Failure modes of valve-regulated lead/acid batteries in different applications

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Abstract

Failure modes of valve-regulated lead/acid batteries are discussed and methods are suggested to overcome the problems. Many of the failures are associated with the positive plate, i.e., grid corrosion, and softening or sulfation of the active mass. Other failures include drying out, thermal runaway, and corrosion at the negative grid/top-bar connection. This work does not give a complete list of all failures that can occur, but it shows a summary of experiences gained from the practical use of valve-regulated batteries in different applications.

Keywords: Failure modes; Valve-regulated lead/acid batteries

1. Introduction

Lead/acid batteries have been used for a long time in many different applications of the technical world. Over the decades the performance of this energy-storage system has been raised steadily so that, in spite of extensive work on many alternative electrochemical storage systems, the lead/acid battery remains the world's most important secondary power-source. Although there have been many changes and improvements to nearly all parts of the battery, the basic electrochemical system consisting of lead, lead dioxide and sulfuric acid is still the same as that used in the first design more than 130 years ago.

Among the many improvements (for example, increase in energy density, extension of cycle life, reduction of self-discharge, automation of processing and assembling which reduces greatly the production costs), the introduction of lead/acid batteries of the gas-recombination type (called, nowadays, valve-regulated batteries) is probably one of the most important advances in the battery technology. The development of valve-regulated batteries makes it possible to use lead/acid batteries for new applications where a standard battery with flooded cells cannot be used because a 'clean' battery without any risk of acid spillage is needed.

There are further advantages with recombination batteries. For example, topping up with water is not necessary over the whole life of the battery, and the batteries can be designed to survive a 30 day short-circuit test so that, after recharge, the battery has the same capacity as before the test. Due to the marked reduction in water decomposition, there is only a very small release of hydrogen gas and a very low rate of self-discharge. Many studies on valve-regulated batteries have been published in recent years; some examples are given as Refs. [1–10].

Growing markets for valve-regulated lead/acid batteries include uninterruptible power supplies, telecommunication systems, consumer batteries, solar power applications, electric vehicles and many others. There is also a probability that recombination batteries will eventually replace flooded-electrolyte designs of automotive batteries.

In spite of all this enthusiasm over the advantages of valve-regulated batteries, it should be kept in mind that some important problems have to be overcome in order to avoid difficulties when this technology is used in the field. An important feature is that the batteries require a manufacturing process that has to be more precisely controlled than that employed for flooded batteries. Although this fact is well known by battery experts, it is sometimes not so easy to convince the people involved in the production process of the need to introduce more precise manufacturing. Baudo [11] has made the pertinent statement that valve-regulated

batteries do not forgive mistakes that are made during processing. Moreover, mistakes that are without, or of only minor, importance for flooded cells can have tremendous consequences for valve-regulated batteries.

In general, more precise processing means, at least in the beginning, a higher production cost. Given the possibilities of automation of the processes, however, this might be not so critical as would appear at first sight. Moreover, precise processing helps to increase reliability and to decrease the probability that there will be failure of the battery during the expected lifetime, and that there will be less rejections. Thus, the total costs need not necessarily be higher than today.

Another point is that in addition to failures due to processing, many failures are caused by the incorrect use, or abuse, of the battery. This is often due to some misunderstanding about the meaning of the term 'maintenance free' that is frequently used for valve-regulated batteries. Some customers might themselves conclude (or might have been so persuaded during the purchase) that after buying such a battery it can then be forgotten. This attitude ignores the fact that even during stand-by application some heat is produced by the battery, and that after discharge the battery must be recharged with a specific charging regime.

The term 'sealed battery' is sometimes also used. Again, this can give rise to some misunderstanding. The name ignores the fact that there is always some hydrogen produced at the negative electrode (although, usually, at a very low rate). This hydrogen leaves the battery either through the container walls or during open periods of the pressure-release valve, which opens for a short time when the pressure inside the battery becomes too high. Brief opening periods of the pressure-release valve take place especially with new gelled-electrolyte batteries or, in general, when a severe charging regime is used with high voltage. At the end of charging, the latter involves a current that can exceed the recombination capability of the cell. Today, therefore, the name 'valve regulated' is used for this type of battery in order to avoid any misunderstanding by the customer.

In this paper, failure modes of valve-regulated batteries are discussed with respect to two main causes; these are design/processing and incorrect use/abuse by the customer. The survey includes virtually all types of valve-regulated lead/acid batteries of both the gel and absorptive glass-mat (AGM) designs. Both technologies have many similarities, but there are also some differences. For example, it is well known that for tall cells only gel can be used, otherwise acid stratification cannot be avoided. For short cells, however, both gel and AGM designs can be used. In practice, it has turned out that in shorter cells, the use of glass-mats gives no risk of acid stratification provided that all the parameters that help to avoid acid stratification are

favoured. Recently, another version of valve-regulated battery called 'granular silica', has been claimed to be better than either gel or AGM [12,13], but there is insufficient evidence at the present to decide whether the use of this new design gives better batteries than either gel or AGM counterparts.

2. Positive-grid corrosion

In general, lead alloys that are virtually free from antimony are used in valve-regulated lead/acid batteries. This is because antimony is released from the positive grid by corrosion and migrates to the negative plate where it lowers the hydrogen overvoltage. As a result, there is an increase in hydrogen evolution and, consequently, higher self-discharge and more water loss.

Nowadays, most battery manufacturers prefer to use lead–calcium alloys for valve-regulated batteries. Calcium acts as a grid-hardening agent. Very often, there is also some tin in the alloy. This improves the casting process and helps to avoid problems at the grid/active-material interface of the positive plate. Therefore, it is better to consider lead–calcium–tin alloy as the most usual alloy for valve-regulated batteries. Some manufacturers also prefer to have some aluminium in the alloy in order to avoid excessive calcium loss from the pot during casting. Recently, it has been reported [14] that a small portion of aluminium also serves to improve casting. It must be emphasized that it is not absolutely necessary to use calcium for grid hardening; there are other alloys that can be employed without any risk of hydrogen overvoltage reduction. Nevertheless, lead–calcium–tin alloy is presently the most common choice.

There is a substantial difference between the corrosion behaviour of lead–calcium–tin and lead–antimony alloys. Tests reveal that antimony generally exhibits a higher corrosion rate, and that the rate decreases with decreasing antimony content. This type of corrosion, which is typical for antimony alloys, is an intragranular corrosion with a quite regular corrosion front over the whole area. In the case of lead–calcium–tin alloys, well-cast samples undergo small corrosion rates, but if the grids are not properly cast there can be a heavy intergranular corrosion. This type of corrosion is not uniform, but penetrates deeply into some parts of the grids. This causes a tremendous growth of the grid which, sometimes, is so heavy that it produces a bending of the lid. In the case of grid growth, it is not the total oxidation of the grid lead to lead dioxide that limits the life of the battery. More often, failure results when the grown grid comes into contact with the negative top-bar to create an internal short-circuit.

During standby duty with very few discharges, another consequence of grid growth can be that the active

material is not able to follow the grown grid and, therefore, contact between grid and material is lost. Fig. 1 shows a positive plate of a battery that has been used in floating service and has developed a grown lead–calcium–tin grid. Due to a poor grid casting, the battery failed after 3 years. During cycling, the active material can maintain contact with the grid so that the whole positive plate, including the active material, grows and again an internal short-circuit between the positive grid and the negative top-bar can limit the life of the battery.

There are many variables influencing grid corrosion. The most important are: (i) alloy composition; (ii) grid design; (iii) casting conditions: (iv) positive active material; (v) impurities that accelerate corrosion; (vi) battery temperature; (vii) potential of the positive plate.

2.1. Alloy composition

Many investigations have been made [15–22] on the influence of alloy composition on the corrosion stability of positive grids in valve-regulated lead/acid batteries. In practice, it has been found that a lowering of the calcium content reduces the corrosion rate. Unfortunately, since a lower calcium content gives slower grid hardening, a compromise is often necessary. A calcium content is used that is sufficiently high to allow handling of the grids during plate processing, but sufficiently low to avoid severe corrosion. In general, this means a rather small acceptable range of calcium content in the pot. Of course, the influences of the other variables mentioned above have also to be taken into consid-

Fig. 1. Positive plate with a grown lead–calcium–tin grid of poor cast quality after 3 years use in floating experiments.

eration. It has turned out that a relatively high calcium content (up to about 0.1 wt.%) can be tolerated if all other conditions are favourable. Conversely, other unfavourable variables (items (ii) to (vii) above) can cause high corrosion rates even with a much lower calcium content. It is a general rule, which has been confirmed by many experiments, that a rather small calcium content helps to keep both corrosion rate and grid growth at low levels.

2.2. Grid design

The influence of grid design on the casting process and on the corrosion behaviour is often underestimated. Particularly for applications where high discharge currents are needed, there is the tendency to improve grid structure to reduce the electric resistance of the grid. This can be calculated quite readily (and with high accuracy) by using computers with the result that it is indeed possible to produce grid structures with markedly lower electric resistance. Unfortunately, it is not so easy to cast well grids that have a minimal electric resistance and this can result in higher corrosion rates. Therefore, changes in the grid structure have to be performed carefully by considering possible casting and corrosion problems.

2.3. Casting conditions

The casting process involves many variables that influence the quality of the cast grid and, therefore, the corrosion behaviour. These variables are, for example, the grid/mould design, the temperature of the pot and the mould, the speed of casting, and the pressure in the case of pressure casting. In general, pressure casting is used for tubular plates and, given that all other variables are not too unfavourable, this produces lead–calcium–tin grids with very low corrosion rates, so that, even after several years in use, there is only a very thin corrosion layer around the spines. Therefore, corrosion of lead–calcium–tin tubular grids has very seldom been the cause of the failure of valve-regulated batteries.

Gravity casting is usually employed for flat positive plates. Flat positive lead–calcium–tin grids are more sensitive and more prone to corrosion. Nevertheless, it has to be pointed out that even for batteries with flat positive plates, corrosion has not often been the limiting factor during cycling. Degradation of the positive material is more critical. In the case of standby applications, drying out could be at least of similar importance to grid corrosion.

An example of the influence of alloy composition and casting conditions on grid corrosion is given in Fig. 2. During this accelerated corrosion test of gravity cast lead–calcium–tin grids in sulfuric acid (60 °C, 1.26
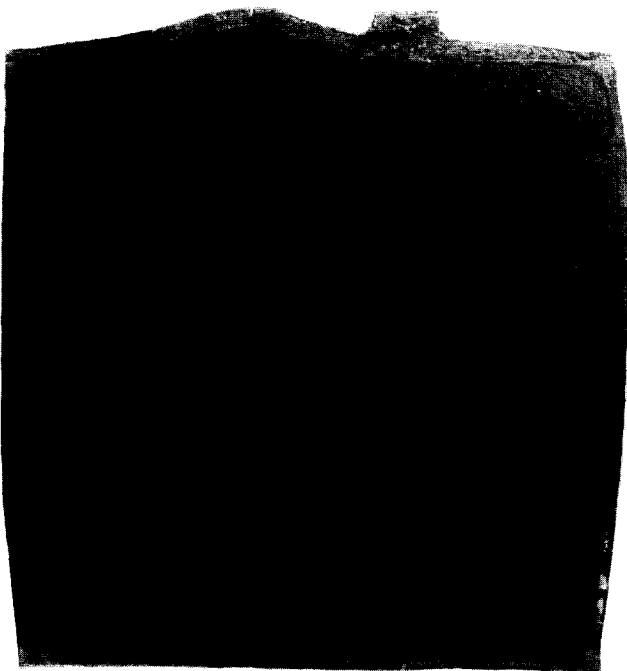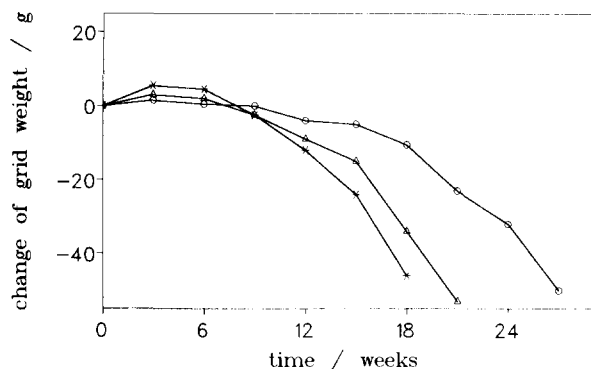
Fig. 2. Accelerated corrosion test of gravity-cast, lead–calcium–tin grids in sulfuric acid (60 °C, 1.26 sp. gr., constant potential 1.85 V against SHE). Change of grid weight measured every 3 weeks without removal of corrosion layer: (*) standard alloy / standard casting; (△) improved alloy / standard casting; (○) improved alloy / improved casting.

sp. gr., constant potential of 1.85 V against SHE) the grids were taken out of the electrolyte every 3 weeks. They were then washed and dried without removal of the corrosion layer and their weight was determined. In all experiments, there was a small increase in weight during the first weeks due to the oxidation of some grid material. The decrease of weight in the second stage of the test can be explained by the shedding of some oxidized material during the progressive oxidation. Normally, a good corrosion stability gives only a small increase of weight in the beginning and shedding starts quite late, whereas a poor corrosion stability gives a higher increase of weight in the beginning followed by a more rapid decrease of weight due to shedding. It can be seen from Fig. 2 that an improvement of the alloy with respect to the calcium, aluminium and tin contents gives a slightly better corrosion stability, but the influence of casting conditions is more distinct.

2.4. Positive active mass

It is not easy to understand completely the influence of the positive active mass on grid corrosion, although some papers have been published about this subject [23–25]. In fact there must be an influence, because results of corrosion tests are different when grids are used with or without active mass. The influence of the mass may be due to an increase in the pH near the grid surface at the end of discharge or, in general, to different acid densities during cycling. This is because there is a limited diffusion capability of the electrolyte in the pores of the mass. Another point is the stress on the grid due to volume changes of the mass during charge and discharge. It also has to be considered that some parts of the grids are in very close contact with the mass, so that no electrolyte can reach these parts. The active mass can accelerate or slow down grid corrosion, but in any case it must not be ignored. Thus,

the results of corrosion tests with well-prepared lead samples in the laboratory can be quite different to the results obtained in batteries.

2.5. Corrosion-accelerating impurities

Impurities that accelerate the grid corrosion rate (e.g., organic acids or chlorine compounds) are well known and there is, in general, no difference between the behaviour witnessed in flooded cells and in valve-regulated cells. Normally, impurities can be excluded rather easily. By comparison with flooded cells, valve-regulated batteries have the advantage that topping up of water is not required and, therefore, impurities cannot be introduced into the cells during use. Of course, manufacturers have to be careful to avoid any marked contamination with impurities during battery fabrication. This is not only important because of accelerated corrosion of grids, but also because there is a marked influence of some impurities on both self-discharge and hydrogen evolution.

2.6. Battery temperature

The features discussed so far are, in general, the responsibility of the battery manufacturer. Beyond these, incorrect use or abuse of valve-regulated batteries is also an important determinant of grid corrosion. The most pertinent factors are temperature and charging voltage or, more correctly, the potential of the positive plate. The influence of temperature is often described by the general rule that a higher temperature gives a higher corrosion rate. This is also valid for valve-regulated lead/acid batteries. During standby service, the expected lifetime is often given at 20 °C, which implies that there is a recommendation to keep the battery around this temperature in order to obtain maximum endurance. It is self-evident but, nevertheless, it should be mentioned here, that the battery temperature and not the temperature of the environment is the relevant factor. If a higher battery temperature cannot be avoided, then at least adjusting the charging voltage according to the instructions of the battery manufacturer is necessary in order to avoid a serious reduction in service life. Regulation of charging voltage can be also necessary if the battery temperature is appreciably below 20 °C.

A typical malpractice is to place batteries as close together as possible in order to save space. As batteries produce some heat, even during floating, tight packing of batteries can produce a situation whereby the heat emission (a combination of heat radiation and heat transport by air convection around the battery) is smaller than the heat produced so that the battery temperature increases. Ignoring the heat produced by batteries can give a marked reduction in service life due to accelerated

grid corrosion, even if the temperature does not reach a level such that drying out or thermal runaway takes place. Although this is valid for flooded cells too, the situation described here can be more dangerous for valve-regulated batteries because, during floating, virtually the whole electric energy is used for the recombination process and is completely transformed into heat.

2.7 Positive-plate potential

The influence of charging voltage on the corrosion behaviour of positive grids has been reported widely. A discussion about the special situation in valve-regulated batteries can be found in Refs. [9,26–28]. The minimal corrosion rate does not depend on the charging voltage alone but also on the recombination efficiency. The latter influences the charging current and, therefore, the potential of the positive plate, which is the determining factor for corrosion. Fig. 3 shows the polarization of the positive electrode at different cell voltages for flooded, gel and AGM cells. For a flooded cell, the assumption is made that the overvoltage of the positive and the negative plate is nearly the same. In the case of gel and AGM cells, one example is given of a high and one of a low recombination efficiency. It must be emphasized that this is only a schematic representation of the behaviour. In reality, the situation can be more complicated [9].

Adapting the charging voltage to acid density, and vice versa, is very important [28]. In the case of traction applications, the charging voltage is not so critical for grid corrosion as traction batteries usually suffer from other failure modes. By contrast, the effect of the charging voltage on positive-grid corrosion is very important in standby applications. The situation becomes quite different if the positive active material is also taken into consideration. In order to keep the positive active material in good condition the charging voltage,
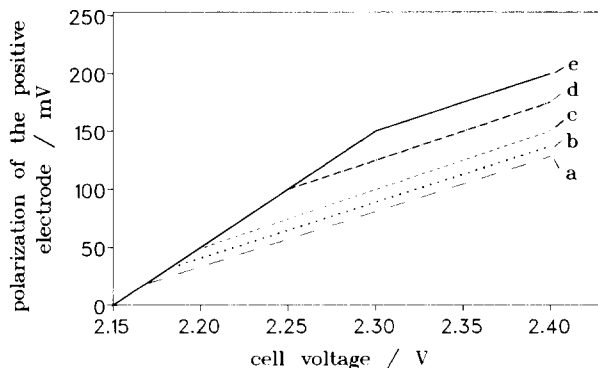

Fig. 3. Schematic of positive electrode polarization of flooded, gel and AGM cells (assumed acid density: 1.30). (a) flooded cell, (b) gel, new cell; (c) AGM, low recombination efficiency; (d) gel, after prolonged periods of use, (e) AGM, high recombination efficiency.

or more specifically the charging regime, is also very important in traction duties. This is discussed in the following section.

3. Runaway effect/drying out

Drying out is mostly connected with a too severe charging regime, often in combination with high cell temperature. The best way to overcome this problem is to prevent very extreme situations in battery operation. This means, for example, the avoidance of high-rate charging, especially after deep discharge and at high battery temperatures. In the case of high temperatures, the use of special cooling systems might even be required, especially when the battery is used for heavy traction applications. In general, drying out reduces the capacity of the cell and finally limits the lifetime. Drying out also increases the recombination efficiency and this can be a severe problem in UPS applications where an excessive recombination efficiency can increase dramatically the temperature of the batteries. This could lead to the so-called thermal runaway effect that can be exhibited by valve-regulated lead/acid batteries in UPS service. The best way to avoid drying out and runaway is to remember that during floating the battery produces some heat. An important point is that it is not advisable to pack the batteries closely together. It is much better to have a distance between each battery of at least 10–20 mm. Keeping the batteries at such a distance normally allows an effective dissipation of the heat.

As discussed in more detail below, a high charging voltage is helpful for reducing the charging time and for avoiding sulfation. Nevertheless, it must be remembered that under this condition a higher current flows through the cell, which promotes the risk of runaway/drying out. Therefore, a higher charging voltage is only allowed for a restricted period after discharge. A charger which automatically reduces the charging voltage after a given time would be an appropriate way to overcome this problem.

The best way to avoid the runaway effect is to monitor the battery temperature and to change the charging voltage or charging current automatically, according to the measured temperature. It is strongly recommended to use the measured battery temperature and not the room temperature for controlling the charging voltage or the charging current. In the case of AGM batteries, it is also important to have a good control of the degree of saturation of the separator during processing, as it is well known that a too low level of saturation will give a very high recombination efficiency and will result in high currents, even at quite moderate charging voltages. The fact that, with the same floating voltage, quite dissimilar currents can flow through the cell as

determined by the recombination efficiency has been discussed previously [9]. The situation in a gel battery is different in the beginning because of a rather low recombination efficiency. After some water loss, however, the recombination efficiency will increase. If too much water is lost (drying out), the recombination efficiency can be at the same high level as that exhibited by AGM cells which have insufficient saturation.

Gel batteries with tall plates and heavy cycling usually require a special charging regime to avoid sulfation, especially in the lower parts of the positive plates. This charging regime has to be chosen carefully, so that there is not too much water loss and drying out. A pressure-release valve with a high opening pressure could be helpful in reducing water loss but the effect is not sufficient to justify other problems that must be faced with high pressures in the cell. In general a pressure between 100 and 200 mbar seems to be a good compromise to avoid excessive loss of water.

4. Barrier layer

Some decades ago, when lead/acid batteries with positive lead–calcium grids without antimony had first been placed on the market, there was a major disaster in terms of a very poor cycle life. Investigation of the phenomenon revealed that the cause of the failure was the formation of a barrier layer of lead sulfate between the positive grid and the active material. Since this occurred more easily when antimony was excluded from the battery, it was called the 'antimony-free effect'. Following those unfortunate experiences with the early lead–calcium batteries, the antimony-free effect and the influence of grid alloy composition on the behaviour of the positive plate during charging and discharging has been the subject of many investigations and much research activity [29–34]. An important result of these studies was the discovery that a lack of antimony has not only an effect on the grid/positive-material interface, but also on the whole crystalline structure of the positive active mass [32] and on the so-called mass 'softening' process. Nowadays effects that are promoted by using grids without antimony are collectively termed 'premature capacity loss' (PCL) [33]. At present, there are many research efforts worldwide to overcome the PCL problem.

In electric vehicle service, high pulses of discharge-current are required and these place an extreme load on the battery. Accordingly, the phenomenon of softening of the positive material has often limited the lifetime of traction batteries. At present it appears that softening of the positive material is a more severe problem than the development of barrier layers. As result of many research activities in the past (e.g., improvement of the curing process, the paste formu-

lation and the alloy composition, especially the tin content and the use of additives), it seems that barrier layers no longer have a marked effect on the life of valve-regulated lead/acid batteries, even when the batteries are used in heavy cycling applications. This is contrary to the generally held belief that lead/acid batteries without antimony fail principally through the formation of lead sulfate barrier layers at the positive grid/mass interface.

5. Positive-mass softening and sulfation

These failures are mainly a problem of the cycling application. In general, it is possible to determine clearly whether the failure mode is softening or sulfation. Although the acid density cannot be measured directly in valve-regulated batteries, the open-circuit voltage (OCV) is a useful measure for any decrease in the acid density due to sulfation. It is important to realize that the OCV after the end of charge is much higher than after a longer rest period. Even after a rest of 24 h, the OCV does not report exactly the acid density in the cell because of the rather slow diffusion of sulfuric acid in the glass-mat or in the gel. Nevertheless, given this slow electrolyte exchange in valve-regulated batteries, the OCV, even if it is measured at a relatively short time after the end of charge, yields sufficient information to estimate, at least roughly, the actual acid density.

5.1. Softening

Softening of the positive material can easily be distinguished from sulfation as such failure does not produce any reduction of acid density in the cell. This is because the soft mass consists predominantly of lead dioxide and the content of lead sulfate is generally quite low. Softening of the mass means that PbO_2 particles lose contact with each other, so that parts of the active mass become electrically isolated and cannot participate any longer in the discharge process. Therefore, batteries with softening of the positive mass have the nominal OCV but a lower available capacity.

Fig. 4 shows the results of a cycle test on an initial string of 10 batteries (Drysafe Multicraft; 12 V, 60 Ah) that were subjected to a high discharge current (50 A). This duty promotes softening of the positive mass. After every 50 or 100 cycles, a capacity test was performed and one battery was removed for analysis. To distinguish between soft material and hard material, water was poured onto the plates so that all the soft material was washed away. The quantity of soft material at different numbers of cycles is given in Fig. 5. Softening always starts from the outer part of the plate with subsequent progress into the inner parts with an in-
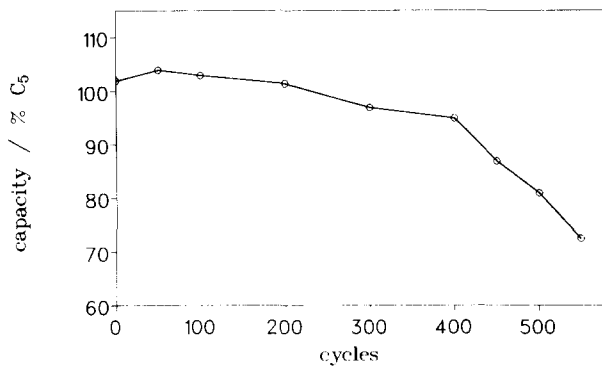
Fig. 4. Cycle test with Drysafe Multicraft batteries (12 V, 60 Ah at C/5 rate). Discharge: 50 A down to 9.40 V; charge: IU, 15 h, $I=2\times I_5$, $U=14.40$ V; 30 °C; C/5 test every 50 or 100 cycles.
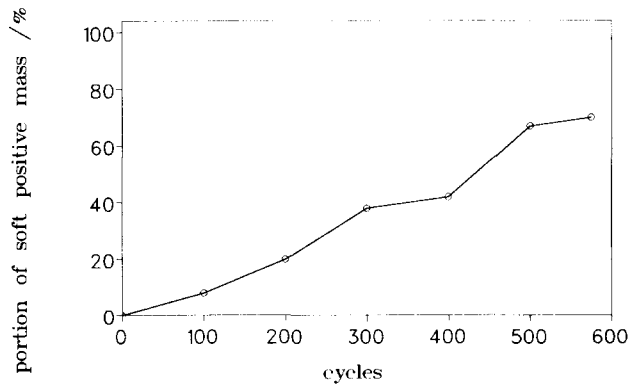

Fig. 5. Amount of soft positive mass during cycling according to conditions given in Fig. 4.
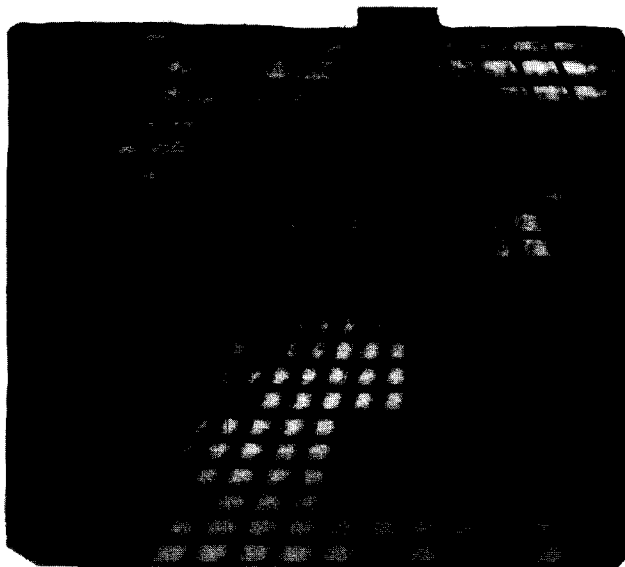

Fig. 6. Positive plate after 500 cycles (according to conditions given in Fig. 4) and removal of the soft material.

creasing number of cycles. After 100 cycles, there was only a thin layer of soft material on both sides of the positive plate. After 200 cycles, this layer had become thicker and after 500 cycles more than 70% of the positive active material was soft. Fig. 6 shows a plate

after 500 cycles and after washing away all the soft material with water. It can be seen that appreciable quantities of material were removed from different parts of the plate.

A comparison between the capacity results and the amount of soft material shows that the marked decrease in capacity during the latter stages of cycling is directly associated with increasing amounts of softened material. No significant quantities of lead sulfate were found in all the plates investigated. Thus, softening alone was the cause of the observed decrease in capacity. The grid/positive-material interface was also investigated in order to discover whether there was any form of barrier layer between the grid and the active mass. It turned out, however, that the interface grid/mass was in a very good condition.

The cause of softening of the positive mass (which means a loss of contact between the lead dioxide particles) has been the subject of many investigation during the last few years. In some papers, the so-called 'Kugelhaufen' theory has been formulated to provide an explanation for the degradation of the positive mass [32,35–38]. This theory uses a model in which the positive active mass is considered to be a network of agglomerates of sphere-like particles with narrow contact zones. It would appear that this is a good approach towards describing the changes in the crystalline structure of the positive active mass that take place during charge and discharge. For a complete understanding of the softening phenomenon, there might be the problem that, in reality, the active mass consists not only of sphere-like particles with smooth surfaces, but there is also a marked microstructure on the surface of the particles. A second theory considers [34,39,40] the active mass to be a mixture of crystalline parts and gel parts. It is assumed that there is a significant portion of hydrogen in the mass of the gel zones and that changes in these gel zones during cycling could be the cause of the loss in contact between the particles of lead dioxide. The influence of hydrated zones and of so called X-ray 'amorphous' material on the behaviour of the positive active mass during cycling had been discussed in earlier papers [41–45].

Although both theories allow a better understanding of the degradation of the positive active mass during cycling, even today it is not completely clear which parameters are the most important in avoiding softening, or at least in slowing down the softening process. Some battery types exhibit very early softening of the positive mass, in other types the progress of softening is very slow. Clearly, a target area for future research will be to understand exactly why some batteries are so good in cycling with slow softening of the positive mass while others are not. Although it is often found that softening is promoted by high discharge rates, the effect sometimes happens even when rather small discharge currents are
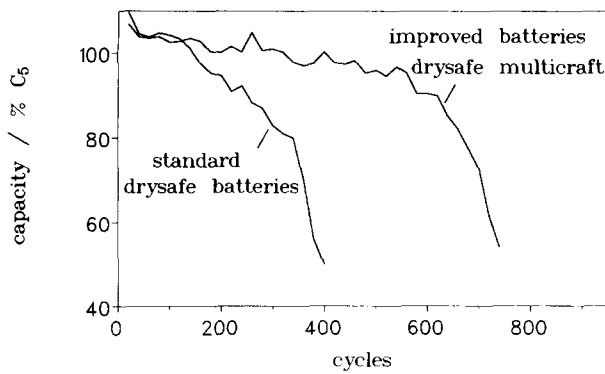
Fig. 7. Cycle test with Drysafe Multicraft batteries (12 V, 38 Ah at $C/5$ rate). Discharge: 42 A down to 9.50 V; charge: IU, 15 h, $I=2\times I_5$, $U=14.40$ V; 25 °C; $C/5$ test every 25 cycles.

used. In general, however, it is true that high discharge pulses accelerate the softening process.

It seems that there are several parameters that strongly influence the speed of softening. These parameters include the design of the battery, the type of application, and the charging regime. Some studies on the influence of charge have recently been published [36,37]. The influence of battery design is a very important point. It has been shown that by using the same charge and discharge regime, batteries with rather small differences in design can fail by softening after a relatively small number of cycles while others are in good condition even after 700 cycles (Fig. 7). In the latter, the life was terminated by grid corrosion. In addition to the design of the battery, rather small deviations in processing can exert a marked influence on softening. This again emphasizes that good process control is absolutely necessary to make sure that all batteries will have a long cycle life. In any case, the results in Fig. 7 for Drysafe Multicraft batteries (12 V, 38 Ah) in a standard and an improved version demonstrate clearly that there is no principal reason why valve-regulated lead/acid batteries cannot be used for deep-discharge cycling. The observed performance of 700 cycles (100% DOD) for batteries with a reasonably high energy density (32 Wh kg^{-1} at $C/5$ rate), with flat positive plates and with lead–calcium grids without antimony is much more than many people would have expected in the past.

5.2. Sulfation

Sulfation of the positive mass is often caused by a charging regime that does not match well the application of the battery. It is particularly a problem with batteries used for heavy cycling (i.e., for batteries discharged to 80% or even more during every cycle), and where customers expect a rather short charging time without having the facilities to start with a high initial charging current [9]. In this case, there is often only a small

range between overcharging, which results in water loss and eventually drying out, and undercharging that produces sulfation of the positive mass. Fig. 8 shows the results of a cycle test for batteries that have been charged with three different charging regimes. It can be seen that the use of a higher charging voltage has been helpful in keeping the batteries in a good condition for a long time. The water loss was always very small even with a charging voltage of 14.4 V.

There are some battery applications that require a duty that is intermediate between standby service, with only a few discharges during the whole life of the battery, and heavy cycling with an extensive discharge every day. Between these extremes, there are for example solar power applications, load levelling duties, or standby operations with rather frequent discharges. With such applications, there is often the problem that a high charging voltage promotes grid corrosion and drying out, whereas a low charging voltage can encourage sulfation. It is therefore often a good compromise to use a charger that automatically switches the charging voltage to a lower value after the battery has been charged for a given time period at the higher level. For example, the charging voltage can be changed from 2.4 to 2.3 V/cell after 12 h of charging. The charging time and different initial charging currents to return a Drysafe Compact Plus battery to 100% of the discharged capacity are given in Fig. 9. The Drysafe Compact Plus is a recently developed AGM battery that will be used mainly for standby applications. It combines high energy density, high power density and good charge acceptance with an exceptionally long lifetime of about 10 years. Due to its good charge acceptance, the battery can be charged quite fast if there are available proper chargers that can change automatically the charging voltage.

Sometimes valve-regulated batteries with tall plates, which are virtually always gel cells due to their better behaviour against acid stratification, suffer from sulfation in the lower parts of the positive plate. This
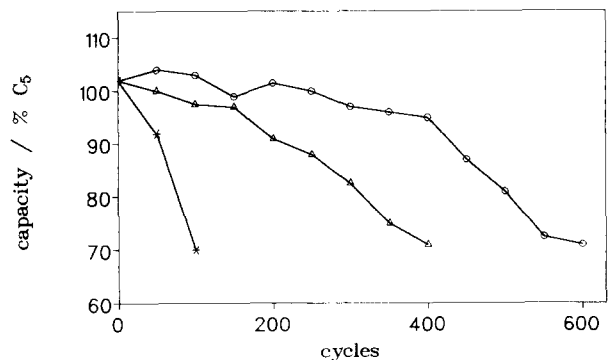

Fig. 8. Influence of charging voltage on cycle life of Drysafe Multicraft batteries (12 V, 25 Ah at $C/5$ rate). 25 °C; $C/5$ test every 50 cycles; discharge: 5 A down to 10.20 V; charge: IU, 15 h, $I=2\times I_5$, $U=$(*) 13.80 V, (△) 14.10 V, (○) 14.40 V.
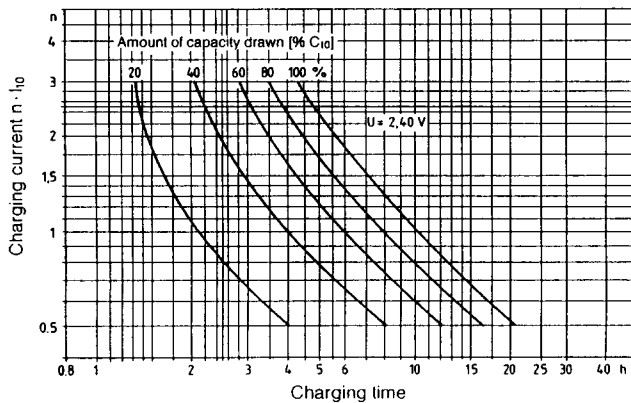
Fig. 9. Charging time and initial charging currents to return a Drysafe Compact Plus battery to 100% of discharged capacity after different depths of discharge.

results in a decrease of capacity during cycling. Again the use of a proper charging regime is helpful in avoiding this effect. In some applications, however, and in heavy duty with deep-discharge cycles, there is always a delicate balance between a too drastic charging regime that will cause drying out and a too moderate charging regime that will result in sulfation. To overcome this problem, and to make the 'knife edge' broader, there has been considerable efforts to improve cell design so that complete recharge of the positive plates becomes possible and, therefore, no accumulation of lead sulfate occurs at the bottom of the plates.

6. Failures of negative plates

In comparison with the situation at the positive plate, failures seldom occur with the negative plates. This applies to both cycling and standby duties. In most cycle tests, the lifetime of the battery has been limited by the positive plate. The negative plate is virtually always in a good condition, even after more than 1000 cycles [9]. When there were failures of the negative plate, these problems were due mainly to the fact that the pressure-release valve was not in a good condition. In these cases, the valve did not close correctly after opening so that oxygen entered the cell and oxidation of the negative mass gave sulfation of the negative plate during storage of the battery. To avoid this problem, the pressure-release valve has to be controlled carefully before it is fitted to the battery. This is also important with regard to the risk of drying out during battery use.

A corrosive attack at the lug/top-bar area is another problem that causes failure of the negative plates of valve-regulated lead/acid batteries, especially if alloys with antimony are used for the top lead. This phenomenon has been discussed in several papers [10,46–48]. It is a type of corrosion that is similar to the so-called 'crevice corrosion' at the positive post of

lead/acid batteries when there is a relatively tight covering around the metallic lead that leaves a crevice into which the sulfuric acid can penetrate. Under these conditions, there is only a thin electrolyte film on the lead, and when an electrochemical reaction takes place in this region an ionic current flows along the thin film and causes voltage drops that shift the potential to a range where corrosion is accelerated. The corrosion at the lug/top-bar area can be so heavy that the connection is completely destroyed and there is no longer a contact between the plate and the top-bar. In order to avoid this latent danger, impurities in the top-bar that promote electrochemical reaction and enhance the ionic current along the thin film have to be excluded. Antimony is particularly deleterious in the top-bar and, therefore, it is advisable to avoid the use of this element in this critical area.

There is another important feature, namely, the use of a proper technique for welding or cast-on-strap (COS). It is well known that the welding of lead–calcium alloys is not an easy subject and, therefore, special techniques have to be used to get a good bonding between the lug and the top-bar. If COS is used, good cleaning of the surface of the lug (i.e., a proper fluxing process) is necessary to achieve a good bonding. Of course this is valid for both positive and negative plate groups, since a poor connection also gives problems in the positive lug/top-bar sections. Therefore, the use of an appropriate alloy for the top-bar, together with a good top-bar/plate-group bonding, reduces markedly the risk of any corrosion in this part of the battery.

7. Short-circuits

A short-circuit inside the battery virtually always results in a failure. Avoidance of this is the responsibility of the battery manufacturer. Formerly, there were sometimes short-circuits through the separator from the growth of lead needles, especially if the battery had been deep-discharged. Nowadays, this is no longer a severe problem, for with the addition of special ingredients to the electrolyte (in general, sulfate salts), the problem of growing lead needles can be overcome completely and there is no longer any risk of a short-circuit through the separator.

In order to increase the volume energy density, plate dimensions have been increasingly extended. Often, the plates are standing directly on the bottom of the case, because a mud space is no longer needed in valve-regulated batteries. If glass-mats are used as single sheets, there is always a latent danger of short-circuits at the bottom of the cell. Enveloping of at least one of the two polarities of the plate (either the positives or the negatives) by glass-mats is a good way to overcome this problem. The use of enveloped plates has reduced failures by short-circuits at the bottom of the cell virtually

to zero. In order to increase the energy density even more, extreme values have been taken for both the width and the height of the plates. This means that the dimensions of the glass-mats do not exceed by much those of the plates and, therefore, during assembly of the cell, the glass-mats have to be adjusted quite carefully between the plates in order to avoid any short-circuits at the sides or the tops of the plates.

8. Conclusions

Much experience has been gained with valve-regulated lead/acid batteries. Sometimes, this has been quite painful, especially in the beginning when valve-regulated batteries were first placed on the market. The causes of many of these rather bad experiences have been discussed in this paper. By learning from every mistake, valve-regulated batteries have been improved steadily and, in collaboration with customers, incorrect use or abuse of this battery type has been reduced markedly. In principal, there appears to be no reason why valve-regulated lead/acid batteries cannot replace flooded cells in nearly all applications. Even now, there are some types of valve-regulated batteries that have a better performance than equivalent flooded-electrolyte types. For example, this is true for the cycle life of flat positive plate batteries. The corrosion behaviour of positive lead–calcium grids can also be improved, provided that the correct alloys and casting conditions are used. In applications where positive-grid corrosion is the limiting factor, the low corrosion rate of properly cast lead–calcium grids can give a better lifetime in comparison with flooded cells with antimony alloy grids. Thus, it is indeed probable that the valve-regulated lead/acid battery will replace the traditional flooded type in many — if not all — applications.

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