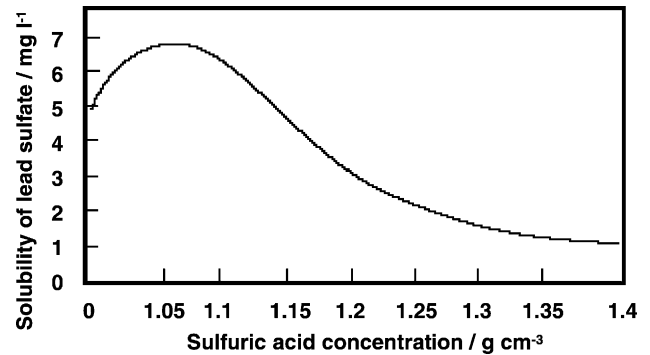


Fig. 10. Solubility of lead sulphate in sulphuric acid.

acts by the common ion effect to prevent the harmful depletion of sulphate ion which is a danger in the discharge of acid-starved batteries. The addition of sodium sulphate provides an ‘inventory’ of sulphate ions that are available without increasing grid corrosion [9]. The solubility of lead sulphate increases significantly as the concentration of the sulphuric acid electrolyte decreases, as shown in Fig. 10. The solubility increases more than four-fold as the sulphuric acid density decreases from 1.300 to 1.100 g cm<sup>-3</sup>. Under certain conditions of overdischarge, the amount of dissolved lead sulphate may be such that, on recharging, the reduced lead will form metallic bridges between the plates. The addition of sodium sulphate will reduce this risk.

Alternative electrolyte additives may be used, which have a different modes of operation. This class of additives is known as ‘dendrite prevention additives’ (DPA) [13]. These operate by actively seeking out and deactivating the growth of lead dendrites. They are polar organic compounds that are believed to deactivate lead growth by coating the tips of the lead crystals with a layer of oriented molecules. Once lead growth is deactivated, these molecules are available to move to new sites.

## 7. Separator optimisation

### 7.1. General comments

Separator properties have a critical impact on acid filling and jar formation [5]. Any change in the physical properties of the separator material can drastically change the quality of the filled and formed cell or battery. The type of separator used is dictated more by the intended battery application, but its properties can also partially determine the filling and formation conditions that are employed.

During the filling process, the acid wicking rate is important. The rate is primarily a function of the mean pore size of the glass-mat separator. The pore size, in turn, is largely a function of the fibre mix (represented by the fibre specific surface area as measured by BET), the density of the glass mat, and the compression level in the unfilled plate stack. In practice, wicking is only directly applicable for ‘top-down’

gravity and ‘bottom-up’ filling methods in which wicking is the primary mode of fluid transport. Although separator properties also play a role in soft- and hard-vacuum filling techniques, the vacuum level and filling speeds are additional control factors, as are the electrolyte temperature and its resultant viscosity. A further variable is the use of 10–20% organic fibres mixed with glass, as in the Hovosorb IIP-15 material produced by Hollingsworth and Vose. The organic fraction confers greater tensile strength and also facilitates filling due to the hydrophobic nature of the organic fibres. Since the organic fibres are not wetted by sulphuric acid, the electrolyte is not ‘held’ as strongly as by glass fibres. This clearly facilitates filling, but it can result in flooding of the pores in negative plates with acid so that electrolyte regurgitation and spray may be significant during formation.

The actual separator compression in the plate group will influence the ease of acid filling and jar formation, and will also affect the performance of the battery. High compression has been shown to be beneficial in extending the life of VRLA batteries by inhibiting positive-plate expansion, but unfortunately the process of filling the battery with acid becomes more difficult. When the separator is compressed, it reduces the pore size significantly and also reduces the space available for electrolyte between the plates. This adversely affects the wicking properties of the electrolyte. On the other hand, smaller pores and higher compression may mitigate variations in saturation and acid strength in the vertical plane (stratification). It is also important to optimise the ratio of plate and separator pore volumes to ensure sufficient electrolyte.

The easiest filling is achieved by using a combination of glass and organic fibres with a low specific surface area ( $\sim 0.8\text{--}1.4\text{ m}^2\text{ g}^{-1}$ ) in a low-density material (i.e. high percent porosity of  $\sim 95\%$  or more) that has a relatively low compression level (25–30 kPa dry, or less) in the assembled, unfilled plate stacks. This gives an open structure that is not completely wetted by the electrolyte and, thus, offers the best chance for uniform fluid distribution. Such a separator would be best suited to gravity filling. This type of separator and cell construction is also most susceptible to electrolyte drainage and stratification, particularly in deep-cycling applications. On the other hand, the best separator to minimise drainage and stratification is a high surface area ( $\sim 2.0\text{--}2.6\text{ m}^2\text{ g}^{-1}$ ), high density (90–92% porosity) all-glass with high compression. This will give excellent deep-cycling results, but it is extremely difficult to fill, particularly in large batteries. It might be thought that a high-vacuum fill would be the most suitable for this separator but, in fact, this would only be true in relatively small VRLA batteries ( $\sim 25\text{ Ah}$  or less) due to the large amounts of heat that are generated in short times in high-vacuum fills. If the battery configuration cannot dissipate the large burst of heat generated by the filling process, there can be permanent damage in the form of plate buckling, separator staining by paste and/or expander, bulging of the case, and destruction of terminal seals; internal cell temperatures in excess of  $110\text{ }^\circ\text{C}$  can be achieved for relatively long periods of

time. Gravity fills with this type of separator system will take much longer (possibly up to 30–40 min), but thermal issues will be minimal.

Typical design parameters are as follows:

Volume porosity	92%
Saturation	95%
Compression	30%
Acid utilisation	8.8–9.5 ml Ah <sup>-1</sup>
Separator calliper	Related to inter-plate spacing and required degree of compression
Separator grammage	>2 g Ah <sup>-1</sup> is preferred
Separator surface area	>2 m <sup>2</sup> g <sup>-1</sup> is preferred to minimise stratification, but filling will be more difficult
Jar formation Ah input	Four or more times the rated capacity; it is necessary to restrict overcharge during formation, otherwise the positive plates may become damaged and the overall relative density of the acid may increase

## 7.2. Separator compression

Research work conducted by the Advanced Lead–Acid Battery Consortium (ALABC) has shown that high compression battery designs can extend battery life by maintaining a high pressure against the positive plates and eliminating or minimising the phenomenon known as ‘premature capacity loss’. In fact, it is more relevant to refer to ‘plate-group pressure’ rather than ‘% compression’. Some recent separator designs are less compressible, but may be able to maintain a higher pressure against the positive plates than conventional glass separators [10]. Unfortunately, a design with high plate-group pressure and high compression may also be more difficult to fill. A higher compression will generally result in lower fill rates. When the separator is compressed, it reduces the pore size significantly and also reduces the space available for electrolyte between the plates. This adversely affects the wicking properties of the electrolyte.

Another issue that may need to be considered is that of changes in plate-group pressure during formation. There are changes in the volume of both positive and negative active materials during the formation process as the lead oxides are converted to lead at the negative plates and lead dioxide at the positive plates. This may have some effect on the separator compression and applied plate-group pressure. This needs to be taken into account in the design of the battery, and in the specification of the separator and the initial compression level. Recent ALABC research has shown, however, that under some circumstances the separator compression may drop significantly after formation [11].

The exact cause(s) of this behaviour is (are) are still to be determined, but may be related to a relatively low initial plate-group pressure. There may be a critical compression that holds the fibres in place (for a particular separator) and if there is significant gassing at the end of the charging process, there may be a loss of integrity in the fibre mat.

While this problem is not yet fully understood, the following design issues need to be considered to minimise the risk of loss of plate-group pressure during jar formation:

- assemble cells with the maximum practicable plate-group pressure (>40 kPa);
- maximise available acid volume and increase separator grammage to  $\geq 2 \text{ g Ah}^{-1}$ ;
- increase the content of fine fibre in the separator;
- use a formation algorithm that minimises gassing at the end of charge.

### 7.3. Separator surface area

The surface area of the glass mat is very important because it greatly influences wicking during fill and fluid movement in fill/formation. There is a reasonably well-defined relationship between surface area and pore size, as shown in Fig. 11. This curve has been constructed from data on various separator samples from a wide range of manufacturers [12].

The surface area of a glass separator is related to the ratio of coarse-to-fine fibres. A separator with a low surface area (i.e. a high proportion of coarse fibres) has advantages in the filling process, but may have other disadvantages depending on the battery application. A higher surface area correlates to a smaller pore structure and results in a lower wicking rate, but a greater ultimate wicking height [13] (see Fig. 12). The smaller pore structure will also help to decrease stratification within the cell. The pore structure of the separator provides a highly tortuous path which helps to prevent dendrite growth and minimises the size of any dendrites that may be formed. On the other hand, this also creates a tortuous path for acid and air movement that increases the filling time for each cell. A battery designed for deep cycling should use a separator with a high surface area, but extra care will need to be taken

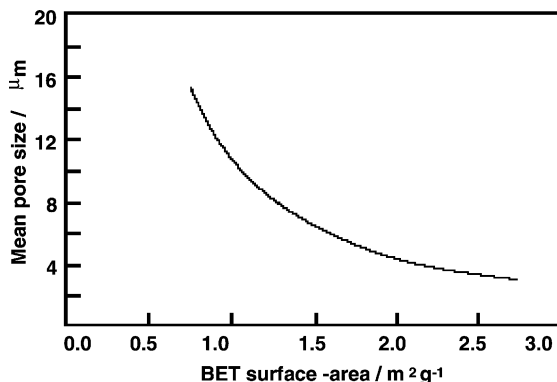


Fig. 11. Mean pore size of AGM as a function of surface area.

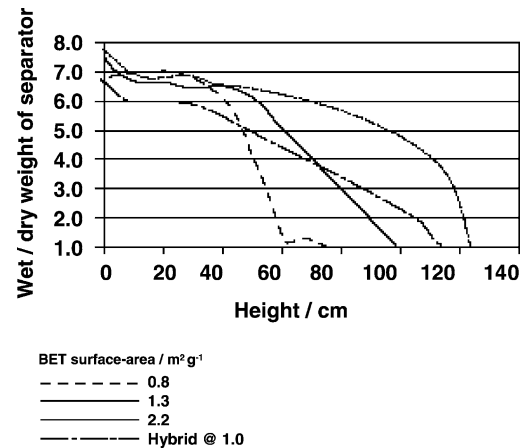


Fig. 12. Wicking characteristics of AGM separators with different specific surface areas.

during the filling process. Such a separator will require additional time to add the acid, since the acid wicks more slowly through finer pores. Also, the method by which acid is added to the battery is critical. If the acid is added too rapidly from the top, the air within the plates and the separator may not have sufficient time to escape, and dry spots may result. If the filling process allows the acid to wick up the separator, entrapped air can escape since it does not have to diffuse through the electrolyte. It is also necessary to allow sufficient time for complete filling of the pores of the separator. With a high surface-area separator, an advantage of the longer time for acid ingress could be a longer time for heat dissipation. The filling procedure is critical to providing a VRLA battery of good quality.

## 8. Separator designs to improve wet formation

The Hovosorb IIP-15 separator has already been mentioned. This is a refinement of the original Hovosorb II material, and has improved puncture resistance. The IIP-15 separator contains a synthetic fibre with reinforcing glass strands; the balance is microglass. The synthetic fibres are hydrophobic and offer sites within the separator matrix that control the wetting properties of the separator and modify the recombination process. It is claimed that this assists the filling and formation process, and allows a 'fill and spill' formation technique to be used. The unformed cells can be flooded with electrolyte prior to formation, and drained of excess free electrolyte after formation. The use of Hovosorb II together with a 'fill and spill' formation system may result in a more uniform cell-to-cell electrolyte concentration than is obtained with volumetrically filled, in-container formed cells. An additional benefit is that recombination can occur even when the separator is fully saturated.

An alternative approach is to use separators that consist of two or more layers of different fibres. This may be helpful in the filling process since layers of coarse fibres are soaked

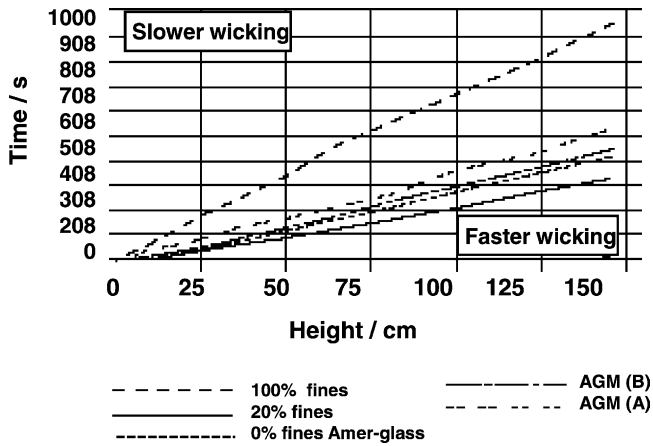


Fig. 13. Influence of fibre mix and segregation on vertical wicking speed of AGM separators. Strips of AGM not compressed. All AGM samples are single-layered, except Amer-glass which is multi-layered.

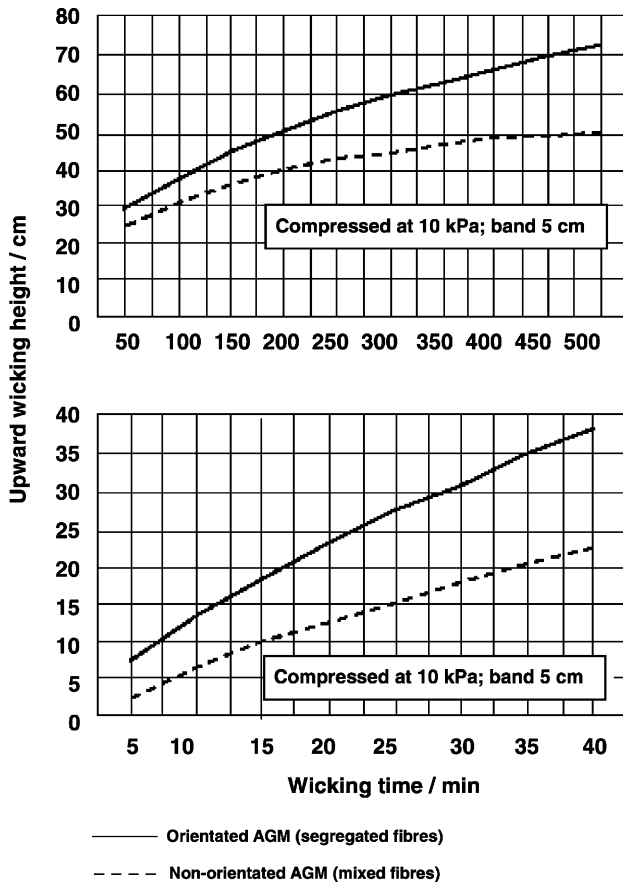


Fig. 14. Upward wicking height for orientated and non-orientated AGM separators.

more quickly. Battery filling is made easier with an ‘orientated’ separator that has separate layers of coarse and fine fibres, the fine fibres are placed against the positive plate, and the coarse fibres against the negative plate. Such a material has a very fast wicking characteristic both upward and downward [6,14]. The influence of fibre mix and segregation on the vertical wicking speed is shown in

Fig. 13. The upward wicking heights for orientated and non-orientated fibres are presented in Fig. 14. During the filling process, the fine fibre component absorbs acid quickly, but when the battery is filled from the top, the looser, coarser fibre structure permits an easier access to the electrolyte which then permeates instantaneously to the fine fibre side. When the process is in reverse, and acid is spilled out of the battery, the forces binding the electrolyte to the coarser fibre structure are weaker, so that electrolyte will be preferentially lost from this part of the AGM. The desired partial saturation of the separator is thus quickly reached. Multi-layered AGM, such as that manufactured by Amer-Sil, has faster wicking properties which may be of great value in the ‘grey zone’ of filling where the ratio of plate height to plate spacing is between 50 and 200.

Another possible option is to include a thin microporous sheet as part of the separator system, as this may help to eliminate the problem of lead dendrite formation. The sheet might also help to control the diffusion of oxygen from the positive to the negative plate. An example of such a microporous separator is the Duragard™ separator manufactured by ENTEK International. Amer-Sil have also developed a composite separator which includes a microporous sheet between two layers of glass. Results with this separator system have been reported in the ALABC research programme.

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