

Discussions on the lead/acid battery No. 6

Physical change in positive-plate material – an underrated contributor to premature capacity loss

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Abstract

In spite of a broad and sustained research effort, premature capacity loss (PCL) remains the major barrier to the long term usage of lead/acid batteries in a range of demanding applications. Of greatest concern today is the manifestation of PCL that results in failure of the porous component of the positive plate. While much of the previous work in this area has focussed on the localized interactions between constituent particles of the porous material, we suggest that important bulk factors, such as plate compression and apparent density, have not received sufficient consideration. Indeed, evidence from experimental studies indicates that apparent density is the critical determinant of positive-plate performance and that compression is the primary means by which density is controlled in contemporary plate designs. Moreover, the extension of positive-plate cycle life depends on maintaining apparent density above a minimum value. In light of this relationship, we present strategies by which gains in plate performance can be achieved.

Keywords: Compression; Apparent density; Lead/acid batteries ; Capacity loss

1. Capacity loss or PCL?

As the importance of making better usage of energy increases, so too does the demand for more reliable forms of energy storage. In particular, energy-storage media must now fulfil a range of demanding criteria. The most fundamentally significant of these is the requirement to perform at high levels of energy density. This criterion has proven to be especially taxing on the lead/acid battery which, despite many years of dedicated research, has so far proved to be unsuited to sustained operation at high energy density (i.e., high material utilization).

The source of the problem is well-known. When operated under repetitive deep-cycling duty, the positive plates of lead/acid batteries exhibit a steady and progressive loss of discharge capacity. The term 'premature capacity loss' (PCL) has been coined as an overall descriptor of this phenomenon. The rate of capacity loss, however, spans an appreciable range: from extremely rapid (~5% of initial capacity per cycle) to

quite low. To avoid any confusion associated with such a broad definition, a classification of two forms of PCL has been proposed [1]. PCL-1 is the severe form of capacity loss in which discharge capacity falls at a relatively high rate. PCL-1 is widely attributed to the development of so-called 'barrier layers' close to the grid. It must be noted that the phenomenon known as 'passivation' can also cause sudden loss of capacity. Passivation can, however, be distinguished from PCL-1 through the application of simple electrical tests. Fortunately, the issue of very early positive-plate failure, due either to passivation or to PCL-1, has been overcome to a great extent. This has been due mainly to the results of detailed studies on the properties of corrosion layers, together with improved manufacturing technologies.

The second form of PCL, namely, PCL-2, applies when positive plates lose capacity at relatively low rates but, the common and readily determinable causes of plate failure (e.g., grid corrosion, irreversible plate sulfation, porous material shedding) are largely absent. Clearly, unequivocal assignment of PCL as the mode of failure becomes more difficult with longer-lived bat-

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teries. This is because degradation associated with the well-known modes of failure becomes more likely. PCL-2 is therefore, by its nature, insidious. Given the success achieved in addressing PCL-1, overcoming this less obvious form of PCL (which we shall refer to simply as PCL from this point on) is now the most urgent task facing researchers in the field.

The purpose of this discussion is to present an explanation of PCL. As we shall show in detail, much of the data on which this explanation is based are to be found in the published literature. In addition, we have initiated specific experimental studies designed to establish the significance of several important aspects of PCL. These studies form part of a research programme sponsored by the Advanced Lead/acid Battery Consortium [2]. We begin with a brief survey of relevant published information.

2. Maintaining positive-plate capacity – key factors

Much has been reported on the broad topic of maintaining plate capacity, and detailed reviews are available [3,4]. From this large body of information, it is relatively easy to extract a list of the major determinants of battery performance: extent of active-material utilization, additive elements (most notably, antimony), charging regimes, depth of discharge, phase composition of lead dioxide, crystallinity and morphology of both lead dioxide and lead sulfate, and compression of the cell plate-group. Each of these factors has been documented to some extent and, as a result, there is detailed empirical understanding of the significance of each with respect to capacity loss. Not surprisingly, years of careful research have also revealed that complex relationships exist between many of these factors. Our intention here, though, is not to delve further into this complexity but, rather, to concentrate on the one factor that allows a simplification of the problem – compression.

The extent to which the plates are held under compressive load during service is arguably the least understood of the factors that prolong battery life. Nevertheless, experimental data indicate that the amount of compression experienced by positive plates during service has a strong (and apparently direct) benefit in terms of cycle life. Perhaps the first detailed study of this relationship was presented by Takahashi et al. [5] in 1983. They described the effects of compressive force on flooded antimonial cells that were operated under a motive-power cycling regime. Compression of the cell group was set prior to formation, at values between 20 and 100 kg dm⁻² (1.0 kg dm⁻² = 0.98 kPa). Cells compressed at the lower value lost approximately 30% of the original capacity within 500 cycles while those

compressed at 100 kg dm⁻² had only just begun to lose capacity after the same number of cycles. For both levels of compression, changes were observed in several important plate parameters: (i) the porosity of the positive material rose; (ii) the total pore volume increased, with distribution of volume biased towards large (>10 μm) pores; (iii) the plate thickness grew appreciably (10–15%), despite the considerable applied forces. Although these changes were noted for both high- and low-compression cells, the magnitude of the change was slightly greater for the latter cells. By comparison, a much more obvious distinction between the two levels of compression was revealed by monitoring the positive-plate resistance. This parameter increased markedly for the cell held under lower compression, but only slightly for the high-compression cell. These results establish two important points: (i) positive-plate resistance is a strong indicator of capacity loss under deep-cycling conditions (this supports earlier findings by the research team at Varta [6]); (ii) small, but significant, increases in the volume to which the plate grows during service appear to determine whether capacity loss will occur. The timing of the changes in plate properties is important – Takahashi et al. [5] noted that all changes were essentially complete early in the cycle life. For the cell with low compression, capacity loss began once the plates had expanded to a certain critical volume.

At around the same time, Alzieu and Robert [7] reported a somewhat less detailed account of the effects of compression. They subjected motive-power cells (commercial units, 5 h capacity = 34 Ah) to a rigorous cycling regime. This involved discharging for ~90 min to a cut-off voltage of 1.5 V, followed by charging at 100 A, with an upper-voltage-limit of 2.65 V. The cycle life was found to reach a distinct maximum at a compressive load of around 100 kPa. This loading is similar to the highest used by Takahashi et al. [5]. Cycle life was extended further (from ~2000 to ~3000 cycles) by deliberately bonding (by a 'hot melt' process) the separator to the surface of the positive plate. In essence, this strategy had the effect of retaining porous material within the boundaries of the plate. Again, it appears that constraining the volume in which the porous mass is held can exert a pronounced effect on cycle life.

In a later study, Alzieu et al. [8] conducted a deeper investigation of the forces within a lead/acid plate-group during long-term cycling service. Rather than apply known levels of compression to cells, the approach in this study was to use a rigid cell container, and then monitor the expansive force exerted by the plate-group. They identified two effects that determine the magnitude of this force: a 'sulfate' effect, that causes the plate to swell during discharging and contract during charging; (ii) a 'thermal' effect that is associated with the opposite changes in pressure. While the former is well-known,

through its relationship to the difference in molar volume of lead sulfate and lead dioxide, the latter is only documented in phenomenological terms. Nevertheless, it was shown that the ratio of the two effects depended on the number of plates in the cell group. Effects of temperature on the performance of positive plates are known, but are generally only considered in terms of enhancement of obvious processes of degradation (e.g., grid corrosion, shedding). The findings of Alzieu et al., however, suggest that temperature contributes to the complexity of forces acting within the plate-group during deep-discharge cycling. While this was an important result, uncertainty remained regarding the distribution of the expansive force between the positive and the negative plates.

Pavlov and Bashtavelova [9] have removed much of this uncertainty through a study of the changes in the properties of the positive material that accompany cycling. Their description of the ‘breathing’ of the porous mass includes the observation that the thickness of positive plates, cycled deeply at the 4 h rate, increased during each discharge and also increased progressively with cycling. Coincident with the increase in plate thickness, as cycling proceeded, was a decrease in the apparent density of the material. Although this study did not examine changes in plate-material properties over a long period of cycling, the results clearly demonstrated that deep-discharge cycling service causes a substantial alteration of the physical properties of the positive plate. Again, the overall effect is that the volume of the plate tends to increase, due to a fall in the apparent density of the (porous) material.

A similar theme was continued by Pavlov’s group in later work on the compression-induced reconstruction of an electrochemically active porous electrode, from finely ground lead dioxide [10]. The pulverized material was packed into the annular volume of an empty tubular-plate element (i.e., spine, gauntlet and end-plugs). A recovery of capacity occurred only in cases where the compressive load was high enough to raise the apparent density above a critical value (3.80 g cm^{-3}). In a sense, the process(es) occurring here can be viewed as the reverse of what happens in plate failure – disintegrated positive material (by analogy, regarded as failed material) is compacted into a coherent, functional porous mass. This view of events adds weight to our arguments about the importance of compression and material constraint. The only aspect on which caution is required is in denying any distinction between ‘failed’ material and the finely ground material used in the reconstruction experiments¹ [10]. It is interesting to recall that similar

concepts were used by Winsel et al. in their development of the aggregate-of-spheres model of porous material structure [6].

3. Compression and apparent density

We commenced the above survey of published data by focussing on the issue of compression. It has emerged, however, that compression is important mainly through its influence on a more fundamental factor – porous-material density. Compression tends to maximize the apparent or packing density of the porous material. The demonstration by Pavlov [10] that a minimum density is required to produce a functional electrode structure highlights the significance of this parameter. In a battery plate, it is the volume within which the positive material is allowed to expand that determines the value of apparent density reached during service. As shown above, this issue has been touched on in the course of several investigations. What appears to be lacking, however, is a detailed investigation of the relationship between changes in positive-material density and degradation of plate performance.

Of particular interest is the fact that none of the major theories advanced in explanation of PCL considers explicitly the effects of changes in material density. The reason is that capacity loss is usually regarded as the result of processes occurring at a level of structure somewhere between the microscopic and the atomic/molecular. For example, in descriptions of both the gel-crystal (GC) [12] and the aggregate-of-spheres (AOS) [6] models, we find an emphasis on the importance of the connectivity between the constituent particles of the porous mass. The maintenance of connectivity between particles (generally sized $<0.1 \mu\text{m}$) is discussed in terms of the ‘bridges’ between particles and capacity loss is treated as a result of the loss of contact in these critical inter-particle zones (‘necks’ in the AOS model). This is certainly an important issue, because ‘connectivity’ in the context of a conducting electrode material, such as lead dioxide, determines the extent to which the electrode can be discharged. Connectivity is not, however, determined solely by the localized interactions between a particle and its nearest neighbours.

The connections between particles, and hence the integrity of the porous structure, are also determined by forces acting on the bulk of the material. The process of sintering provides a good illustration. Another example is the study reported by Winsel et al. on the conductivity of compressed aggregates of metal particles [6]. This work related the conductivity of a porous network of material to the pressure applied to the bulk of the sample, and was used as the basis for the AOS model of positive-plate structure. Pavlov’s group dem-

¹ Those who believe that lead dioxide undergoes some form of ‘de-activation’ during capacity loss will, of course, object to labelling the ground lead dioxide as ‘failed’ material. On the other hand, it should be noted that experimental attempts to establish a meaningful distinction between ‘healthy’ and ‘failed’ lead dioxide have been unsuccessful [11].

onstrated the relevance of this concept to lead/acid positive plates by producing fully functional positive electrodes from finely ground lead dioxide [10]. In both cases, a sensitive relationship was observed between the packing-density/external-packing-pressure and the properties of the porous structure. This relationship, along with the evidence presented from experimental studies, justifies treating the apparent density of the porous mass as a significant determinant of plate capacity.

4. Cycling positive material within a restricted volume

We have set up an experimental programme to obtain more information on the role of apparent density in the loss of plate performance. To do this, it is necessary to monitor the discharge capacity of positive electrodes under conditions where the dimensions of the porous mass are, to a large extent, fixed. The electrode design, shown in Fig. 1, satisfies this requirement.

A typical motive-power positive paste was prepared and forced into the recess of a specially cast epoxy block. The block was machined to a standard B34 (Quickfit) taper so that the electrode can be fitted into a cell with a corresponding B34 (Quickfit) socket. At the narrow end of the electrode assembly, a thread was cut to accommodate a plastic (polypropylene) retaining cap, with the corresponding internal thread. As shown in Fig. 1, this design allows a disc-shaped separator to be positioned between the cap and the porous material. In this way, the volume occupied by the lead dioxide is restricted to a large degree. In fact, the only expansion that is possible in this arrangement is through: (i) compression of the separator against the underside of the retaining cap; (ii) distortion and expansion of the separator so as to form a bulge through the aperture in the retaining cap.

Each positive electrode was cycled against a relatively large sponge-lead negative electrode, in a considerable excess of 5 M H₂SO₄. In order to test the validity of the arguments developed above, a charge–discharge regime that was known to give rise to severe PCL was chosen. The Varta group has conducted extensive studies

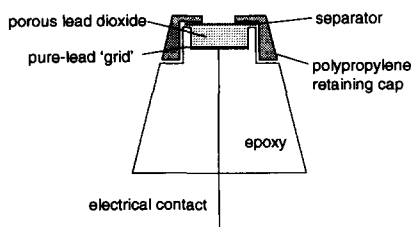


Fig. 1. Schematic diagram of pasted electrode for studies of positive material.

of the regimes that cause rapid capacity loss [4]. Based on the results of those studies, we selected a combination of relatively high-rate discharging and low-rate charging that has been shown to give rise to rapid loss of capacity. Other work in our laboratories, on full-sized cells, has confirmed the severity of this type of cycling regime. Hence, the cells were discharged at approximately the 1 h rate, to a cut-off voltage of 1.75 V, followed by charging at one tenth of the discharging current, with no limit on the upper voltage. The overcharge factor was maintained at around 150%, which is also known to accelerate capacity loss.

As shown in Fig. 2, the discharge capacity of each cell has remained close to the initial value, for nearly 40 cycles. Under similar conditions, workers at Varta have shown [13] that, for different types of positive plate, severe capacity loss occurs within only a few cycles. Clearly, the positive electrodes described in the present study possess a remarkable resilience with respect to capacity loss. This is despite the fact that each aspect of the experiment's design was chosen so as to enhance the rate of capacity loss of the positive electrode, namely: (i) the grid material is pure lead; (ii) both electrolyte and negative material are present in considerable excess. This, we assert, emphasizes the influence of the support and the restriction of expansion that is provided by the physical construction of the electrode.

The importance of the volumetric stability of these electrodes was emphasized further by relaxing the confinement of material in one of the electrodes. This was accomplished by loosening the retaining cap of one electrode, by half of one turn, after it had completed more than 40 cycles. Within a few cycles, the discharge capacity fell sharply, by approximately 25%, and the cell was removed from service. During the same period, the resistance of the positive electrode increased appreciably. Prior to loosening of the cap, the resistance had remained virtually constant throughout most of the cycle life. As noted earlier, several laboratories have also reported that a decrease in positive-plate capacity coincides with an increase in the resistance of the positive material [5,6]. The amount by which the retaining cap was released translates to an increase in volume of between 15 and 20%. For good cycling performance, Pavlov has suggested [3] that expansion of the positive mass should not be allowed to exceed ~ 15%.

5. Why is apparent density so important?

Having illustrated the effect of active-material density/volume on plate performance, it is important now to consider the underlying reasons for this effect. Ultimately, we can then devise ways of minimizing the loss

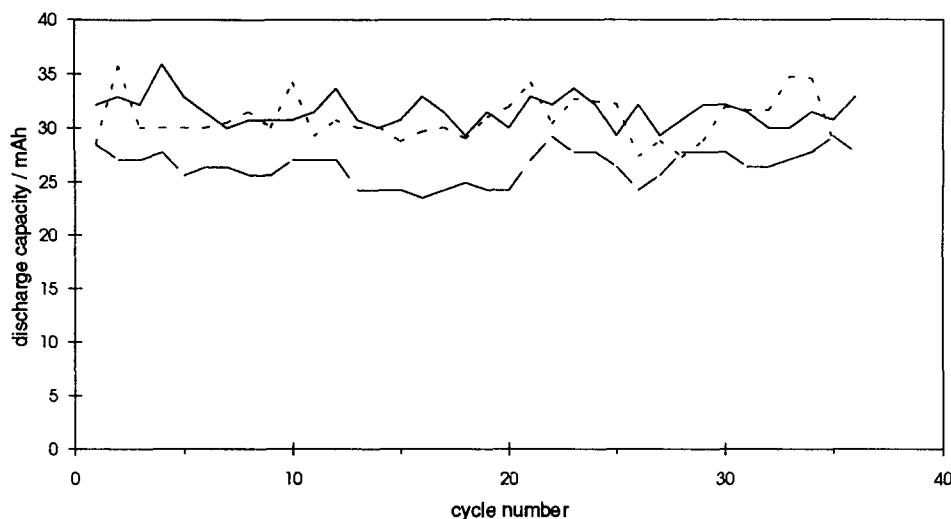


Fig. 2. Plots of capacity against cycle number for small pasted electrodes.

of discharge capacity that arises when density is not controlled. The following discussion is presented in terms of resistance/conductivity because this is the property that essentially defines the discharge-ability of a porous electrode.

The conductivity of a porous body, i.e., one that is comprised of particles of a conductive material, is known to be a function of the packing density of the particles. This dependence is derived from the relationships that exist between packing density and the number of points of contact between neighbouring particles. Percolation theory provides a mathematical description of these relationships and has been used to model accurately the behaviour of several well-known systems [14]. For example, when finely-particulate mixtures of niobium and alumina are sintered under pressure, the conductivity of the resultant composite increases rapidly above a certain minimum ratio of conductor (Nb) to insulator (Al_2O_3) [15]. Below this threshold value, there is not enough metal present for the establishment of a conducting network.

More recently, Aoki et al. [16] invoked a percolation-based model to explain the behaviour of conducting polymers. In many ways, conducting-polymer electrodes behave similarly to battery electrodes such as the lead/acid positive plate. In particular, both are porous electrodes in which a conducting phase is converted into an insulating phase, via electrochemical reactions at an electrolyte interface. Important comparisons can, therefore, be made between the behaviour of the two systems. Aoki et al. [16] have found that significant portions of the conducting component of a polyaniline film are left isolated from the substrate electrode when a reduction of the film, back to the insulating state, is attempted. As conversion of conductor to insulator takes place, there is a decrease in the the number of connections between the conducting regions and the

base electrode (analogous to the grid for a battery electrode). At the percolation limit, i.e., the threshold value (defined above), a significant number of these regions become electrically isolated and no further conversion takes place. Clearly, a percolation model is a useful way of accounting for the fact that much less than 100% material utilization is achieved in the discharge of battery plates.

In terms of capacity loss, similar arguments can also be used to describe changes in the porous structure that determine the percolation limit. It is interesting to note that conducting polymers exhibit phenomena that influence their charge-transfer characteristics. For example, Aoki et al. [16] describe a 'slow relaxation' process in which the polymer structure is re-organized so that some of the isolated conducting material again becomes accessible for conversion, to the insulating state. Relaxation-like processes are also known for lead/acid positive plates. Pavlov and Bashtavelova [9] found that the expansion of positive plates during discharging relaxed when the plates were allowed to stand at open circuit in the discharged state. [This was quantified by measurement of the slight contraction in the thickness of the plates during standing.] The clear analogy between the behaviour of conducting polymer and lead dioxide electrodes indicates that the theoretical description of the former, in terms of percolation theory, can also be applied to the lead/acid electrode. At the very least, such a treatment should yield important data on relationships between compression, apparent density (both before and during service), and maximum levels of utilization for positive plates.

6. A fresh approach to capacity loss – PCL revisited

We have proposed that moderate forms of capacity loss are the result of significant changes in the volume

occupied by the positive mass. In particular, once the apparent density of the porous material falls below a critical value, set by principles similar to those expounded in percolation theory, then capacity falls steadily. The loss of capacity is due to a progressive, mutual isolation of the constituent particles of the porous mass. From this perspective, it is now useful to re-evaluate some of the key aspects of PCL that have received attention in the past.

The benefits of antimony on positive-plate cycle life have until now been discussed in terms of crystal-chemical effects. These include the influence of antimony on: α -PbO₂/ β -PbO₂ ratio; the properties of PbO₂ per se; the bonding between particles of PbO₂. In simpler physical terms, though, the superior strength of Pb–Sb grids should be an important factor in retaining the porous material within a given (sub-critical) volume. Specifically, the strength of the perimeter member of a grid determines how much growth/expansion occurs in the plane of the plate. If such expansion is restrained, and the cell group is held under some compression, then the plate-material volume is regulated to a large degree. Antimony, as a grid-strengthening agent, clearly plays an important role in this parameter of plate behaviour.

The known ability of tubular plates to provide long cycle lives is clearly consistent with the proposed benefit of restricting the expansion of the porous material. Further, it has been reported that antimony-free tubular plates can give a cycling performance to rival that of antimony-containing equivalents. Such a situation is, however, difficult to reconcile with a purely chemical explanation of antimony's benefits. By comparison, if constraint of material volume is the major determinant of cycleability, then the effects of antimony will become less universally important. And of course, tubular plates eventually fail during cycling service. Interestingly, the common modes of failure (e.g., fracture and splitting of gauntlets, movement of tube end-plugs) are indicative of volume increase due to expansion of the porous mass.

Some comment is also required on the incidence of severe PCL and/or passivation. It is probable that these phenomena will occur in cases where a relatively large increase in the volume of the active material occurs early in service. The resultant opening-up of the porous structure will then aggravate effects at the interface (such as passivation) by allowing electrolyte to penetrate close to the grid. Such a scenario is probably the cause of reported instances of 'preferential discharge' in which a high concentration of lead sulfate forms early in discharging, close to the grid [17]. In situations like this, conditions may then be established for the development of 'barrier layers' of α -PbO, below the layer of lead sulfate. Meissner has outlined a similar chain of events in his review of the AOS theory [4].

The main point of these arguments is that the barrier-layer component of PCL is in fact a secondary effect that requires a particular set of conditions within the plate. Tin appears to ameliorate this severe form of PCL through modification of the electrical properties of barrier compounds, such as α -PbO. But, once a plate has survived this critical period, i.e., a barrier layer has not formed, the capacity loss of the plate is determined by operational factors that act to restrain changes in the volume/density of the active material.

Another ameliorating effect is high paste density. This parameter is, in essence, the starting point from which expansion takes place. Clearly, a plate produced from high-density paste will be able to undergo more expansion before reaching the critical value that causes severe capacity loss. Conversely, it is well-known that plates produced from very-low-density pastes perform poorly under cycling regimes. Such plates begin life very close to the critical density and reach the limiting density quickly.

A final point for discussion is the so-called 'softening' of positive-plate material. This is regarded as the step that precedes shedding of porous material. Accordingly, it is generally viewed as being synonymous with degradation and loss of function of the material. A variety of means for determining the degree of softening have been proposed. Each is based on subjecting the positive plate to a disruptive force (e.g., a jet of water, ultrasonic waves, etc.) and measuring the amount of material that is dislodged from the plate. The data presented here, though, cast doubt on the significance of this concept. For example, Takahashi et al. [5] recorded a measure of 'cohesion' of the positive mass, using a disruptive technique, and showed that changes in this parameter were virtually complete within 50 to 100 cycles, for plates held under high and low compression. Yet, both types of plate survived several hundred cycles. In addition, Alzieu and Robert [7] were able to extend the cycle life of their positive plates by ~1000 cycles, through physically preventing material from shedding off the plate. By definition, a considerable portion of the porous material in a positive plate affected by PCL is not electrically connected to the current collector. On the basis of experimental data, however, it cannot be concluded that this un-dischargeable material has 'softened' and can be removed easily from the plate. On the contrary, strategies that retain friable/softened/loose material within the porous mass have been demonstrably effective in extending cycle life. Preliminary results in our laboratories strengthen this conclusion.

7. Concluding remarks

Until now, it would appear that the importance of restricting the expansion of the porous mass of the

lead/acid positive plate has not been fully appreciated. We have presented strong evidence, from both published reports and the initial results of our own studies, that capacity loss becomes rapid once the apparent density of the porous material falls below a critical value. Therefore, in order to obtain improved cycling performance, we suggest that the design of positive plates should place a greater emphasis on methods for maintaining dimensional stability throughout service.

For pasted (Fauré) plates, it is suggested that the most effective improvement is to increase the strength of the grid frames. This would restrict expansion in the plane of the plate. Application of pressure at right angles to the plate plane (as normally provided by packing of the plate group in the container) ensures that the plate is restrained in all three dimensions. It is, however, unclear at this stage whether the amount of compression afforded by the separator-glass-mat combinations in current usage is sufficient to restrain expansion in a given situation. Clearly, the strength and elasticity of the separator are key factors. In some designs, it may be desirable to also include some form of 'compression plate' in order to optimize the force exerted on the plate group. This raises the prospective benefit of some form of active compression that maintains a pre-set value throughout cycle life.

For tubular plates, present designs appear to be close to optimum. As indicated above, though, attention may have to be paid to the long-term durability of the gauntlet material, as well as to the secure fitting of the end-plugs.

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