Technical Note

Aspects of lead/acid battery technology
6. Designing for capacity

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Abstract

The factors that determine the capacity of a cell are reviewed and the influence of cell design on the end-of-discharge specific gravity and attainable capacity is examined. The effect of predominantly deep or shallow discharging is assessed for cells with either flat or tubular positive plates. The contribution, or otherwise, of the various sections and components of a cell is evaluated and a detailed design breakdown is made for (i) a tubular positive plate cell rated at 100 Ah/plate and (ii) a flat positive plate cell rated at 66 Ah/plate. The effect of production tolerances on components is discussed and a method for estimating the probable spread in capacity for bulk production is described.

Introduction

The capacity of a cell depends on the following features: (i) an excess of positive active material over theoretical; (ii) an excess of negative material over theoretical; (iii) sufficient electrolyte to support the capacity required and maintain an acceptable voltage, and (iv) sufficient diffusion characteristics in the active material/separator/electrolyte/separator/active material cell element to allow the available capacity in the electrolyte to be fully attained.

Although the exploitation of the electrolyte capacity will vary with the rate of capacity withdrawal on discharge, it can also be affected by the type and method of separation that is employed.

Low-rate discharges, i.e., slow withdrawal of capacity, will suffer less from the constraint placed on the electrolyte diffusion by the separation, the active-material porosity and the pore-size distribution than will high rates that attempt to denude the cell of its charge capacity very quickly.

There is a limit to the extent to which the positive and negative active materials can be reacted and cycled satisfactorily. The product of the discharge reaction is lead sulfate which forms first on the surface of the material and later on the walls of the pores within the active material. Lead sulfate is a very poor conductor of electricity and the more the compound is formed from the discharge reaction the more difficult it is to initiate and maintain the subsequent recharge reaction.

Cells that are required, by design, to deliver a good discharge capacity at low rates are usually expected to give a long cycle life. In such cells, there is usually a

lower limit to the porosity of the active materials below which the cycle life of the cell suffers. This limit is, to some extent, dictated by the amount of support given to the active materials by the separation and plate armouring. Active material porosities are directly related to the apparent densities of the formed materials. The latter can be readily measured and controlled on the shop floor. For example, the minimum apparent density for a flat-plate traction positive formed material with the support of a layer of glass wool held against it under slight compression should not fall below 4.1 g cm^{-3}. This gives a porosity of 56%. Similarly, the matching density for the negative should not be less than 3.7 g cm^{-3} if the back of the separation conforms closely to the profile of the plate. This gives a porosity for the negative material of 67%.

The type and nature of the separation determines the degree to which the available electrolyte can be denuded of sulfate ions. For example, it is common in a tubular positive traction cell to use a single-ribbed separator with a back-web thickness of ~0.1 cm assembled with the ribs against the tubes of lead dioxide. This arrangement gives a relatively large reservoir of electrolyte immediately adjacent to the positive material and a free path for the electrolyte above the cell element to diffuse downwards assisted by gravity. With such an assembly, it is possible to react the electrolyte until the concentration of sulfuric acid has fallen to ~9 wt.% (1.060 sp. gr.).

By contrast, in an obsolete design of flat-plate traction cell where the positive material was armoured with a relatively thick glass-wool sheet and the separation consisted of a shallow-ribbed, synthetic material separator with a thin, treated wood veneer interposed between the separator and the negative plate, the minimum end-of-discharge concentration at the same low rate of discharge barely reached 20 wt.% (1.140 sp. gr.). Modified forms of separation permit the electrolyte to be reacted to varying extents within these upper and lower limits.

These limits must be fully recognized in any estimation of cell performance since the capacity equivalent of one litre of electrolyte made available by design will vary considerably and will depend on how far the separation design will permit the electrolyte to be reacted. If, for example, the initial electrolyte concentration is 37.5 wt.% H_2SO_4 and the separation conforms to each of the extremes quoted above (i.e., to give an end-of-discharge concentration of 9 and 20 wt.%, respectively), then the capacity equivalents of the electrolyte would be 104 and 68 Ah l^{-1}, respectively. These are very large differences and they can determine success or failure in exceeding the level of the capacity provided by competitors' products.

A broad guide to the effect of separation and material porosity on the extent to which the material can be reacted is given in Table 1. The data are based on discharges at the 5-h rate. The higher figures are usually fixed by the type and thickness of the separator shim and/or glass-wool retainer mat used in conjunction with the ribbed separator. The lower figures are more dependent on the formed density of the positive active material, i.e., the amount of electrolyte absorbed within the pores of the material.

The design for capacity can be based on optimizing the element assembly by accepting that the cost of new tools for grids, pillars, etc. is part of the design or by employing existing grids, pillars and readily available separation, etc. to reduce, as far as practical, the cost of tooling, jigs, fixtures, etc. The latter is a compromise and confirms the feasibility of meeting market demands using, wherever possible, standard components. The reasons for choosing one or the other approach must be fully understood by management since the compromise approach may not give the competitive edge that is sought and the designer might, therefore, be wrongly accused of failing to meet the company need.

TABLE 1

Effect of separation and material porosity on acid utilization

Nature of separation/plate interface	Final acid sp. gr.
Single-ribbed separator against a tubular positive	1.080–1.090
Single-ribbed separator against an unarmoured flat-plate positive	1.080–1.090
Single-ribbed separator against a glass-wool armoured (0.5 mm) flat plate	1.090–1.000
Single-ribbed separator against a thicker glass-wool armoured (1 mm plus) flat plate	1.100–1.110
Double separation (separator plus wood shim) against thin glass-wool (0.5 mm) armoured flat plate	1.110–1.120
Double separation against thicker glass-wool armoured (>1 mm) flat plate	1.120–1.140

When estimating capacities, it is convenient to consider a single plate pitch and to determine the capacities that can be obtained for varying plate lengths and varying amounts of electrolyte over the plate, rather than to attempt from the start of the design to allocate portions of the full container height to the individual working and nonworking sections.

The basis of a working relationship between positive and negative plates and the associated electrolyte depends on balancing the minimum safe formed densities of the active materials with the maximum safe utilization of those materials within a working electrolyte of sufficient volume to support the desired capacity. In the case of flat-plate (grid type) cells, the balancing of formed material density with utilization (or specific formed material weight in g Ah^{-1}) can be readily controlled by design since the controlling factor is the grid. Take, for example, a negative traction plate in which the minimum safe formed density is deemed to be 3.9 g cm^{-3} and the minimum specific formed material weight is 11.5 g Ah^{-1} contained in a grid of specific grid weight of 6 g Ah^{-1} (excluding the lug).

For a 100 Ah (5-h rate) plate, the grid weight would be 600 g and the formed material weight 1150 g. The volume of the grid metal would be 600/10.8 cm^3, where the density of the grid alloy is 10.8 g cm^{-3}, i.e., 55.6 cm^3. Similarly, the volume of the active material, based on a formed density of 3.9 g cm^{-3}, would be 294.9 cm^3. Thus, the combined volume will be (55.6 + 294.9) cm^3, i.e., 350.5 cm^3.

The average plate thickness will be given by dividing the combined grid and material volumes by the superficial area of the plate, i.e., average plate thickness = 350.5/850 cm^2, where the negative plate is matched against a positive of 850 cm^2, a value that is typical of many positive plates.

The greatest difficulty arises in knowing what are safe specific formed material weights. This is because it is easier to react more of the material of an automotive plate than a traction plate on account of the large differences in plate thickness, even though the same formed density has been adopted in both cases. It is also easier to react more of a less-dense material, but with the limitation that below a certain formed density the electronic conduction between adjacent particles becomes uncertain and, consequently, the performance and the life attainments are unstable.

A further factor, applicable particularly to traction cells, is the ability to initiate and sustain an effective recharge after a full discharge. This can become a reality in
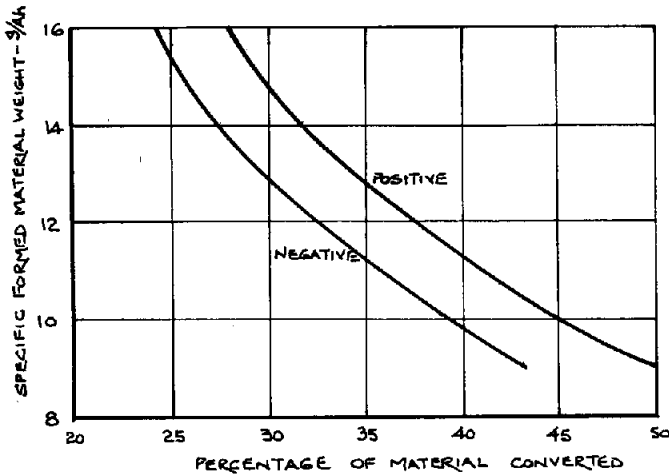
Fig. 1. Relationship between specific formed material weight and the percentage of formed material converted.

traction cells when the materials have been repeatedly discharged so that 35%, or more, of the formed material has been converted into lead sulfate.

In the above calculations, the convention of specific grid and specific formed material weights has been adopted since they convey rapidly to the designer the usage levels of the basic raw materials. There is a relationship between specific formed material weight and the percentage conversion of those formed materials in a complete designed discharge. The relationship is shown in Fig. 1.

Design parameters for flat-plate (grid type) negatives

Taking into account the effect of plate thickness and material density on the ease, or otherwise, of reacting the material provided, Fig. 2 indicates the order of variation in the specific formed material weight when discharging at the 5-h rate that is applicable to different thicknesses of active material at differing material densities. The same data are given in Fig. 3, except that the ordinate is the percentage of active material converted in a full discharge. Some designers prefer this parameter.

Automotive plates not subjected to deep discharging can accept lower formed densities than propulsion and traction plates. Below 3.4 g cm^{-3}, there are real dangers of material sinkage unless inert supporting additives, such as chopped Dynel fibres, are incorporated in the paste mix. This is particularly noticeable in the case of dry-charged negatives.

At one time, traction plates were commonly processed with formed negative densities of 4.2 to 4.4 g cm^{-3} but, with programmed paste mixing and better support, densities have been reduced below 4.0 g cm^{-3} and as low as 3.6 g cm^{-3}.

Whatever formed density is chosen for the plate design, allowance must be made, in formulating the paste mixing, for the densification of the material after passing under the pasting hopper so that the ratio of starting water and sulfuric acid will, in practice, produce the chosen design density. Without this confirmation, the calculations become a paper exercise with no relation to reality.
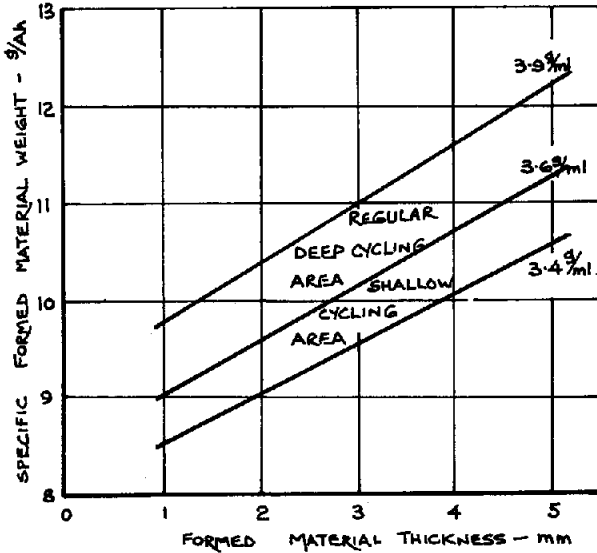
Fig. 2. Variation of specific formed material weight for negatives with formed density and material thickness.
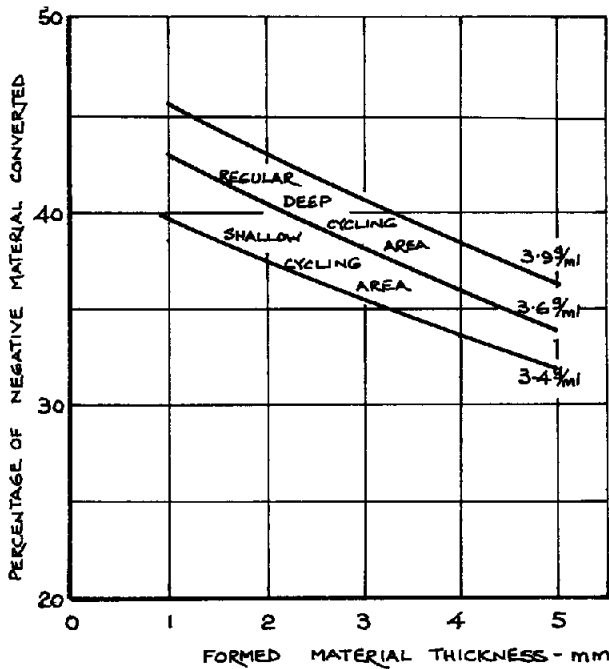

Fig. 3. Variation of percentage of negative material converted with formed density and material thickness.

An empirical guide to negative plate design is as follows:

(i) Automotive plates up to 2 mm thick, with shallow discharging (i.e., up to 40% conversion) in general and few and infrequent deeper discharges:
minimum formed density = 3.4 g cm^{-3}
specific formed material weight = 9.0 g Ah^{-1} at 5-h rate, and
= 7.6 g Ah^{-1} at 20-h rate.

(ii) Automotive plates thicker than 2 mm, with a degree of relatively deep-cycling:
minimum formed density = 3.7 g cm^{-3}
specific formed material weight = 9.7 g Ah^{-1} at 5-h rate, and
= 8.2 g Ah^{-1} at 20-h rate.

(iii) Traction or propulsion plates up to between 2 and 4 mm thick, with regular deep-cycling:
minimum formed density = 3.7 g Ah^{-1}
specific formed material weight = 10.8 g Ah^{-1} at 5-h rate.

(iv) Traction plates over 4 mm thick:
minimum formed density = 3.8 g cm^{-3}
specific formed material weight = 11.5 g Ah^{-1} at 5-h rate.

The above values are reasonably safe ones, but there are commercial examples, particularly with plates over 4 mm thick, of specific formed material weights as low as 10.5 g Ah^{-1}. Experience has shown that this order of specific formed weight demands a very close control of processing in order to restrict the inevitable spread in production. Without this, under onerous working conditions, the poorest cell in a series assembly will fail prematurely with repeated cycling, mainly through too rapid a build-up of irreversible lead sulfate, particularly in the lower area of the plates.

Design parameters for flat-plate positives

Characteristic curves that link the formed material thickness with plate thickness and type of work pattern, similar to those given in Figs. 2 and 3 for negatives, can be produced for positives. The main difference is that the formed densities tend to be higher since the positive material often does not have the same amount of physical support as the negative and the cementation bonds between particles are less secure.

Figure 4 gives broad guidelines for positives using the convention of specific formed material weight to identify the degree to which the material is used. The previously adopted usage patterns, regular deep cycling and shallow cycling, have been extended to underline the effects of inert binders incorporated in the pastes, and also the degree to which the positive material is supported by retainer mats. The data of Fig. 4 have been replotted in Fig. 5 with the specific formed material density replaced by the percentage of formed material that is converted during a full discharge.

There are dangers in working at formed densities much below 3.8 g cm^{-3}, unless inert fibre binders are incorporated in the material. This density should be taken as the minimum for specification tolerancing. For regular deep-cycling duties, a minimum formed density of as high as 4.2 g cm^{-3} is recommended in those cases where the positive material cannot be guaranteed to be always under real compression after the cell has been filled with electrolyte. This figure can be reduced to 4.0 g cm^{-3} when a generous thickness of glass-filament retainer mat holds the material firmly against the grid structure. This distinction is important since the surface of a positive readily expands with the volume changes that accompany successive discharges and recharges.
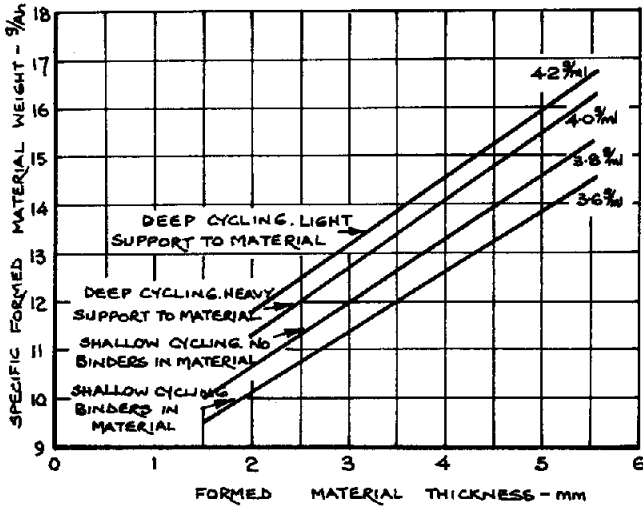
Fig. 4. Variation of specific formed material weight for positives with formed density and material thickness.
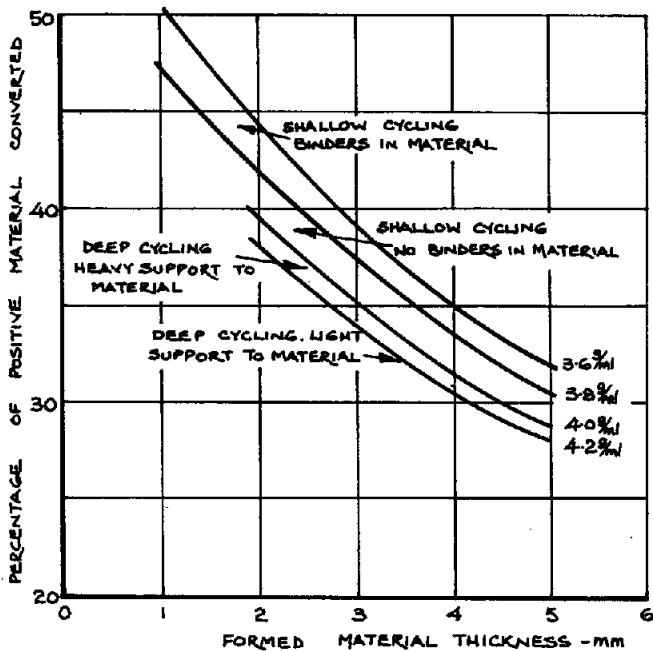

Fig. 5. Variation of percentage of positive material converted with formed density and material thickness.

Without real and permanent compression, the surface density can change appreciably and decrease to a sufficient extent that surface silting and loss of good particle-to-particle conduction becomes a reality.

The following empirical guidelines for flat-plate positives are suggested:

(i) Automotive plates up to 2 mm thick, with shallow cycling and few and infrequent deeper discharges:

formed density (minimum) = 3.8 g cm^{-3}

specific formed material weight = 10.5 g Ah^{-1} at 5-h rate, and
= 8.8 g Ah^{-1} at 20-h rate.

(ii) Automotive plates with inert fibre binders:

minimum formed density = 3.6 g cm^{-3}

specific formed material weight = 10 g Ah^{-1} at 5-h rate, and
= 8.4 g Ah^{-1} at 20-h rate.

(iii) Propulsion plates up to 3 mm thick with retainer mat support:

minimum formed density = 3.8 g cm^{-3}

specific formed material weight = 11.2 g Ah^{-1} at 5-h rate, and
= 9.9 g Ah^{-1} at 20-h rate.

(iv) Traction plates 3 to 4 mm thick with compressed retainer mat support:

minimum formed density = 4.0 g cm^{-3}

specific formed material weight = 13.5 g Ah^{-1} at 5-h rate.

(v) Traction plates 3 to 4 mm thick with lightly compressed glass-filament retainer mats support:

minimum formed density = 4.2 g cm^{-3}

specific formed material weight = 14 g Ah^{-1} at 5-h rate.

(vi) Traction plates over 4 mm thick with heavily compressed retainer mat support:

minimum formed density = 4.0 g cm^{-3}

specific formed material weight = 15 g Ah^{-1} at 5-h rate.

(vii) Traction plates over 4 mm thick with lightly compressed retainer mat support:

minimum formed density = 4.2 g cm^{-3}

specific formed material weight = 15.5 g Ah^{-1} at 5-h rate.

Some small reductions in these values are possible but any decision to make such a decision should be backed by adequate experimental evidence since the financial repercussions from taking too great a reduction can be large.

Design parameters for tubular traction positives

Whilst it is a relatively simple matter to equate formed density and specific formed material weight in flat plates, this is not the case with tubular positives. Often, the tubes are bought in as proprietary items and the choice is to accept the standard lines or pay a premium on that price to obtain a deviation from the popular standard. It is necessary in such cases, first, to assess the order of improvement in performance the optimum tube diameter would produce, and then to decide whether the price differential can be justified against the market requirements. If, with the standard tube, the market requirements of performance cannot be met, then the decision which tube to purchase is already made.

With tubular positives operating at pitches from 15.6 to 19 mm, it is generally agreed that the absolute minimum formed density for an acceptable commercial life of 4 to 5 years under onerous working conditions is 3.6 g cm^{-3}. The latter cannot be taken for design calculations since, under production conditions, there will be variations either side of the specified value. Some success has been obtained with formed densities as low as 3.4 g cm^{-3}, but the erratic nature and level of premature

failures on life precludes it from being accepted as the lower limit without recourse to additives in the filling material.

It is not uncommon for the variation in the formed density of the material in individual tubes of a plate, and between plates, to be of the order of ± 0.2 g cm^{-3}, even when the filling technique is carefully controlled. This indicates a prudent minimum formed density for design purposes of 3.8 ± 0.2 g cm^{-3}. Whether or not this level of formed density can be obtained in practice depends very much on the flow properties of the filling powder and its tamp density. For example, a Barton-pot oxide will generally flow more readily than a ball-mill oxide. Where a blended filling powder is adopted with red lead and/or litharge additions, the origin of these materials can be significant since it is common for either of the additives to be roasted from Barton-pot oxide, ball-mill battery quality oxide, or out-of-specification 'fines' from either system.

Ball-mill oxides are rarely used on their own as their characteristic platelet-shape hinders free flow. With such oxides, undiluted by any other material, it is even often difficult to reach a formed density of 3.6 g cm^{-3} and the incidence of voids is high. In order to exploit the lower cost of ball-mill oxide compared with, say, red lead, the oxide is usually blended with litharge and/or red lead made from Barton-pot oxide to enhance the flow properties. Barton-pot oxide alone, approaching 80 wt.% PbO, has been used with reasonable success.

The choice of tube diameter will dictate, at the chosen formed density, the degree of excess material over theoretical that will be obtained in production and the proportion of material converted to lead sulfate on discharge. This percentage needs to be limited. This is because a considerable amount of poorly conducting lead sulfate will seriously reduce the conductivity of the discharge material, will clog the pores and deny free access to electrolyte and, overall, will cause difficulties with effective recharging after deep discharge.

Where the capacity output is limited by the available electrolyte (and this is the case with most tubular positive cells), an active-material utilization factor of 35% for a full discharge will keep a cell free from recharge problems. This is equivalent to a minimum formed material weight of 4.46/0.35 g Ah^{-1}, where 4.46 g Ah^{-1} is the theoretical weight of lead dioxide to support 1 Ah, i.e., 12.7 g Ah^{-1}. This figure will refer to the safe minimum formed density of 3.6 g cm^{-3}. With a production tolerance of ± 0.2 g cm^{-3} to give a specification density of 3.8 g cm^{-3}, the mean specific formed material weight for design purposes becomes 13.4 g Ah^{-1}. Before this value can be adopted for design purposes, it needs to be checked against actual densities derived from filling trials with the powder normally used. It could well be higher, given that it is determined by the combination of the flow and packing qualities of the powder, the type of vibrator, tamper or other filling means that is used. If this is found to be so, it is advisable to re-examine the powder blend and to modify it, usually by increasing the red lead content, so that a reduction can be made to both the specific formed material weight and the cost of the positive material.

Where there is not a statutory demand for the full rated capacity to be attained within, say, the first five cycles of charge and discharge and the competitive situation is difficult, it is often possible to meet the average work load with an initial capacity below the rated value, and then work up to the rated value slowly. In those circumstances, some easement in the allotted proportion of positive material reacted in a full discharge can be permitted. For design purposes, however, it is not recommended to take a figure higher than 40% of material to be reacted. The easement is based on the increase in capacity that takes place with cycling with most filling powders. Taking

the amount of material reacted with a full discharge as 40% would require the design to be optimized. This entails a critical look at both the particle-size distribution of the oxide and the electrolyte volume displacement of the separator.

Figure 6 shows the possible effect of the pitch of the plates on the average capacity per decimetre of formed material based on a tube with an internal diameter of 8 mm and holding material with an average formed density of 3.8 g cm^{-3}. The central spine diameter is 3 mm and the sp. gr. of the electrolyte when fully charged is 1.280 at +25 °C. A drooping characteristic is obtained with plate pitch and this indicates that there should be an optimum tube diameter for each plate pitch. The effect of reducing the internal diameter of the tube is to reduce the amount of formed material and, with a shorter path from the outside of the material to the central spine, some improvement is gained in the utilization of the material and an increase in the electrolyte present, per unit length of tube. Initially, the nett result is an increase in the capacity per unit weight of formed material, up to the point where the extra proportion of lead sulfate formed as a result of the discharge reduces the conductivity of the material and clogs the pores. At this point, the voltage losses increase rapidly and the effective capacity decreases.

It is difficult to be precise about the proportion of lead sulfate in a discharged plate that will produce this decrease in capacity output. For flat plates ~3 mm thick discharging at the 5-h rate, the value appears to be close to 40%, provided the separation, etc., allows a sufficiently free access for an adequate volume of electrolyte to support this level of reaction. It always has to be recognized that the higher the percentage of lead dioxide reacted (and sponge lead in the negative), the greater is the risk of ineffective recharging.

Consider the case of a nominal 4-year guaranteed life tubular positive cell, where the spine diameter is 3 mm and the cell components are so arranged that the utilization of the lead dioxide reaches 40%. If d cm is the diameter internally of the tube, then:
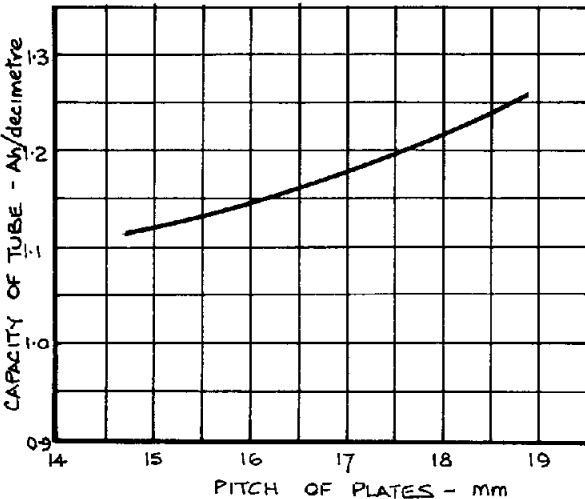

Fig. 6. Variation of capacity per decimetre of formed positive material density 3.8 g cm^{-3} enclosed in tubes with an internal diameter of 8 mm using spines of 3 mm diameter.

cross-sectional area of formed material = $\pi/4(d^2 - 0.3^2)$ cm^2

volume of formed material per decimetre length of tube = $7.854(d^2 - 0.09)$ cm^3

weight of formed material per decimetre at density 3.8 g cm^{-3} = $3.8 \times 7.854(d^2 - 0.09)$ g = $29.85(d^2 - 0.09)$ g

If the internal diameter of the tube is varied from 7 to 9 mm, the amount of formed material and the displacement of electrolyte by that material will vary. Above a diameter of 8 mm, the decrease in the amount of electrolyte available will reduce the capacity since the cell performance will be strictly limited by the volume of electrolyte present. Below 8 mm diameter, the volume of electrolyte will increase and, eventually, the available active material will need to be reacted beyond 40% if all the electrolyte available enters fully into the reaction. In order to evaluate the effect of the electrolyte changes with change in the internal diameter of the tubes, an approximate capacity equivalent for the electrolyte of 11.5 cm^3 per Ah can be taken for an 8 mm tube, based on typical cell geometry. This is equivalent to the electrolyte sp. gr. changing from 1.280 to 1.100 as the result of the discharge reaction. Many designs of tubular positive cells can be discharged until the electrolyte sp. gr. reaches 1.060 before the minimum acceptable voltage is reached and the assumption represents realism and not hopeful anticipation.

The effect of changes in the pitch are summarised in Table 2 for a pitch of 18 mm. These data are plotted in Fig. 7, together with similar data derived for pitches of 15.6 and 19 mm. The locus of the maxima of these curves will define the optimum internal tube diameter for each pitch using 3 mm diameter spines.

These data indicate that for each plate pitch there is an optimum tube diameter and that, for the most effective use of the positive active material, there should be available to the designer the option to vary the tube diameter from the standard based on the greatest commercial demand so that the most favourable active-material cost figures can be engineered into the cell design. The ability to manufacture tubes in house is an advantage since there is no argument against purchasing a reputely 'non-standard' tube if the optimum should deviate from the proprietary standard. Analysis of whether the cost saving in material with using a smaller diameter tube is greater or less than the possible increase in tube cost should be carried out as part of a design exercise.

The examination of the effect of tube diameter on capacity output has assumed the discharge reaction can reach 40% of material conversion. This has recognized that

TABLE 2

Effect of change in plate pitch

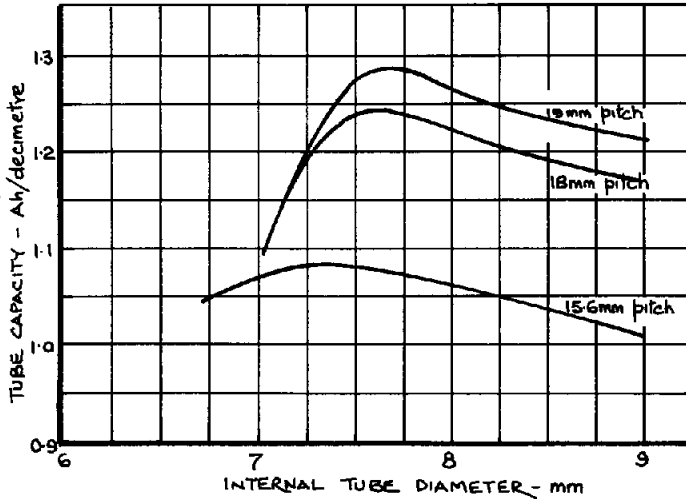| Internal tube diameter (mm)	7	7.5	8	8.5	9
Volume of formed material per dm (ml)	3.14	3.71	4.32	4.97	5.65
Weight of formed material per dm (g)	11.9	14.1	16.4	18.9	21.5
Weight of PbO$_2$ equal to 40% usage (g)	4.76	5.64	6.56	7.56	8.6
Capacity potential of 40% reaction (Ah)	1.07	1.27	1.47	1.69	1.93
Difference in volume of electrolyte displaced compared with an 8 mm tube (cm^3)	−0.48	−0.24	−0	+0.27	+0.55
Estimated capacity equivalent of displaced electrolyte (Ah)	+0.04	+0.02	0	−0.02	−0.05
Capacity equivalent of tube per dm (Ah)	1.07	1.24	1.22[a]	1.20	1.17

[a]From Fig. 6.

Fig. 7. Relationship between plate capacity and internal tube diameter for varying plate pitches. Spine diameter = 3 mm; formed material density = 3.8 g cm^{-3}; specific electrolyte volume for 8 mm tube excluding electrolyte below element = 11.5 cm^3 per Ah.

every assistance has been given by the choice of separator, by the side clearances between the element and the cell container causing promotion of free convection of the electrolyte, etc. It should also be recognized that the effectiveness of recharge becomes a problem with regular deep discharging that involves more than a 35% conversion. The wisdom of fully exploiting the optimum design to achieve a 40% conversion needs to be examined carefully, as well as the risk element of irregular recharging as based on the proportion of regular to irregular deep-discharge customer applications. Furthermore, the degree of irregular deep discharge must be estimated. It is common for customers buying traction batteries to be advised to restrict regular discharges to not more than 80 to 85% of the rated capacity. This is, however, virtually impossible to enforce and some degree of overdischarging (i.e., > 80–85%) is inevitable with heavy users. Some degree of variation between cells in a series assembly is also inevitable and this exacerbates the situation. The maximum depth-of-discharge that the optimum design would support without possible recharge troubles will be 35/40 × 100% = 87.5% of rated capacity. Where the percentage difference between the worst cell capacity and the rated capacity exceeds about (87.5/80 × 100) − 100 = 11%, the low performance cell will almost certainly give early trouble. It is generally prudent to increase the tube diameter marginally to ensure that the sulfate level in the worst cell under arduous working conditions does not exceed that equivalent to 35% conversion of the active material.

Recalculating the figures in Table 2 to limit the conversion of lead dioxide to 35% gives a new curve that relates to the optimum tube diameter to the plate pitch. The curves for both 35 and 40% conversion are given in Fig. 8.

The following conclusions can be reached:

(i) Where the regular duty to which the cells will be put does not involve consistent deep cycling, the 40% conversion figure can be used.

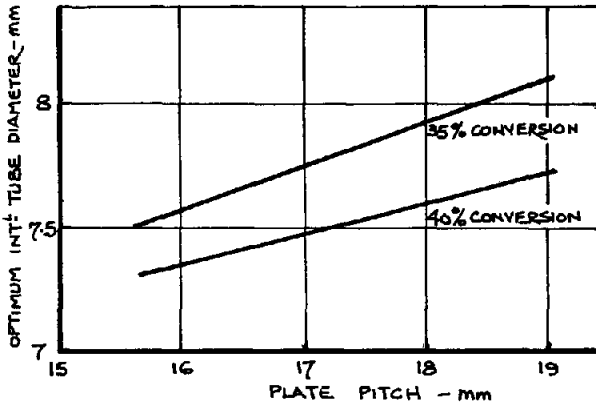(ii) For regular deep cycling, it is prudent to adopt 35% conversion.

Fig. 8. Effect of active material conversion on the relationship between plate pitch and optimum tube diameter. Spine diameter = 3 mm; formed material density = 3.8 g cm^{-3}; specific electrolyte volume (excluding electrolyte below element) = 11.5 cm^3 per Ah.

(iii) Where no control can be exercised over the use to which the cells will be put, the 35% conversion data are appropriate.

The foregoing sets broad guidelines from which to start to derive a basic design of cell.

Estimation of cell performance

Irrespective of the type of cell being considered, it is convenient to estimate cell behaviour on the basis of a single plate pitch. The current international standards call for traction cell ratings to be at 30 °C, but much of the acquired data of the past referred to 25 °C. This is particularly the case with the capacity equivalents of electrolyte of varying concentrations. A higher rating temperature leads to an increased declared capacity due to the greater reactivity of the materials. Taking the electrolyte alone, a charged sp. gr. of 1.280 at 30 °C is equal to a sp. gr. of 1.284 at 25 °C. Reaction through a sp. gr. range of 1.280 to 1.100 at 30 °C will produce a capacity equivalent of 87 Ah l^{-1}, compared with 86 Ah l^{-1} for the same range at 25 °C, i.e., an increase of 1.2% due to electrolyte alone. When the increased material reactivity at the higher temperature is included, the total increase is ~3% and this figure can be safely used for capacity estimations at 30 °C when using data based on 25 °C.

Before any detailed estimations are made, it is helpful to examine the possible sharing of the cell container height between the various discrete areas of cell construction. A typical breakdown of cell container height would include the following:
● thickness of cell container base
● plate support height
● plate height
● overlap of separator over the top of the plates
● height of electrolyte level over the top of the separators
● gassing space
● entry of underside of cell lid into cell container
All these added together should equal the height of the cell container.

In all the above items, only the thickness of the container base and, possibly, the entry of the cell lid into the container are fixed since both of these are usually set by the supplier of the container and lids. All the other items can be varied by the designer. In such areas as the plate supports and overlap of separators over the plate tops, there are no firm rulings. The former is governed by the nature of the separation (whether single sheet, sleeve or envelope), whilst the latter depends on the minimum volume of electrolyte that is necessary to support the rated capacity and the effectiveness of the retention of the active material within the plates.

Plate supports

These are sometimes referred to as prisms or plate racks. The supports were originally incorporated into a cell container to accept shed active material clear of the underside of the cell element where it could form conducting bridges and set up parasitic discharge reactions that would deprive the cell of its full designed capacity. This was particularly so in the case of the slitted, hard rubber, ironclad plates where shedding of the active material commenced early on in life and then continued at an increasing rate. In tall ironclad cells, plate supports as high as 7.5 cm were deemed necessary. This placed a severe restriction on the maximum length of plate that could be accommodated within a specified cell height. Modern tubes for traction positive plates effectively contain the formed material and there is very little lost during life. Similarly, with flat-plate traction cells, wherever there is an adequate layer of glass or inert filaments held against the positive material and maintained under permanent compression, the losses of active material are small. Only a small sediment space is theoretically required with these modern plates. Furthermore, where closed-bottom separator envelopes enclose either the positive or negative plates no sediment space should be needed.

Sediment does not fall evenly over the bottom of the container. This is noticeable where solid supports are used. By perforating the supports, the wash of electrolyte through the support openings with cell movement reduces considerably the variable heights of the sediment. Some designers deliberately adopt loose plate supports moulded with openings so that they can keep the sediment height to a minimum and reduce the risk of bottom short circuits.

Where cells are capable of being heavily worked and the electrolyte sp. gr. at the end of regular discharges approaches 1.080, or less, some of the lead sulfate that arises from the discharge reaction dissolves in the very weak end-of-discharge electrolyte. The minimum solubility of lead sulfate in dilute sulfuric acid occurs at around pH 1.2 and increases as the concentration decreases. The electrolyte containing lead sulfate, being of greater density, sinks to the bottom of the cell. If the sediment space is large, the electrolyte containing lead sulfate is accommodated within that space but, with a small sediment space, the contaminated electrolyte at the lower extremity of the plate element penetrates the separators as well as the active material. With the arrival of higher concentration electrolyte during charge, the lead sulfate comes out of solution in the form of lead sulfate crystals and these permeate the separators. As the charge reaction proceeds, the crystals are converted to metallic lead that bridges the positive and negative active materials in the lower portions of the plates and causes internal discharge. With no plate supports and the cell element resting on the bottom of the cell container, the risk of internal short circuits from such behaviour can be high, even though the separation may be an envelope with a closed bottom. The convection currents that are associated with the movement of increasing concentration electrolyte as recharge proceeds tend to be stronger with a small sediment

space than with a deep sediment space due to the slowing down of the speed of electrolyte movement as it passes from the narrow paths down the side of the element to enter the much greater space available under the element in the latter case. For this reason some space should be provided under the element even though separator envelopes are used in the cell make-up.

A suggested minimum height for plate support of 6 mm is realistic whether either all the positives or negatives are encapsulated in separator envelopes. With this height, good life results although, by tradition, it has been more usual to set the minimum height at 12 mm. The same minimum can be accepted where, in the case of flat-plate traction cells, the positives are well supported by glass-wool retainer mats and the plate/mat assembly is contained in a perforated plastic envelope unperforated at the base and edges, or where the positives are initially armoured with a particularly closely woven retainer mat that is held in position under permanent and firm compression by a more open and resilient outer mat.

Where single-thickness, open-texture, sheets of glass wool are simply held against the positive by a single-sheet separator then, for safety, the minimum height of plate supports should be increased to at least 16 mm and, preferably, to 20 mm.

The production of conducting lead in the lower portions of the separators can be virtually eliminated by limiting the depth-of-discharge and avoiding reaching the critical electrolyte concentration at which the phenomenon occurs. Whilst users can be repeatedly advised of such a recommendation, they cannot be prevented from ignoring it whilst the cell design is such that the situation is possible. It is undoubtedly better to arrange the separation and material densities to limit the minimum electrolyte concentration that can practically be obtained after a full discharge to an acid sp. gr. of not less than 1.140. This will reduce appreciably the effective capacity and may conflict with the market competitiveness of the product. The designer must recognize this and come to an agreement with the marketing personnel on how far the risk can be accepted. The final decision is an economic one and full notice must be taken of the possible cost of funding guarantees based on the likely proportion of very heavy to medium and light users.

With automotive batteries, the risk that deep discharge will occur regularly is slight and material shedding will be small, even though no real support is given to the positive material. Some automotive batteries are subjected to charge/discharge cycling and a compromise sediment depth or plate support height of 8 mm is adequate for all applications. With the use of alternator systems in automobiles, there is virtually no material shedding and the ultimate failure is almost invariably the corrosion and break-up of the positive grid. Nothing is gained by an increase in the sediment depth.

In the case of traction batteries, the emphasis is on minimizing the floor space. As a consequence, the cell height is extended disproportionately to the cross section. It is common for tall cells, when heavily worked, to operate relatively hot compared with the ambient, particularly where boost charging is practised to extend the working duration of a battery. A deep sediment space with its relatively large volume of electrolyte will act as a heat sink that absorbs an appreciable portion of the heat generated. As a result, such a cell will be noticeably cooler than the same size of cell with a smaller sediment space. For example, in a pair of cells with the same elements but with sediment spaces of 16 and 75 mm depth, respectively, and container heights of 560 mm, a temperature difference of up to 5 °C has been recorded after sustained, but not excessive, heavy working. The stable temperature in the hotter cells was 37 °C.

Although the lower temperature effect was welcome, it was found that the electrolyte in the deeper sediment space increased in concentration over a period of time to a greater extent than in the shallow space. The increased concentration was considerable and subjected the active material in the lower area of the plates to a direct chemical attack that gave rise to a slow, but significant, increase in the unconvertible lead sulfate content of the material. The effect of this is to throw a greater strain on the remaining material in the plates. As a result, the life potential of the plates in some cases is reduced to less than the corrosion life of the positive grid or spines. The two phenomena oppose each other and the designer has to seek a compromise. This is often solved pragmatically by adjusting the plate supports or sediment height to allow the use of currently standard pillars but, in the absence of such artifices, the following is suggested for traction cells:

    (i) traction cells with plates up to 200 mm in length:

with separator envelopes (mm)	12
without envelopes (mm)	20

    (ii) traction plates more than 200 mm in length, but not exceeding 500 mm:

with envelopes (mm)	16
without envelopes (mm)	25

    (iii) traction plates above 500 mm in length:

with envelopes (mm)	20
without envelopes (mm)	30

Gassing space

Above the electrolyte, there must be provided enough clear space so that acid-laden gas bubbles, that break through the surface tension at the liquid/air interface at top-of-charge, lose sufficient kinetic energy and burst before reaching the underside of the vent plug to allow their liquid and solid contents to fall back into the cell and their gas contents to escape through the vent holes provided. If insufficient energy losing distance is provided, the finer acid-laden droplets penetrate the gas escape holes in the vent plug and emerge to fall back on to the upper surface of the cell lid. The result is the formation of an electrically-conductive wet coating on that surface which can, and often does, lead to tracking across the path and, in bad cases, to charring of the lid material.

The volume of gas evolved is directly proportional to the charging current, whilst the rate of emergence of gas through the electrolyte is inversely proportional to the surface area of the electrolyte. The velocity of emerging gases will increase as the height of the cell increases. There is a need to allow an increasing amount of space above the electrolyte with increasing cell height in order to keep the cell lid free from undesirable conducting electrolyte films.

The amount of space allowed will depend very much on the vent plug design, the degree of internal baffling provided, and the water repellent nature of the plastic material from which the plug is made. The space must always well exceed the amount required to accommodate the temporary rise in the electrolyte level caused by that volume of gases, produced by charging, which has not penetrated the surface film at the liquid/air interface. This rise in traction cells will vary with the height of the cell and the magnitude of the charging current. The variable of cell height can be ignored in automotive batteries.

In the absence of experimental data for a given company product, a change in electrolyte level of about 2 mm per 100 mm of plate length can be assumed for design purposes under normal gassing charge conditions of $\sim C/15$ A, where C is the rated

cell capacity. The minimum clearance between the increased electrolyte level and the underside of the vent plug for clean operation can be taken as 20 mm. This suggests the following broad guidelines:

(i) for up to 300 mm plate length allow 26 mm minimum between the topped-up electrolyte level and the underside of the vent plug, and

(ii) increase the above value by 20 mm for each increase in plate length of 150 mm and in proportion for intermediate lengths.

Level of electrolyte above separators

The amount of electrolyte over the tops of the separators has to be sufficient to:

(i) provide enough electrolyte above the plates for a hydrometer reading to be taken at any time during charge and discharge;

(ii) provide a reasonable period of time to elapse before the cell requires further water additions;

(iii) allow for a reduction in electrolyte volume of about 1 ml for every 1 Ah taken out of the cell during discharge;

(iv) accept the increase in volume of the active materials that occurs during discharge, and

(v) allow for a drop in level as gas, held as bubbles in the electrolyte and in the pores of the active materials, is released during discharge.

Items (iii) and (iv) above are roughly equal and can be ignored.

The minimum volume of electrolyte to enable a hydrometer reading to be taken depends on the size and type of hydrometer used but, for design purposes, a notional volume of 20 ml can be used since most portable hydrometers will operate satisfactorily in this volume. In a cell with an internal width of 190 mm and a plate pitch of 18 mm, this suggested volume sets the minimum permissible level after a discharge at 6 mm above the top of the separators. For practical cells, a minimum of 8 mm is suggested. To this must be added a further component to cover electrolysis losses over the chosen intervals for topping-up. In installations where there are trained maintenance staff for the charging process, topping-up becomes a daily routine and no added component is necessary. If, after making the allowances above, it is found that there is not enough electrolyte in the cell to support the full discharge reaction, the height of the electrolyte above the separators must be increased.

Choice of operating specific gravity of electrolyte

It is good practice not to allow the specific gravity of the electrolyte at top of charge to exceed 1.300. This figure has been accepted for a very long time and derives from the days when wooden separators were used and were subject to direct oxidation in contact with lead dioxide and sulfuric acid, and also when there was a desire to limit the rate of direct chemical attack on the negative material to what was considered to be reasonable proportions. Since wooden separators are no longer used and the present synthetic separators are greatly improved as regards oxidation, this factor is no longer valid.

Vinal [1] quotes figures for the weight change in negative materials in various concentrations of electrolyte saturated with lead sulfate. These figures can be reworked to give comparative rates of weight increase, i.e., direct chemical attack at the differing electrolyte concentrations. These reworked data are shown in Fig. 9 where the comparison factor is the ratio of the weight loss at each electrolyte concentration to the weight loss at 1.300 sp. gr. at 25 °C.
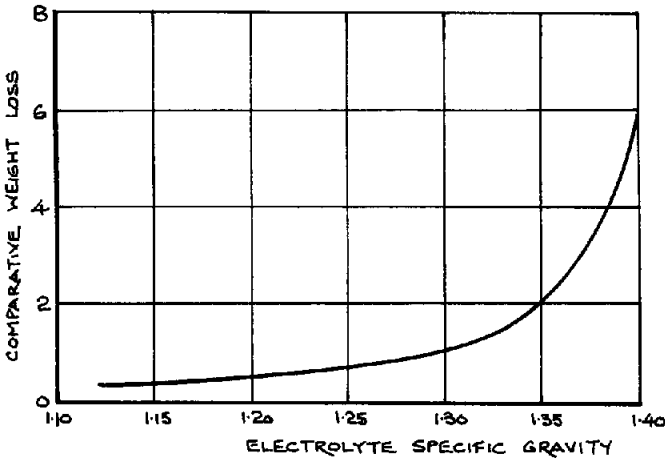
Fig. 9. Comparative weight loss in negative active material due to local action. Comparative weight loss=weight loss at stated sp. gr./weight loss at 1.300 sp. gr.

These data suggest that the weight loss would double in moving from a top-of-charge sp. gr. of 1.300 to 1.350. This increased weight loss shows up as an increase in open-circuit losses. These losses could be troublesome if the cells are subjected to long standing periods in service use. The 1.280 sp. gr. for the charged electrolyte specified by most makers is a prudent choice to provide an initial working tolerance of ±0.010, and to allow for any further increase that is derived from the release of sulfate ions to the electrolyte as a result of the formation of small amounts of unformed material that are initially present.

Some manufacturers argue that open-circuit losses are relatively unimportant in a traction cell where daily recharges are regularly applied, and point out that there will be an inevitable migration of antimony from the positive grid to the negative material that can produce increases in the open-circuit losses many times greater than those produced by increasing the working electrolyte sp. gr. to even as high as 1.350. Such manufacturers tend to set their operating specification at 1.320 sp. gr. on the basis that the initial open-circuit losses are only about 25% higher than for 1.280 sp. gr., and that these losses are unlikely to be noticed or be a serious hazard to battery life. Such manufacturers are the exception and the majority work within the sp. gr. range 1.260 to 1.280. The practice is to adjust the sp. gr. at the factory to the lower figure before release of the batteries to customers and to allow the sp. gr. to rise to the higher figures with cycling in service.

Working on the assumption that the initial sp. gr. is 1.280 and that the maximum sp. gr. caused by water losses through electrolysis will not exceed 1.300, the acid needed to produce this change is 0.077 l per l of electrolyte and can be derived from Standard Density Composition Tables. For a 100 Ah positive plate with a total electrolyte volume per pitch of, say, 1250 ml, this volume would apply to the topped-up condition. The permissible reduction in volume through loss of water through electrolysis will then be (1250 − 1250/1.077) ml, i.e., 89.4 ml. Referred to a cell container with an internal width of 190 mm and a plate pitch of 18 mm, the change in the electrolyte level becomes 2.6 cm. This order of permissible change is usually greater than the designer can accept within the height dimension of the cell container. If so, there is an in-built safeguard against the development of too high an electrolyte concentration

in service use. Any restriction in the permissible rise and fall of the electrolyte level will lead to an increase in the frequency of topping-up.

Wherever possible, a permissible change in the electrolyte level approaching the calculated value should be allowed, but it should not be exceeded without the backing of experimental data from life tests.

Where, for other reasons, the normal sp. gr. is set lower than 1.280, the risk of high levels of sp. gr. developing through a poor topping-up discipline are reduced, but the cell capacities will be lower.

Rigorous adherence to the above would require a different set of upper and lower levels for each size of plate. This is inconvenient for an economic production as it would greatly inflate the stock inventory. A reasonable compromise would be to set the upper electrolyte level to about 30 mm above the top edges of the plates, and to control the lower level by adjusting the overlap of the separators over the tops of the plates. In the latter, the emergence of the top edges of the separators is used as an indication that the lower permissible level of the electrolyte has been reached and that topping-up is necessary.

Effect of plate height on performance

It is convenient to use standard components in as many cells as is realistically possible to maintain the smallest stock inventory. It also increases the length of the production run on each component and helps the overall economics of manufacture. The designer who adopts this expedient has to deviate from optimum designs for some cell sizes and to evaluate the possible loss of performance arising from such deviation. Disadvantages include a reduced voltage at the higher rates of discharge with tall cells and a higher cost of lead components with short cells. Typical design expedients are the use of a common spine casting for tubular positive cells and cropping the casting to the required length for the plate, the use of common pillars over a wide range of cell sizes, and the use of a universal burning comb to produce the same thickness of plate strap irrespective of the current demands of the cells.

Although the prime design requirement for most traction cells and many stationary cells is often maximum low-rate capacity at the 3-h rate, there are occasions when the cells are required to operate closer to the 20- to 30-min rate for vehicle starting or the 3-min rate for switch closing duties in power stations. Any design for low-rate capacity should take note of what other duties may be required since these may dictate the way the design should proceed, even though it is at the expense of optimizing the low-capacity design.

The floor area that is available for many trucks is severely restricted and there is no alternative but to use very tall cells. Every increase in height introduces an added grid resistance factor and reduces the terminal voltage on discharge. At the higher rates, this can substantially reduce the power available to specified voltage end points. Before proceeding to standardize on a common spine diameter or a vertical rib section in a lattice grid, it is important to estimate the price to be paid in terms of lost performance.

It is common practice for manufacturers to display in their brochures a standard curve showing the average voltage performance claimed for their product. This curve will tend to reflect the behaviour pattern of the popular cell size at the time the brochure was produced. It generally follows that this curve does not match the voltage performance of the shortest or tallest cells with the result that, under onerous discharge conditions, the performance of the tall cells can be at best marginal compared with the claimed performance.

Consider the case of a range of tubular positive cells in which the spine casting is cut from a common casting to produce plates varying in length from 175 to 730 mm in a standard cell box of width 160 mm. Assuming the popular cell length is one with plates 335 mm in length and the common cell size has a capacity of 370 Ah (5-h rate), a typical voltage curve could be as in Fig. 10 when discharged at 417 A at 30 °C (30-min rate) to 1.5 V.

Consider four plate lengths of 175, 335, 530 and 730 mm giving rated capacities of 26, 53, 86 and 120 Ah per positive plate, respectively, with the following dimensions:

mean diameter of spine (mm)	3.5
mean pitch of spines (mm)	9.2
mean dimensions of bosses at top of spines (mm)	8.25 (diameter)×4.5
mean dimensions of top bar (mm)	8×7.2×138
lug dimensions (mm)	28×5×30
resistivity of 9 wt.% Sb alloy at 30 °C (Ω cm)	2.2×10^{-5}

Based on the nominal plate capacities, the 30-min rate discharge currents will be equivalent to $1.125C_5$ A, where C_5 is the numerical value of the capacity at the 5-h rate. This gives 29.1, 59.4, 96.3 and 134.4 A, respectively, for the various plate lengths. An allowance has to be made for the depth of the top bar and bosses and the entry of the base closure.

Taking an allowance of 23 mm, this gives the following spine lengths corresponding to the chosen plate lengths, given in Table 3.

The resistance of the spine metal is given by the relationship: $R_s = \rho(l/A)$, where R_s is the resistance of the spine (Ω), ρ is the alloy resistivity (Ω cm), l is the spine length (cm), and A is the cross-sectional area of spine (cm^2).

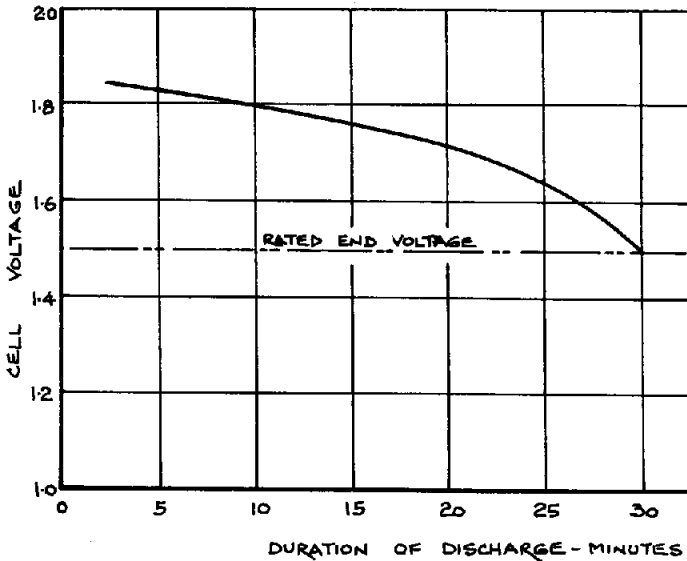The bosses at the top end of the spines can be taken as an enlargement in series with the spine. Then:

Fig. 10. Voltage performance of a 2 V/370 Ah cell with tubular positives discharging at the 30-min rate (417 A) at 30 °C.

TABLE 3

Spine lengths vs. chosen plate lengths

Plate length (mm)	Spine length	Spine resistance (Ω)
175	152	0.0035
335	312	0.0072
530	507	0.0117
730	707	0.0163

TABLE 4

Voltage losses in spine

Plate length (mm)	Current per plate (A)	Voltage loss per plate through the spine (V)
175	29.1	0.0034
335	59.4	0.0143
530	96.3	0.0380
730	134.4	0.0730

$$\text{resistance of a single boss} = \frac{2.2 \times 10^{-5} \times 45}{\pi/4 \times 0.825 \times 0.825} = 0.00002 \ \Omega.$$

The current in a single spine builds up from the bottom where it is zero to full value at the top where the spine joins the top bar. When estimating voltage losses in a spine, due to spine and boss resistances, the average current over the full length of the spine will be half the full current. Since the plate will have 15 spines the current leaving the top end of a spine will be one-fifteenth of the discharge current. Using the average currents, the voltage losses in the spine and bosses per plate are listed in Table 4.

There will also be losses in the top bar where the current increases progressively from the free ends of the bars to the lug take off. The position of the lug will affect the way in which the current builds up. As an example, the lug position is assumed to be as given in Fig. 11. This gives an approximate current distribution as shown where i A is the current through one spine. The nearer the lug position is to the centre of the top bar, the more symmetrical will be the current distribution.

The voltage losses can be estimated by multiplying the resistance of a spine pitch section of the top bar by the sum of all the individual current increments along the bar. A spine pitch in the example will have dimensions 9.2 mm (long) × 8 mm (deep) × 7.2 mm (thickness). Thus, the resistance of a pitch increment = $2.2 \times 10^{-5} \times 0.92/(0.8 \times 0.72)$ Ω = 0.000035 Ω.

The sum of the individual currents passing through an equivalent spine pitch increment will be, counting from right to left of the top bar, $i(1+2+3+4+5+6+7+8+9+10+11+12+3+2+1)$ A = 82i A. The voltage loss in the top bar = 82i × 0.000035.
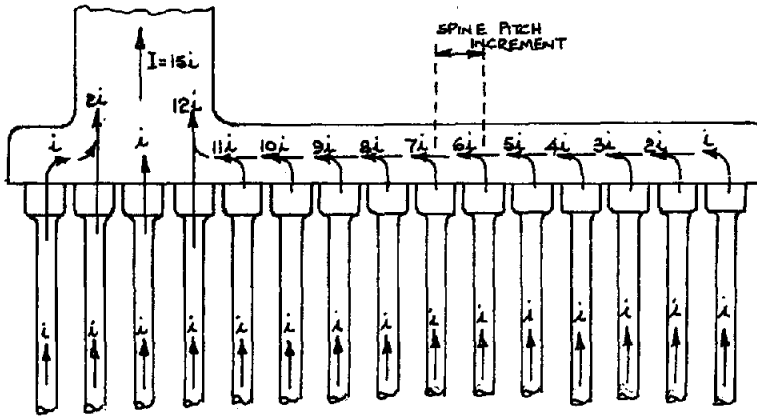
Fig. 11. Current distribution along the top bar of a tubular positive plate. Current per spine: i A; total current per plate: $I = 15i$ A.

TABLE 5

Voltage loss in top bar

Plate height (mm)	Plate current (A)	Spine current (A)	Voltage loss in bar (V)
175	29.1	1.94	0.0056
335	59.1	3.96	0.0114
530	96.3	6.42	0.0184
730	134.4	8.96	0.0257

TABLE 6

Voltage loss in lug

Plate length (mm)	Plate current (A)	Voltage loss in lug (V)
175	29.1	0.00096
335	59.4	0.00196
530	96.3	0.00318
730	134.4	0.00444

From this relationship can be calculated the voltage loss in the top bar for each length of plate at the 30-min discharge rate. These are given in Table 5.

In addition to the top bar there is a voltage loss in the plate lug, i.e.,

$$\text{resistance of lug} = \frac{2.2 \times 10^{-5} \times 3}{2.8 \times 0.72} \; \Omega = 0.000033 \; \Omega.$$

The voltage loss in the lug will be directly proportional to the plate current as shown in Table 6.

The sum of the separate losses in spines, top bar and lug gives the order of voltage loss that is to be expected from the casting when a single spine casting is used for all plate lengths. These are presented in Table 7.

The 30-min rate voltage curve given in Fig. 10 referred to a plate with a length of 335 mm. This compared with that cell, the performance of the 175 mm plate (cropped from the common casting) would be enhanced by about 0.02 V, whilst that of the 530 and 730 mm plates would be reduced by 0.03 and 0.07 V, respectively. The effect of this on the declared voltage performance curve would be as shown in Fig. 12. Unless in practice there is an excess of performance (i.e., duration) with the production cells for which the declared curve applies, the tall cells could become the subject of disagreement between manufacturer and supplier wherever the cells are supplied against an applied specification.

The example covers the effect of the positive plate only and a similar voltage variation could be experienced with the negative plate if common vertical rib and frame sections are used, irrespective of plate height. Added to this is the practice of using standard pillars for a variety of plates.

TABLE 7

Voltage losses in complete casting

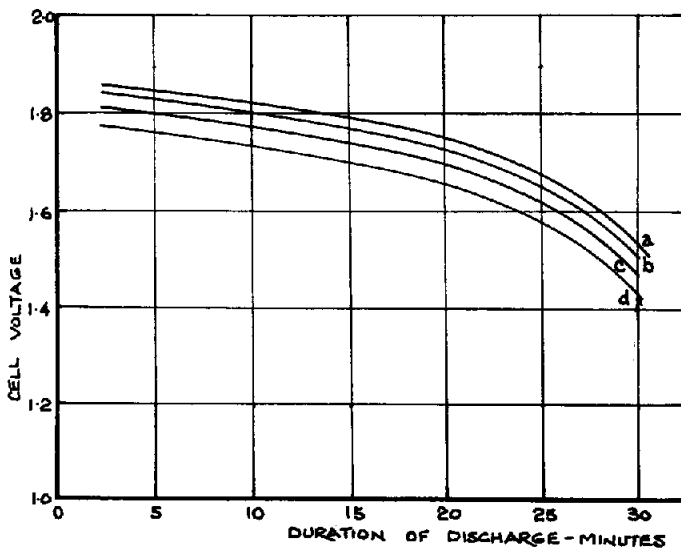| Plate height (mm)	Voltage loss (V)			
	Spines and bosses	Top bar	Lug	Complete casting
175	0.0035	0.0055	0.001	0.01
335	0.0140	0.0115	0.002	0.03
530	0.0380	0.0185	0.003	0.06
730	0.0730	0.0255	0.0045	0.10

Fig. 12. Effect of positive plate length on the voltage performance at the 30-min rate of discharge of a tubular positive type cell. Plate length: (a) 175, (b) 335, (c) 530 and (d) 730 mm.

Changes were made to the grid designs in a particular tubular positive range of cells to counteract the effect of varying plate height on the 30-min performance for, although the main criterion was the capacity at low rates, there still was required the ability to start the battery driven trucks for which the range of cells were used. The specific grid weights of positive and negative grids exhibited a progressive increase with plate height, as shown in Fig. 13. The taller cells needed longer pillars to provide an adequate gassing space for a clean lid and this necessitated an increase in the cross section of the pillars to keep the voltage loss to an acceptable level.

Estimation of the capacity of tubular traction cells

Consider a traction cell rated at 100 Ah per positive (5-h rate) assembled in a container 199.5 mm wide and 565 mm high, with a plate pitch of 18 mm (DIN 43567). Some proprietary makes of cell container have a base thickness of 4 mm, and a proprietary matching lid enters the cell container 10 mm measured from the under surface of the vent plug. These dimensions will be accepted for the example.

Using the minimum criteria previously stated for plate supports, gassing space, etc., the build-up of the cell container height would be as follows:

- base of container (mm)   4
- plate supports, assuming the use of envelopes (mm)   16
- plate length (mm)   not known
- electrolyte height over plates (mm)   30
- gassing height (mm)   46
- entry of lid into container (mm)   10

The total of these will equal the container height. As the various dimensions are minima, the plate height will be a maximum. Thus, the maximum plate height = $565 - (4 + 16 + 30 + 46 + 10)$ mm = 459 mm.
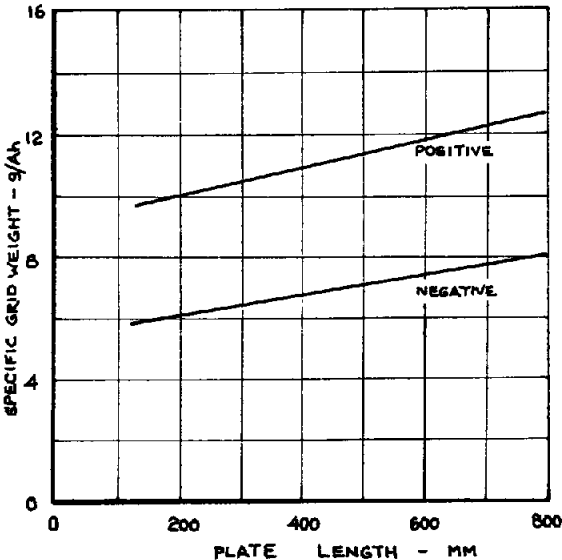

Fig. 13. Progressive changes in specific grid weights of tubular positive cells to maintain good 30-min rate voltage characteristics, irrespective of plate length.

In the make-up of the positive plate, the only effective dimensions that determine capacity are the total length of the pencil of lead dioxide and the cross-sectional area of the active material. There are two options: (i) to choose an appropriate tube diameter to the plate pitch to give the optimum capacity, and (ii), if (i) is not a proprietary standard, take the nearest commercial standard diameter above the optimum to obtain the lowest piece price, but an increased material content. From the data given in Fig. 8 and restricting the amount of positive material converted to lead sulfate to 35% with a full discharge to cover onerous working conditions, it can be found that a tube diameter of 7.95 mm applies. This is so close to the 8 mm standard to make it unnecessary to consider option (i) above.

The length dimension of a tubular positive plate includes the inert base closure, the entry of the cast lead bosses into the tubes and the thickness of the cast top bar.

In one make of positive casting, the depth of the top bar is 9 mm (average) and the entry of the bosses is 5 mm into the tubes. A typical injection moulded base closure enters 5 mm into the bottom of the tubes and projects 4 mm beyond the tubes. These dimensions provide sufficient entry into the tubes to cater for subsequent stretching of the spines during the active cell life without exposing any section of the spine to direct oxidation from contact with the electrolyte. The geometry also imparts adequate strength to the closure across the width of the plate to prevent distortion. All these dimensions added together (i.e., boss entry, depth of top bar and total closure depth) are lost dimensions to producing capacity. They equal 23 mm and the difference between the plate length and this dimension will give the maximum length of a pencil of lead dioxide, i.e., 436 mm.

The internal width of the container will dictate the number of pencils of lead dioxide in each plate. In determining this number, an allowance has to be made for the thickness of the tube and, in the case of a plate made up of a number of single tubes, the lack of straightness or, in the case of multitubes, the space taken by the interweaving or heat sealing.

For the example, assume that it has been decided to use multitubes with a dimension of 1.5 mm between tubes, including the tube thickness. A clearance between the plate width and the internal width of the container is needed to allow the electrolyte to circulate, freely from top to bottom. A reasonable clearance at either side is 5 mm. Allowance has also to be made for the thickness of the container walls. For hard-rubber containers, a typical thickness is 4 mm. Thus, the permissible plate width = 199.5 − 2(4 + 5) mm = 181.5 mm. The effective tube pitch will be (8 + 1.5) mm, i.e., 9.5 mm. Therefore, the number of tubes per plate = 181.5/9.5 = 19.1. Take the lowest whole number, i.e., 19 tubes per plate.

A typical spine diameter for 1500 charge/discharge cycles to 80% depth-of-discharge is 3 mm when using an alloy containing from 7 to 9 wt.% Sb:

internal cross-section area of pencil of $PbO_2 = \pi(0.8^2 - 0.3^2)$ cm^2 = 0.432 cm^2

volume of formed PbO_2 in maximum plate length of 436 mm = $(19 \times 43.6 \times 0.432)$ cm^3 = 357.9 cm^3

Adopting a formed density for PbO_2 of 3.8 g cm^{-3}, the weight of PbO_2 in the maximum plate length will be (357.9 cm$^3 \times 3.8$ g cm^{-3}), i.e., 1360 g. This weight of PbO_2 would provide a specific formed material weight of 13.6 g Ah^{-1} if there is sufficient electrolyte available to support a discharge capacity of 100 Ah.

This specific formed material weight is higher than necessary and some reduction can be made without prejudicing the ability of the plate to deliver the rated capacity. This reduction will release space for a little more electrolyte and enhance the ability of the plate to perform its specified capacity. If the specific formed material weight

is reduced to 13.4 g Ah^{-1}, the pencil of lead dioxide will be shortened in proportion. The new length of the pencil of lead dioxide becomes 430 mm and the plate length 453 mm. This will increase the gassing space by 6 mm, or the height of electrolyte over the plates by 6 mm. The latter offers the option of increasing the total electrolyte previously mentioned.

Referring back to the capacity data given in Fig. 6, the capacity of a single tube for an 18 mm pitch is given as 0.122 Ah cm^{-1} and, thus, the projected plate length would be: $100/(0.122 \times 19) = 431$ mm. This is in good agreement with the above calculations.

At this stage, the total solid material comprising a positive plate can be calculated. For the plate design, the following dimensions, based on service experience, can be determined:

(i) average cross section of top bar = 9 mm deep × 6 mm wide;

(ii) length of top bar = 19 × pitch of tubes = 180.5 mm;

(iii) diameter of cast bosses on top bar accepting the top of the tubes will be a clearance fit in the tubes, i.e., 7.95 mm;

(iv) average depth of entry of top bosses into tubes = 5 mm;

(v) average diameter of spine = 3 mm;

(vi) entry of base closure into tubes = 5 mm;

(vii) entry of spines into base closure = 3 mm; leaving 1 mm of material sealing off the closure;

(viii) diameter of bosses on base closure = 7.95 mm;

(ix) cross section of base closure outside tubes = 4 mm × 9 mm and

(x) length of base closure equal to top bar = 180.5 mm.

Volume of grid metal

This can be broken down into the separate volumes of top bar, top cast bosses and spines, i.e.:

volume of top bar = (18.05 cm × 0.9 cm × 0.6 cm) = 9.7 cm^3

volume of 19 top bosses = $(19 \times \pi/4 \times 0.8^2 \times 0.5)$ = 4.8 cm^3

length of spines = length of pencil of PbO$_2$ + 5 mm + 4 mm = 439 mm

volume of 19 spines = $(19 \times \pi/4 \times 0.3^2 \times 43.9)$ cm^3 = 58.96 cm^3

total volume of casting = (58.96 + 9.7 + 4.8) cm^3 = 73.5 cm^3

Assuming the metal is a Pb–9wt.%Sb alloy with a density of 10.8 g cm^{-3}, the weight of the casting, excluding the lug, will be 793 g. This gives a specific grid weight of 7.93 g Ah^{-1}. This is a low figure compared with what is common in the industry. Nevertheless, it is acceptable as the cross section of the top bar is greater than five times the total cross section of the 19 spines, and is more than adequate to outlast appreciably the corrosion life of the spines. The strength of the top bar will withstand the stresses associated with most vibrator filling systems but, if any distortion should occur during the filling operation, then some increase in the top bar dimensions may be necessary.

Volume of active material

The weight of the formed material has been fixed at 1340 g. The density of PbO$_2$ is 9.4 g cm^{-3} and this gives a true volume of PbO$_2$ of 142.6 cm^3.

Volume of tube material

A typical weight of a 19-tube multitube (or as some suppliers call them, anode bags) is 10.5 g per 100 mm of single tube length. Tubes of length 440 mm applicable to the proposed plate with a yarn density of 1.3 g cm^{-3} will have a volume equal to $(10.5 \times 4.4)/1.3$ cm^3, i.e., 35 cm^3.

Volume of base closure

The base closure consists essentially of an outer strengthening bar with 19 integrally moulded, hollow, cylindrical bosses entering into the lower ends of the tubes and receiving the lower ends of the spines. Normally, it is simplest to obtain a suitable sample of a closure and estimate the volume of displacement of water. Assuming the bottom bar is a flat bar, and the bosses are hollow cylinders, then, the volume of base closure = volume of bosses + volume of bottom bar = $19(\pi/4 \times 0.8^2 - 0.3^2 \times 0.5) + (18.05 \times 0.9 \times 0.4)$ cm³ = 8.76 cm³.

Volume of lug below the electrolyte level

The electrolyte level is usually 30 mm above the plates. Two arrangements are possible: (i) the lugs are extended so that the plate strap is above the electrolyte level, and (ii) short lugs are fitted and the plate strap is immersed in the electrolyte displacing electrolyte. Option (i) gives a more resilient cell element and more readily accommodates manufacturing tolerances. It is preferable and will be adopted for the example.

Before the lug volume can be estimated, the cross section has to be fixed. An acceptable current density in the lug, based on the 5-h rate of discharge, would be 15 A cm⁻². Where a single casting is cropped to produce a number of plate lengths with a single lug dimension, the design has to be based on the largest plate to be made from the common casting.

It is assumed that the spine casting is exclusive to the 100 Ah plate. The designed cross section will be proportional to the 5-h discharge current, 20 A, and will be 20/15 cm² or 1.33 cm².

Volume of lug below the electrolyte level = 1.33×3 cm² = 4 cm³.

Total solid volume of plate

The total solid volume of the positive plate will be given by the sum of the grid, active material, tube material, base closure and immersed lug volumes. Volume of plate = 263.9 cm³. The outline dimensions of the negative plate should preferably mirror the pencils of lead dioxide in the positive plate. The portion of the negative plate within the outer frame should have about the same dimensions as the length of a pencil of lead dioxide and the same width as that of 19 tubes. For the proposed negative plate, allowing 3 mm as the width of the top, bottom and side frames of the lattice grid, the dimensions become 186 mm wide × 436 mm long.

Earlier, it was stated that a separator envelope was being fitted. This envelope can be fitted to either positive or negative plate. The advantage of enveloping the positive is an economic one as there are less positives than negatives in a normal cell. Most envelopes require a side clearance of at least 5 mm in order to avoid interference between the edges of the envelopes and the cell container wall. It is usually more difficult to modify the width dimension of the positive, particularly when using proprietary tubes and, if the positive is close to the borderline of the minimum clearance between plate and cell container walls, then it is prudent to envelope the negative. This may mean the width of the negative grid may need reducing to ensure an adequate free space between cell element and container for ease of assembly and electrolyte convection.

The internal cell container width is 191.5 mm and the dimension to achieve matching with the positive will give insufficient clearance. The negative grid width should be reduced to 180 mm.

Instead of entering into a full grid design at this stage, it is convenient to postulate a specific grid weight (in g Ah⁻¹) within the skills of the operators. Any reduction

on this will introduce a training factor. Take a value of 7 g Ah^{-1}, which should not be outside the skill of average and not highly skilled operators. This gives a grid weight of 700 g.

There is no technical need for high antimony or highly corrosion resistant alloys for negatives as there is no oxidation corrosion product and a greater degree of surface imperfections can be tolerated than for positive grids. The choice of alloy rests mainly with the skill of the casting and pasting operators, as well as the expertise of machine setting and control. Assume that a 5 wt.% Sb alloy is acceptable with a density of 11.07 g cm^{-3}, then: volume of negative grid = 700/11.07 cm^3 = 63.2 cm^3.

If the cell is required for regular deep discharge, then a specific formed material weight of 11.5 g Ah^{-1} is recommended, together with an apparent formed density of 3.9 g cm^{-3}:

    weight of negative formed material = 100 Ah × 11.5 g Ah^{-1} = 1150 g

    apparent volume of material = 1150/3.9 = 294.9 cm^3

    true volume of formed material = 1150/11.3 = 101.8 cm^3

If t cm is the average pasted thickness of a negative plate and the superficial plate dimensions are 18 cm × 43.6 cm, then the apparent volume will be $(18 \times 43.6 \times t)$ cm^3. This must equal the sum of the grid volume and the apparent volume of the formed material, i.e.: $18 \times 43.6 \times t = 63.2 + 294.9$; $t = 0.46$ cm. Thus, the matching negative will be 0.46 cm thick.

The amount of electrolyte displaced by a negative plate will be equal to the sum of the grid volume, the true active material volume and the volume of the wetted portion of the lug. The latter will be the same as for the positive, i.e., 4 cm^3.

Total solid volume of plate = 63.2 + 101.8 + 4 = 169 cm^3.

Separation

The choice of separation can have a profound effect on the rate of migration of antimony from the positive grid to the negative material, and the subsequent corrosion life of the positive grid or spine. Only truly microporous separators, such as microporous hard rubber, poly(vinyl chloride) or phenolic-filled polyester separators with a dominant pore size <2 μm are acceptable.

Full allowance must be given to permitted dimensional tolerances for each of the components forming a complete plate pitch (i.e., one positive, one negative and two separators) when determining the overall separator thickness. This is because it should be possible to accommodate all the components at their maximum dimensions in a cell element without having to exert undue pressure to enter the element into the container. There is some difficulty in defining 'undue pressure' since individual understandings can vary tremendously. A generally accepted standard of tightness of an element in a container is defined by stating that a cell element should fall under its own weight between halfway and two-thirds down the container and require hand pressure, firm but not excessive, to move the element down on to the plate supports. Naturally, this situation cannot be met at every level of tolerance but, for trouble-free assembly, it should apply when all tolerances are at their maxima and inert side shims (inserted on either side of the element to compensate for element slackness) when dimensions are below the maximum permitted.

Undesirable cost additions can be incurred in large plateage cells as the excursion in cell element thickness from the minimum to the maximum can be large and involve appreciable costs of shims and the labour in inserting the shims. Some easement in this extra operation can be obtained by a study of the quality control data of the frequency distribution of component dimensional variations. Based on this data, an

upper element thickness can be derived that will be less than that obtained when all components are at their maximum values. It is usually adequate to take the routine quality control data of plate thickness variations over, say, one month, and accept the dimensional variation over $\pm 2\sigma$ limits as design limits. The upper dimension ($+2\sigma$) is then used as the effective separator thickness in calculation of the average separator thickness.

It is usually simpler when determining the separator thickness (or separator plus retainer mat or porous spacer) to reduce the plate pitch by the design upper tolerance (as distinct from maximum tolerance), and subtract from that value the sum of the nominal positive and negative thicknesses. Half the remainder will be the nominal separator thickness.

The positive-plate thickness is determined by the wall thickness of the enclosing tubes for each specified internal diameter. Material wall thicknesses vary among proprietary tubes from 0.27 mm for single woven glass-fibre tubes to as high as 0.60 mm for nonwoven tubes. High tensile strength, polyester filament, woven tubes average 0.30 mm. The tolerances on wall thickness are generally of the order of ± 0.05 mm for woven tubes, but can increase to ± 0.1 mm for nonwoven tubes.

Assume as an example, a woven polyester tube with a maximum wall thickness of 0.35 mm. This will give a maximum plate (positive tubular) thickness of 8.7 mm. Negative plate tolerances can be kept at ± 0.1 mm with good pasting machine settings, followed by compression rolling before flash drying. This will give a maximum negative plate thickness of 4.7 mm in the example under consideration. Typical tolerances for proprietary separators are ± 0.07 mm. In summary, the cumulative tolerances above the nominal thicknesses are:

positive plate (mm)	0.10
negative plate (mm)	0.10
separators (two) (mm)	0.14
total (mm)	0.34

This leaves (18–0.34) i.e., 17.66 mm to accommodate the nominal thicknesses of a positive and a negative plate and two separators. The thickness of two separators = 17.66 − (8.6 + 4.6) mm. Thus, the nominal separator thickness = 2.22 mm. Take the nearest standard separator thickness below this value. Assume, for the example, that a standard thickness of 2.2 mm is available. Figure 14 shows sections through two satisfactory traction separators.

No manufacturer, from choice, can afford to rely exclusively on one make-and-design of separator. A prudent cell design should accept at least two makes of separator, albeit of differing profiles. The cell design should operate with the separator with the greatest electrolyte displacement in order to give some freedom of purchase. The total solids material for each design of separator needs to be evaluated, and the highest used for subsequent capacity estimations. Taking the separator profiles of Fig. 14, separator (a) can be broken down for volume calculations into main ribs, back web and minor ribs facing the negative plate. It could be argued that using minor ribs against the negative would deny the negative material the necessary support it needs to prevent uncontrolled expansion and loss of designed apparent density. The surface of the negative material presented to the back of the separator does not marry intimately with the surface of the separator. The points of contact are the high spots or areas of the material surface. Gases emerging from the surface of the active material on charge can be, and often are, trapped between the surface of the material and a flat back separator surface. The trapped gases deny the active material adjacent to them contact with the electrolyte so that the normal volume changes associated with charge
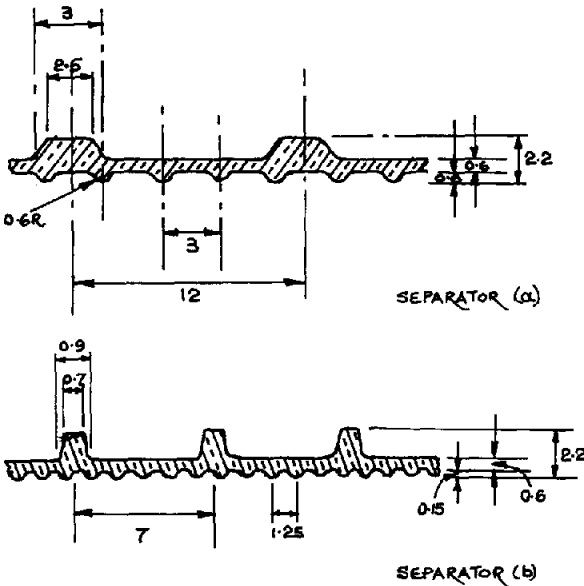
Fig. 14. Typical microporous traction separators, dimensions in mm.

and discharge do not occur. The result is an unevenly expanded material, often with a reduced capacity. The provision of shallow ribs on the back of the separator adjacent to the negative material allows the evolved gases during the early life of the cells to escape readily between the separator and the plate, and allows the whole surface of the active material to enter into the reaction. The result is an even expansion over the whole of the plate with the active material, in due course, expanding into the spaces between the shallow ribs to marry intimately with the separator. Thereafter, the evolved gases on charge pass through the pores of the separator to escape as a cloud of minute bubbles via the positive excess electrolyte. The volume between the shallow ribs is insufficient to cause any appreciable alteration in the apparent density of the expanded material.

Some shallow ribbing should always be present on the back face of traction separators. The spacing of the shallow ribs in separator (a) of Fig. 14 is probably as wide as can safely be adopted; a closer spacing as in separator (b) gives a better control of negative material expansion. Nevertheless, separator (a) has given good results in service use.

The separator must overlap both positive and negative plates and readily enter the cell container at its narrowest dimension. In the example under consideration, it must not be less than 180.5 mm nor greater than 191.5 mm in width.

For a width of 185 mm and with the major ribs in separator (a) at 12 mm pitch, there will be 15 major ribs. With the minor ribs at 3 mm pitch, there will be 61 minor ribs. Since the pitch of the tubes is approximately 9.5 mm, a separator with vertical ribs at 12 mm pitch will have ribs that coincide with the crests of about 6 positive tubes over the full 19 tubes. The result of this poor lining-up of the ribs on the separator and the crests of the tubes is that an uneven and erratic pressure over the full separator denies the surface of the negative material, the essential support that is needed to control the rate and evenness of its expansion. Areas will develop over

the surface of the material that differ appreciably in apparent density and porosity. The areas that expand the most will have an excess of electrolyte available to them, whilst those that cannot expand as much will have a reduced supply of electrolyte. The former will support a greater discharge capacity and will be more heavily worked than the less expanded areas. Initially, the cells will behave more or less normally, as far as can be determined by average electrolyte concentration measurements, but the proportion of lead sulfate in the more heavily worked areas will be greater and may not be fully converted in the subsequent recharges. A point is reached when recharging becomes incomplete and the capacity decreases. An examination of the negative material will show discrete areas of high lead sulfate content within apparently normal negative material. The overall result is usually an erratic and unpredictable life expectancy.

An artifice that reduces considerably this undesirable condition is to angle the major ribs away from the vertical. The greater the deviation from the vertical, the greater will be the number of contact points between the separator ribs and the positive tubes, and the greater will be the support given to the negative material. With too great an angle, however, there is a danger that evolved gases cannot escape readily and entrapped gases will blank off areas of the negative material from participating in the discharge reaction. A compromise has to be made, and one supplier of diagonal ribbed separators has standardised on 10° from the vertical. The effect of this with a plate of length 255 mm is to increase the number of contact points from about 6 to about 75 in the case of a rib pitch of 12 mm. The number of contact points will increase with plate length. Coupled with a relatively stiff separator, the 10° angle will give an acceptably even pressure over the negative material surface with minimal entrapment of gases, even with the shortest plates common to traction cells in general use. The way in which the diagonal ribbed separator assists in distributing pressure over the plate width is shown in Fig. 15.

The choice of rib pitch is arbitrary, but with a diagonal rib design, the narrower the rib pitch the greater will be the number of contact points but the greater also will be the electrolyte displaced. Taken to an extreme of rib pitch reduction, this could result in an unacceptable loss of capacity potential. A reduction in the rib pitch should be accompanied by a reduction in the rib width. For example, if the rib pitch is reduced from 12 mm to 7 mm, the rib width would need to be reduced from an average of 2.75 mm to an average of 1.6 mm for an equal displacement of electrolyte, provided that the material porosity is unaltered.

The value of using a diagonal ribbed separator lies in restricting the separation to a single item instead of using a flat or finely-ribbed separator shim with a perforated, inert spacer such as the corrugated and perforated PVC spacer used by some makers. The diagonal-ribbed true separator would be the first choice where the distance between plates is too great to be bridged by a flat or finely-ribbed separator shim. This is because corrugated and perforated spacers tend to flatten under high-temperature working and the designed support to the negative material is lost.

The adoption of a 10° diagonal for the main ribs increases the length of each main rib compared with the separator length by an amount equal to 1/cos 10 times the length of the separator. This should be allowed for when calculating the volume displacement of the separator.

In the example used above, it was decided to allow the electrolyte to be 30 mm over the tops of the plates. The top of the separators will come between the top of the plates and the surface of the electrolyte. An overlap of separator over the top of the plates is required since, during the working life of the cells, some active material
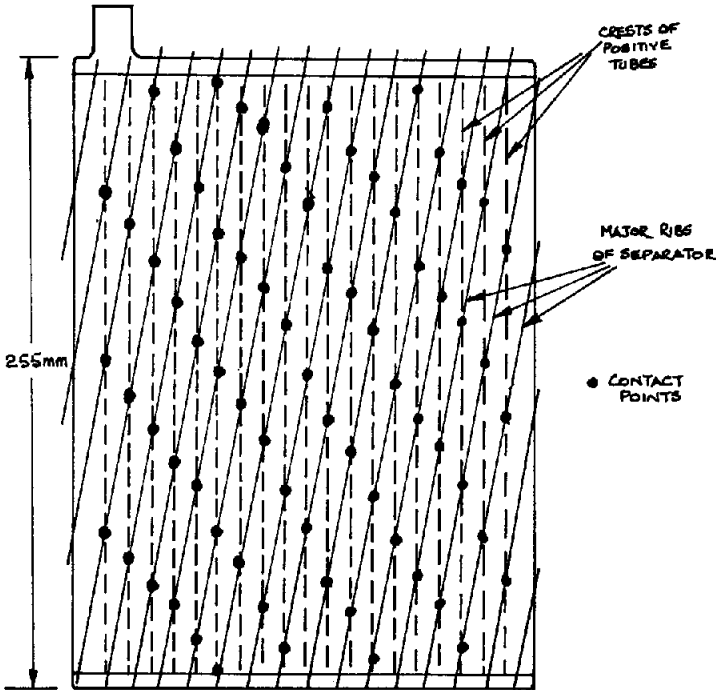
Fig. 15. Pressure contact points between the crests of the positive tubes and the major ribs of a diagonal ribbed traction separator. Angle of major ribs of separator to vertical: 10°; pitch of major ribs: 12 mm.

will be dislodged from the plates and will be carried upwards by the rising gas bubbles. When the gas bubbles burst, this material will fall back into the cell and some will lodge on the top of the element, in the cavities bounded by the separators. Sufficient collecting space should be provided by the overlap of the separators over the plates at the element top to prevent the formation of conducting bridges of active material between plates of opposite polarity. There is a limit to the maximum overlap since, in a good design, there has to be sufficient space over the separators to permit a hydrometer reading to be taken of the electrolyte sp. gr. A reasonable height of electrolyte over the separators is 15 mm per 100 Ah of capacity per single positive plate.

For the design being considered, accept 15 mm head of electrolyte over the separators leaving the separators 15 mm longer than the longest plate, i.e., 453 + 15 = 468 mm. The electrolyte level will then be 483 mm over the plate supports.

Take the three sections of separator (a) of Fig. 14 individually:
    (i) main ribs:
        length of main rib = 468(1 + 1/cos 10) = 475 mm
        cross-sectional area of rib = average width × height of rib = 0.275 × 0.1 = 0.0275 cm^2
        apparent volume of 15 ribs = 15 × 47.5 × 0.0275 = 19.6 cm^3
    (ii) back web:
        apparent volume of back web = 46.8 × 18.5 × 0.06 = 51.9 cm^3

(iii) back ribs:

number of minor ribs is approximately 61, semi-circular with a radius of 0.06 cm:

apparent volume of back ribs $= 61 \times 46.8 \times \pi/2 \times 0.06^2 = 16$ cm^3

Total apparent volume of two separators per pitch $= 2(19.6 + 51.9 + 16) = 175$ cm^3. Separators are highly porous and, although figures of 70 to 85% are quoted for volume porosity, these tend to be optimistic and, in estimating capacities, a more conservative figure of 60% is generally more reliable for most traction separators. It is helpful to check volume porosities of the types of separators most readily available by weighing in the dry state and after soaking in water to confirm the validity of the above assumption and also to categorize the various types of separators. In cases where it is very difficult to meet the capacity ratings, the most porous of the available separators should be considered irrespective of cost.

Using the assumed figure, the true volume displacement of two separators will be $0.4 \times 175 = 70$ cm^3. Before accepting this figure, a similar calculation should be made for the alternative separator (b) of Fig. 14. This separator can be broken down for calculation into main ribs and back web. Included into the back web would be the fine ribbing which is roughly symmetrical and has an average thickness of close to 0.075 mm.

The true solid material in separator (b) that displaces electrolyte works out at 58.2 ml. This is less than for separator (a) so that, for estimation purposes, the larger displacement volume should be taken.

Electrolyte volume

The electrolyte in the sediment space is virtually static and contributes little, if anything, to capacity. It is ignored in calculating the capacity equivalent of the electrolyte.

The working electrolyte can now be estimated by subtracting the total volume of the solid components of the cell element per pitch from the volume per pitch from the top of the plate supports to the electrolyte level.

The electrolyte is 483 mm above the plate supports and the internal width of the container will be $199.5 - (4 + 4)$ cm^3, i.e., 191.5 cm^3.

The internal container volume per pitch occupied by element and electrolyte (cm^3) = $19.15 \times 48.3 \times 1.8 = 1665$.

The solids volumes are then:

positive casting (cm^3)	73.5
positive tube material (cm^3)	35.0
positive active material (cm^3)	142.6
positive base closure (cm^3)	8.8
positive lug (cm^3)	4.0
negative casting (cm^3)	63.2
negative active material (cm^3)	101.8
negative lug (cm^3)	4.0
two separators (cm^3)	70.0
total volume (cm^3)	502.9

The volume of working electrolyte (cm^3) = $1665 - 502.9 = 1162.1$

Earlier, it had been stated that with a single separator against a tubular positive it is common for the electrolyte specific gravity at the end of a full discharge at the 5-h rate to be of the order of 1.080–1.090. A finishing sp. gr. of 1.100 is accepted to provide a small safety margin.

Vinal [1] gives a table of the electrochemical equivalents of solutions of sulfuric acid. From that data, a family of curves can be derived that give the initial volume of electrolyte necessary at any starting specific gravity to provide 1 Ah of discharge capacity for various finishing specific gravities (Fig. 16). Referring to this characteristic curve starting at 1.280 sp. gr. and finishing at 1.100 sp. gr., the volume of electrolyte necessary to produce 1 Ah will be 11 cm^3 Ah^{-1}. Taking the calculated electrolyte volume of 1162.1 cm^3 for the design example gives a capacity potential for the design of 105.6 Ah at +25 °C when discharging at the 5-h rate. This is in excess of the rated capacity and the design offers a reasonable basis for bulk manufacture, provided that the manufacturing tolerances fixed for bulk production are adjusted to ensure the poorest cells will also meet the rated capacity. This must be verified.

It must be recognized that, when checking the sp. gr. at the end of a discharge, a reading, taken immediately after the discharge is complete, will be false. This recorded reading will be that of the free electrolyte and not that of the electrolyte within the pores of the active material. The latter will be appreciably lower than the true average sp. gr. whilst the former will be higher. A more accurate value for the finishing sp. gr. will be given some 2 h or more after the discharge has been terminated. By this time, the more concentrated free electrolyte will have diffused into the pores of the active material and mixed with the absorbed electrolyte.

Effect of production tolerances on cell capacities

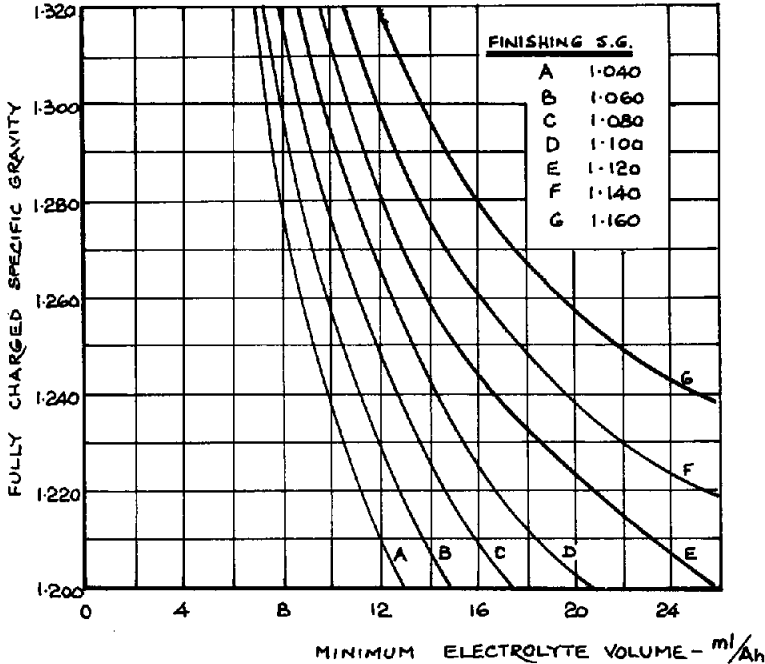The following are production tolerances that are realistic in a well-controlled factory:

Fig. 16. Variation of the minimum electrolyte volume to support 1 Ah of discharge capacity with starting and finishing specific gravities.

(i)   positive formed density (g cm^{-3}) ± 0.2
(ii) negative formed density (g cm^{-3}) ± 0.1
(iii) positive plate thickness (mm) ± 0.1
(iv) negative plate thickness (mm) ± 0.1
(v)   electrolyte specific gravity ± 0.010

Assume these are applicable to the design example.

The change in the positive-plate thickness derives from the permitted variation in the positive formed density and will not necessarily alter the electrolyte displacement volume. The minimum and maximum capacity outputs will occur when items (i), (ii) and (iv) above are all on the maximum and minimum tolerances, respectively, at the same time.

Based on a positive formed density of 3.8 g cm^{-3}, the effect of an upward change of 0.2 g cm^{-3} will be to increase the solids content by a factor of 0.2/3.8. Thus, the change in positive volume $= (0.2/3.8) \times 142.6$ cm$^3 = 7.6$ cm^3.

Similarly, a change of 0.1 g cm^{-3} in the negative formed density will produce a change of 2.6 cm^3 in the solids' volume, based on a specified density of 3.9 g cm^{-3}.

A change of 0.1 mm in the negative-plate thickness is most likely to occur when the cast grid thickness is high. The change in volume will therefore apply to both grid and active material. Applied to a plate 4.6 mm thick, the increase in the solids volume becomes $0.1/4.6(63.2 + 101.8) = 3.6$ cm^3.

The cumulative effect of all these is to produce a solids' volume change of ± 13.8 cm^3 in the volume of the electrolyte previously calculated at 1162.1 ml. These give the excursion of the electrolyte volume due to the effect of cumulative tolerances from 1148.3 to 1175.9 cm^3.

An increase in the electrolyte sp. gr. from 1.280 to 1.290 will not significantly alter the finishing value, neither will a decrease to 1.270. The main factor that determines the completion of a discharge is the voltage. The latter is a function of the final electrolyte sp. gr. Starting from 1.290 sp. gr. and finishing at 1.100 sp. gr., the volume of electrolyte to produce 1 Ah will decrease from 11 to 10.2 cm^3 per Ah, whilst starting from 1.270 sp. gr. will require an increase in the electrolyte volume to 11.7 cm^3 per Ah.

The minimum capacity will occur when the formed densities and negative-plate dimension are on the plus tolerance and the electrolyte sp. gr. on the minus tolerance, and vice versa. The minimum capacity will then become, through the full play of the tolerances, $1148.3/11.7 = 98.1$ Ah, and the maximum capacity $1175.9/10.2 = 115.3$ Ah at $+25$ °C.

On the basis of the design dimensions and allowing for the full interplay of the permitted tolerances, the bulk production output can vary from 98.1 Ah to as high as 115.3 Ah. If the minimum capacity has to meet the rated figure, then either the tolerances have to be tightened or the design has to be modified to give the higher capacity. In general, $\pm 2\sigma$ limits statistically are reasonable production standards for capacity maintenance and the probability of up to about 4% of production cells failing to reach the minimum acceptance capacity does not present a high financial risk. The above capacity variations can be plotted on probability paper taking the calculated values as the 2σ limits and assuming the distribution of cell capacities will be close to a Gaussian distribution, Fig. 17. From this plot can be derived the probable cumulative distribution curve that is representative of controlled production, Fig. 18. The curve illustrates the importance of designing a cell to produce an excess of capacity over rated as the particular geometry will show up to 7% of all cells produced likely to fall below the rated capacity. To meet the $\pm 2\sigma$ limits with no cell having less than
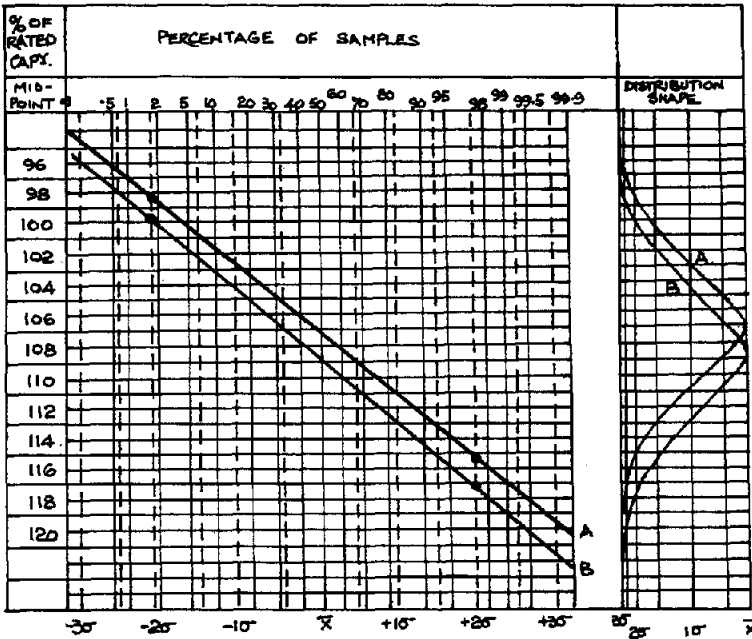
Fig. 17. Probable distribution of capacity for the bulk production of 100 Ah/positive cells made within the following tolerances: formed material density: positive 3.8 ± 0.2 g cm^{-3}, and negative 3.9 ± 0.1 g cm^{-3}; negative thickness: $4.6 - 0.1$ mm; electrolyte sp. gr.:1.280 ± 0.010. Curve (A) initial design, and curve (B) plate length and electrolyte level increased by 6 mm.

the rated capacity, the design capacity has to be increased from 106.7 to 108.5% of the rated value.

Previously, when adjusting the formed material weight of the positive to 13.4 g Ah^{-1} and retaining an average formed density of 3.8 g cm^{-3}, the length of the pencil of lead dioxide was reduced from 436 to 430 mm and the 6 mm reduction was added to the gassing space. This was an expedient and not a necessity; by reverting to the original length some easement in the capacity is possible. The extra electrolyte that would accrue from this step would be the volume of a 6 mm high section of the cell container less 6 mm of two plate lugs per pitch. Extra electrolyte volume = $0.6(19.15 \times 1.8) - (2 \times 1.33) = 19.1$ cm^3. The minimum capacity will occur when the electrolyte sp. gr. is at the lower limit, i.e., 1.270, when the volume of electrolyte to support 1 Ah is 11.7 cm^3. The maximum capacity is when the sp. gr. is 1.290 and requires 10.2 cm^3 per Ah. Hence the minimum capacity increase = $19.1/11.7 = 1.6$ Ah, and the maximum capacity increase = $19.1/10.2 = 1.9$ Ah.

By this change the $\pm 2\sigma$ limits will be raised to 99.7 Ah through to 117.1 Ah, as shown in curve (B) Fig. 17. This design does not ensure that every cell made to the permitted tolerances will fully meet the rated capacity value, but that the possible percentage of cells failing will have been reduced to about 2.5%. This level is not dangerous since it is based on all cells having to meet regular deep cycling. In service use, the pattern of working is not universally hard and this mitigates the apparent failings in capacity. Where cells are intended mainly for industrial trucks that operate
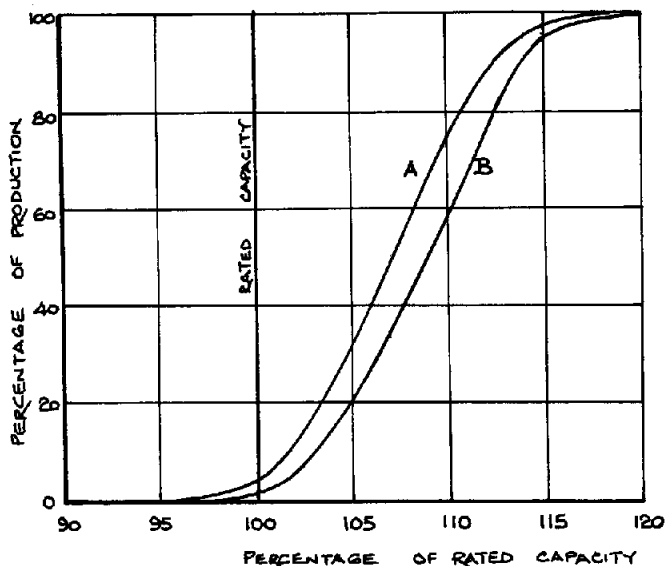
Fig. 18. Cumulative distribution curve of probable cell capacities from the bulk production of 100 Ah/positive cells made to the following tolerances: formed material density: positive 3.8 ± 0.2 g cm^{-3}, and negative 3.9 ± 0.1 g cm^{-3}; negative thickness: 4.6 mm -0.1 mm; electrolyte specific gravity: 1.280–0.010. Curve (A) initial design, and curve (B) plate length and electrolyte level increased by 6 mm.

on a 5-day week, it is doubtful whether the initial design without the increased plate length would have given cause for financial concern. The situation where the predominant usage is with road vehicles and the working pattern is invariably hard is different, and it would be prudent to adopt the longer plate. It is therefore necessary to analyse the market and to assess the proportion of industrial truck users to road vehicles before finalizing the design. The commercial danger attached to choosing the longer plate design with a capacity spread fully capable of meeting sustained heavy duty operation, is that the average life can be so extended that the size of the annual replacement market on which the future prosperity depends can be steadily eroded to the detriment of the future of the whole industry.

Effect of change of pitch on cell design

In the above example of a design of a tubular positive cell, it was fortuitous that the designed tube diameter was so close to a standard proprietary tube diameter that the latter could be accepted as satisfactory. There are global cell designs based on both 19 and 15.6 mm pitches and the proprietary standard tube will not necessarily be the most economical either in the usage of the active materials or the exploitation of the electrolyte.

Consider the smaller pitch of 15.6 mm where the optimum tube diameter is 7.5 mm internally with 35% material conversion for heavy usage, and 7.3 mm and 40% conversion for light operation. Two options are available, namely: (i) to specify

a non-standard tube diameter, and (ii) to accept a standard tube and distort it into an approximate ellipse or rectangle of reduced cross-sectional area.

Take, for example, a 7.5 mm internal diameter tube or its equivalent distorted 8 mm tube. As discussed above for 18 mm pitch, allow 1.5 mm between each tube to cover the thickness of material, lack of straightness, etc. Also allow 4 mm for the cell container walls and 5 mm clearance between the element and those walls. The permissible plate width for a nominal cell width of 160 mm that is applicable to the smaller pitch will be: $160 - 2(4 + 5) = 142$ mm. The number of tubes per plate will be: $142/(7.5 + 1.5) = 15.8$ tubes; take the lower number of 15 tubes. The apparent volume of formed material per decimetre of tube length will be: $10 \times 11(0.75^2 - 0.3^2) = 55.5$ cm^3. This apparent volume can be obtained by using a tube of 8 mm internal diameter distorted into a crude ellipse of external width (minor axis) 7.5 mm and external length (major axis) 9.3 mm. This corresponds to internal tube dimensions of 8.7 mm by 6.9 mm with 14 tubes per plate instead of the 15 tubes with a circular tube.

Optimizing the tube dimensions instead of using a standard tube produces a saving of about 6.7% in the active material, and adopting the crude elliptical saves one tube per plate. The elliptical tubes present a flatter surface to the separators and the volume of electrolyte between the plates is increased. Although the approximate rectangular form of tube presents a stiffer form than the elliptical version, it is not possible to produce an acceptable form using the 8 mm standard tube. In many suppliers standards, however, there are larger circular tubes from which acceptable rectangular tubes can readily be produced. A subsidiary advantage stems from the natural tendency for the elliptical and rectangular tubes to return to their original shape and, wherever there is some slack in the fit of the element in the cell container, the tube will distort to take up the slack and, thereafter, will remain under light compression. This situation is ideal for negatives that would otherwise expand on the surface mainly to achieve the same result but, in so doing, the surface material in a slack fitting cell element would become loose and readily leave as sediment. The surface expansion would then be repeated to the detriment of cell life. Any distortion occurring in the tube shape reduces the formed density and helps to improve the capacity output.

An alternative is to manufacture the tubes from thicker nonwoven material and to hold the outer diameter close to that of the woven standard. There is a small disadvantage in this as the solids' volume of the nonwoven tube tends to be greater than that of the woven equivalent and, thereby, displaces slightly more electrolyte than the latter.

Flat-plate traction cells

Consider a cell container 535 mm high and 199 mm wide as specified in DIN 43567 Blatt I to accommodate a range of flat-plate cells with a plate pitch of 15 mm and a positive-plate rating of 66.6 Ah at the 5-h rate. The design life is to be not less than 4 years, or 1500 charge/discharge cycles, under discharge conditions not regularly exceeding 80% of the rated capacity. This means the positive material will require firm support from glass-wool retainer mats. For the purpose of the example, it is proposed to enclose the positive plate in a separator envelope to eliminate failures prematurely from the formation of conducting bridges of active material at the sides and bottom of the cell element.

From the previous statements the following parameters of design would apply:

(i) specific positive grid weight (g Ah^{-1})	11
(ii) positive formed density (g cm^{-3})	4
(iii) positive specific formed material weight (g Ah^{-1})	15
(iv) specific negative grid weight (g Ah^{-1})	6.7
(v) negative formed density (g cm^{-3})	3.8
(vi) negative specific formed material weight (g Ah^{-1})	11.5
(vii) plate support height (mm)	16
(viii) electrolyte height over plates (mm)	30
(ix) maximum gassing height (mm)	46
(x) entry of lid into container (mm)	10
(xi) thickness of material in container base (mm)	4
(xii) plate length	not known

Positive plate

The maximum plate length will be the difference between the container length and the sum of the dimensions (vii) to (xi), above. This gives a maximum length of 429 mm.

There must be a clearance between the plate and the envelope and also between the envelope and the cell wall. Allow 3 mm for each of these on either side of the plate and 4 mm for the thickness of the container walls. This gives a plate width of 179 mm.

Based on the capacity rating of 66.6 Ah per positive, the weight of positive grid (less lug) = $66.6 \times 11 = 732.6$ g.

If it is assumed that the alloy contained 7wt.% Sb with a density of 10.97 g cm^{-3}, then:

volume of positive grid (less lug) = $732.6/10.97 = 66.8$ cm^3

weight of formed active material required will be $66.6 \times 15 = 999$ g, with an apparent formed density of 4 g cm^{-3}

apparent volume of positive material = $999/4 = 249.8$ cm^3

total volume of plate = $66.8 + 249.8 = 316.6$ cm^3

If t cm is the average pasted and formed plate thickness, then total apparent volume of plate = $42.9 \times 17.9 \times t$ cm^3 and thickness of plate, $t = 316.6/(42.9 \times 17.9) = 0.412$ cm.

Take 4.2 mm as the effective thickness of plate. This, being greater than the calculated thickness, could indicate that a small reduction in plate length is possible to accommodate the required volume of formed active material, i.e., revised plate length = $(0.412/0.42) \times 429 = 421$ mm. Thus, the revised plate dimensions will be 421 mm long, 179 mm wide, and 4.2 mm thick.

It is necessary to derive the solids' volume per pitch in order to derive the capacity per pitch. Using the empirical rule for the dimensions of the plate lug based at holding the 5-h discharge current density at about 15 A cm^{-2}, the cross-sectional area of lug becomes 0.89 cm^2.

The plate length was reduced by 8 mm when the thickness was rounded up to 4.2 mm. Initially, this can be added to the height of electrolyte above the plates to make this dimension 38 mm instead of the 30 mm that was originally proposed.

Assuming the straps connecting together the plates are set at the electrolyte level, 38 mm of lug will be below the electrolyte and will displace electrolyte. Thus: volume of lug below electrolyte = $3.8 \times 0.89 = 3.4$ cm^3.

Although the formed density of the positive material was set at 4 g cm^{-3}, the actual density of lead dioxide is 9.4 g cm^{-3}. Thus, actual solids volume of formed material = 999/9.4 = 106.3 cm^3.

The solids' volume displacing electrolyte then becomes:

grid (cm^3)	66.8
lug (cm^3)	3.4
formed material (cm^3)	106.3
total (cm^3)	176.5

Negative plate

Accept a negative grid with the same length and width as the positive grid so that the superficial area of active materials match each other. Based on the capacity rating of 66.6 Ah/positive: weight of negative grid = 66.6 × 6.7 = 446.2 g.

Assume there is sufficient casting expertise available to cast economically using an alloy with 4.5 wt.% Sb and a density of 11.08 g cm^{-3}, then:

volume of negative grid (less lug) = 446.2/11.08 = 40.3 cm^3

weight of formed negative material = 66.6 × 11.5 = 765.9 g

apparent volume of formed material = 765.9/3.8 = 201.6 cm^3

Let the average formed plate thickness be t cm, then:

total apparent volume of plate = 42.1 × 17.9 × t cm^3 = 201.6 + 40.3 cm^3

thus: plate thickness, t = 241.9/(42.1 × 17.9) = 0.32 cm

The negative plate dimensions will therefore be 421 mm × 179 mm × 3.2 mm.

Although the formed material density is 3.8 g cm^{-3}, the true material density is that of lead, 11.3 g cm^{-3}, thus: actual solids' volume of formed material = 765.9/11.3 = 67.8 cm^3. The volume of lug material displacing electrolyte will be the same as for the positive plate, i.e., 3.4 cm^3. This gives the total solids' volume of a negative plate displacing electrolyte as:

grid (cm^3)	40.3
lug (cm^3)	3.4
formed material (cm^3)	67.8
total (cm^3)	111.5

Glass-wool retainer mats

There needs to be a glass-wool retainer mat on either wide of the positive held under compression. A realistic value for the degree of compression is for the original mat to be reduced in thickness by about 15%. Less than this introduces the risk of the fibres slumping under vibration and mechanical shock. Whilst a thick retainer mat improves life expectancy, the more mat material provided, the greater is the loss of effective electrolyte and cell capacity. In practice, an uncompressed thickness of 1 mm tends to be inadequate unless the lay of the fibres is close and very regular. A thickness in excess of this is recommended. An acceptable positive material support can be obtained with mats of 1.8 mm thickness compressed to 1.25 mm.

The equivalent porosity of the mats can vary between 35 and 60%; the value is dependent on the uniformity and closeness of the weave or random lay of the fibres. An average of 50% is usually realistic for capacity estimations, but it is prudent to check that this order of porosity is realized in bulk production stocks. As the retainer mats have to be inserted with the positive plates into the separator envelope, their dimensions will be the same as those of the positive plates, i.e., 421 mm × 179 mm, but the uncompressed thickness will be 1.5 mm. The apparent volume of two retainer

mats = $2 \times 42.1 \times 17.9 \times 0.15 = 226.1$ cm^3 and the true solids' volume of 2 mats = $0.5 \times 226.1 = 11.3$ cm^3.

Separation

The cumulative tolerances on the components comprising a single pitch will be:

positive plate (mm)	0.1
negative plate (mm)	0.1
retainer mats (2) (mm)	0.3 (these tend to be variable)
separators (2) (mm)	0.14
total (mm)	0.64

This leaves $(15 - 0.64)$ mm, i.e., 14.36 mm to accommodate the nominal thicknesses of a positive plate, negative plate, two retainers mats (compressed) and two separators. The thickness of two separators = $14.36 - (4.2 + 3.2 + 2.6) = 4.36$ mm. This gives a nominal thickness for each separator of 2.18 mm. Take 2.2 mm as the nominal thickness that causes the retainer mats to be slightly more compressed than originally intended.

The electrolyte level has been taken as the height of separators over the tops of the plates. Initially, allow 15 mm as the height of separators over the plates; this leaves the electrolyte level as 23 mm above the top of the separators. Allow 5 mm overlap of separator each side of a plate. The separator dimensions then become: 436 mm × 189 mm × 2.2 mm.

Taking the separator (a) profile of Fig. 14, the minor back ribs will again be 0.6 mm deep with the back web 0.6 mm thick and the main ribs 1 mm deep. A normal vertical ribbed separator will be satisfactory.

With a rib pitch of 12 mm, there will be 15 main ribs. Similarly at the back of the separator with a minor rib pitch of 3 mm, there will be 63 minor ribs:

apparent volume of 15 main ribs = $15(0.1 \times 0.275 \times 43.6) = 18$ cm^3

apparent volume of back web = $43.6 \times 18.9 \times 0.06 = 49.4$ cm^3

apparent volume of 63 back ribs = $63(43.6 \times \pi/8 \times 0.06^2) = 3.9$ cm^3

total volume of 2 separators = 142.6 cm^3

Taking into account the volume porosity of 60%, the true solids' volume of two separators becomes 57 cm^3.

Electrolyte volume

As in the exercise on the tubular positive cell, the electrolyte below the element is disregarded in the determination of the working electrolyte. The electrolyte was initially taken as 38 mm above the tops of the plates to give an electrolyte level above the plate supports of 459 mm. The internal cell container width is $(199 - 8) = 191$ mm when the thickness of the walls is taken into account. The internal container volume per cell pitch occupied by element and electrolyte = $19.1 \times 45.9 \times 1.5 = 1315$ cm^3.

The solids volumes per pitch are:

positive plate (cm^3)	176.5
negative plate (cm^3)	111.5
two retainer mats (cm^3)	113
two separators (cm^3)	57
total (cm^3)	458

The working electrolyte per pitch = $1315 - 458 = 857$ cm^3

Cell capacity

With the amount of glass wool adopted for the example, it should be possible with the chosen formed material densities to react the electrolyte down to a sp. gr.

of 1.120 when discharging at the 5-h rate. The use of denser formed materials and thicker glass-wool retainer mats will raise this end-of-discharge sp. gr.

Commencing at a sp. gr. of 1.280 and reacting down to 1.120, the electrolyte will have a capacity potential of 83 Ah l^{-1} at $+25$ °C which is equivalent to 85.5 Ah l^{-1} at $+30$ °C. On this basis, the design will produce a capacity at $+30$ °C of 73.3 Ah which, compared with the design requirement of 66.6 Ah, may seem a generous margin.

Before accepting this design, the effect of permitted manufacturing tolerances needs to be assessed. The following tolerances are realistic:

positive plate thickness (mm)	± 0.1
negative plate thickness (mm)	± 0.1
positive formed density (g cm^{-3})	± 0.1
negative formed density (g cm^{-3})	± 0.1
electrolyte specific gravity	± 0.010

The maximum and minimum capacities will occur when all the above except the electrolyte are on the minimum and maximum values, respectively. In the case of the electrolyte, an increased sp. gr. leads to an increased capacity, and vice versa.

The effect of 0.1 g cm^{-3} tolerance on the positive material will change the solids volume by 0.1/4 and the negative solids volume by a factor of 0.1/3.8.

change in solids' volume of positive material $= (0.1/4) \times 106.3 = 2.7$ cm^3
change in solids' volume of negative material $= (0.1/3.8) \times 67.8 \times 67.8 = 1.8$ cm^3

The change in the grid and material solids' volume of a positive plate due to a change of 0.1 mm in plate thickness will be: $(0.1/4.2) \times (106.3 + 66.8) = 4.3$ cm^3. Similarly, the change in the negative solids' volume will be: $(0.1/3.2) \times (67.8 + 40.3) = 3.4$ cm^3. Cumulatively, these produce a solids' volume change of ± 12.2 cm^3. The lowest and highest electrolyte volumes due to the full interplay of all the permitted tolerances will be 844.8 and 869.2 cm^3, respectively.

Irrespective of the starting sp. gr., there will be little or no change in the finishing sp. gr. This will give electrolyte capacity potentials when starting at 1.270 sp. gr. of 77.5 Ah l^{-1}, and when starting at 1.290 sp. gr. of 87.7 Ah l^{-1}. Thus:

minimum capacity $= 0.8448 \times 77.5 = 65.5$ Ah
maximum capacity $= 0.8692 \times 87.7 = 76.2$ Ah

Assuming these values represent $\pm 2\sigma$ limits statistically, the probable cumulative distribution curve of cell capacities in bulk production will be as shown in Fig. 19.

The distribution curve indicates that even with what appears to be a wide spread of capacities (with the highest-capacity cells over 15% greater in capacity than demanded), there could be up to 5% of bulk production failing to meet the rated capacity. The variation in usage patterns would probably mean that the real level of failures in service will be much lower.

Whilst the design appears feasible, all the conclusions depend on the discharge continuing until the electrolyte sp. gr. has reached 1.120. Having made trial cells to the design and stabilized the capacity by limited cycling, it may be found that discharge at the 5-h rate is terminated by loss of voltage before the stated sp. gr. has been reached. This does not necessarily mean that the design parameters are suspect, but rather that:

(i) there has been a greater densification in the paste when passing through the pasting machine than anticipated; or

(ii) the thoroughness of pasting mixing is suspect; or

(iii) there is a greater variation in the plate weights than planned; or
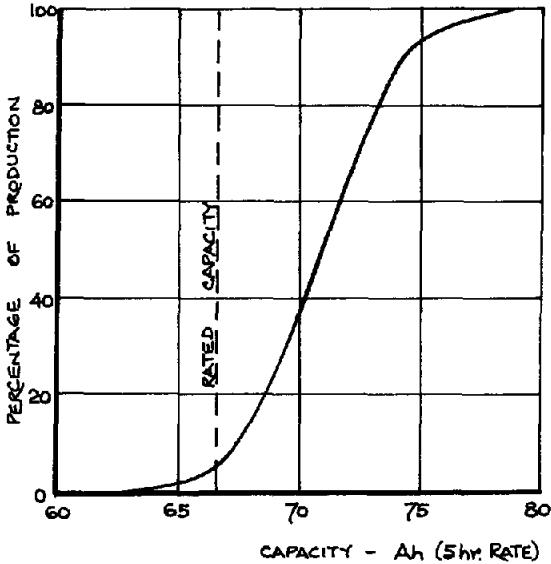
Fig. 19. Cumulative distribution curve for probable cell capacities from the bulk production of 66.6 Ah/positive flat-plate cells made to the following tolerances: formed densities ± 0.1 g cm^{-3}; plate thicknesses ± 0.1 mm, and electrolyte sp. gr. ± 0.010.

(iv) the assembly of plates into an element has been such that there is not a free convection path down the sides of the element and there is poor mixing of the electrolyte within the cell; or

(v) the porosity of the glass-wool retainer mats is lower than the expected value; or

(vi) a combination of some, or all, of the above.

It is expedient when making up trial cells that the plates are selected first by grid weight and then by grid and material weight. They should also be examined for thickness. The separators and glass-wool retainer mats should also be monitored. From the resulting data, an indication will be gained of the probable tolerances introduced into the trial cells and, in turn, the effect of these tolerances on the measured capacities.

References

1 G.W. Vinal, *Storage Batteries*, Wiley–Interscience, New York, 3rd edn., 1945.