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Operational experience with valve-regulated lead/acid batteries

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Abstract

Valve-regulated lead/acid (VRLA) batteries provide the very high levels of reliability required for standby service. Various types are available, in particular: cells with lead–calcium–tin alloy grids and absorptive glass-mat (AGM) separators; cells with pure lead grids and AGM separators; cells with tubular plates and gelled electrolyte. These cell types are subject to a number of factors that affect durability in float service. These factors are reviewed and it is shown that grid corrosion is the usual failure mode. As a result, practical cell and battery designs need to ensure all other potential causes of failure are either eliminated or occur at a slower rate. Test results based on thermal acceleration are presented and have been correlated with real-time tests. The attainment of satisfactory product life under practical conditions is fully demonstrated. Techniques for battery monitoring and surveillance also have a strong impact on reliability and can be used to define the best strategy for replacement. The overall result is better levels of protection which, together with precise specification and careful consideration of the service conditions, enable user requirements to be met in full.

Keywords: Rechargeable batteries; Valve-regulated batteries; Lead/acid batteries; Reliability

1. Introduction

Valve-regulated lead/acid (VRLA) batteries have established themselves as the pre-eminent type for all types of standby application. Nevertheless, there is a perception that they are subject to premature failure. Some of this criticism is based on claims for life that could not be substantiated and were found in some instances to be unfulfilled for earlier generations of product. In addition, premature failure modes that were unique to VRLA batteries became evident and are now well understood such that they have been eliminated by design from batteries made in recent years. The product has reached a stage of maturity such that it is meeting the full range of requirements that are specified, given correct selection and a clear recognition that there are various types of VRLA battery appropriate to different applications.

VRLA batteries may be conveniently grouped into four categories [1], namely, high integrity, high performance, general purpose, and standard commercial. These groupings differentiate products principally by the expected service design life, but also by electrical performance requirements and safety considerations. The specification of these types of batteries has been adopted by Eurobat as a guidance note, but has not been established as a standard.

Work has been in progress to develop an international standard for VRLA batteries. The International Electrochemical Commission (IEC) is developing a standard to be designated as Part 2 of IEC 896, where Part 1 defines requirements for vented stationary batteries. Concurrently, the European Committee for Electrochemical Standardisation (CENELEC) has taken the draft of IEC 896-2 as a potential European standard as EN 50105, but this was recently rejected through the voting procedure and there is no further work being performed. The need for properly recognized standards is self-evident and in the United Kingdom BS 6290: Part 4: 1987 [2] has served a useful purpose in defining requirements for VRLA batteries. This was developed several years ago at a time when the level of experience was less extensive than it is today. Methods of test and appropriate levels of compliance are defined for electrical performance, mechanical integrity and safety requirements. This standard has served as a benchmark for VRLA batteries for a number of years. There was nothing, however, in the standard that defined product life under different operating conditions. With this in mind, a revision to BS 6290: Part 4: 1987 to include methods of test for product life is now under devel-

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opment and, given acceptance, will represent a step forward in giving meaningful data to assess service life.

The favoured method of assessing life is an accelerated life test at 55 °C at a specified floating voltage. An Arrhenius relationship is used to extrapolate from the temperature to the service temperature, assuming a single process with a single activation energy is responsible for degradation across the full temperature range. This can only be assumed by measuring the same level of reduction in performance over a range of temperatures and verifying that the activation energy is unique. In practice, this involves large numbers of trials and a single temperature has been adopted that is neither too high to make extrapolation prone to error nor too low to make testing times unduly prolonged. Testing of this type may also be correlated with real time testing, and work in this area provides a useful further basis for verifying results from accelerated life tests.

In this paper, three types of VRLA batteries, all of which are fully capable of meeting the longest specified service life, will be described. The potential failure modes and how they may be overcome will be outlined. The results of accelerated life tests on these types of battery will be presented and strategies for monitoring and surveillance will be discussed. VRLA batteries are recognized as the principal source of standby power in many sectors and will continue to provide back-up supply in an ever-increasing range of applications.

2. Valve-regulated lead/acid battery types

There are three principal types of VRLA battery: cells using lead–calcium alloy grids and absorptive glass-mat (AGM) separators; cells using pure-lead grids and AGM separators; cells using tubular plates and gelled electrolytes (Fig. 1).

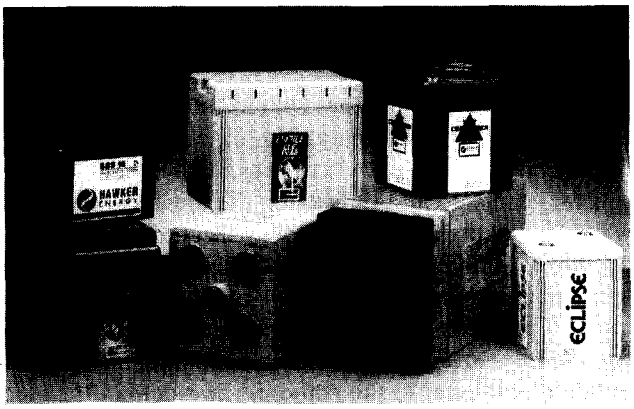

Fig. 1. VRLA batteries employing lead–calcium–tin alloy and pure-lead grids with absorptive glass-mat separators and tubular gel technologies.

2.1. Cells with lead–calcium alloy grids and absorptive glass-mat separators

VRLA batteries of this type use flat, pasted plates with grids cast in either lead–calcium or lead–calcium–tin alloys. Tin-containing alloys are favoured because they enhance castability and, hence, the metallurgical integrity of the grid. Tin also reduces the effects of passivation at the grid/active material interface. The overall effect is to increase life and this is achieved without detriment to recombination efficiency or reduction in the corrosion resistance of the positive plate. Plate thickness is important in the achievement of adequate life. Thicker plates increase life, but at the expense of high-rate performance and active-material efficiencies.

The AGM separators are essential to the correct operation of this type of VRLA battery and ensure that the oxygen transfer necessary takes place efficiently. The fibre mix and separator compression are important to avoid stratification effects. Acid volume and plate separation will determine capacity at both low and high rates.

Venting systems to allow for safe release of small quantities of gas in the forward direction, and to prevent ingress of air into the cell in the reverse direction, are used. High-integrity pillar seals are essential. Containers are generally moulded in flame-retardant, acrylonitrile-butadiene styrene (ABS). This has good mechanical strength, an adequate modulus to resist deflection under pressure and a high level of fracture toughness.

2.2. Cells with pure-lead grids and absorptive glass-mat separators

The need to reduce the hydrogen overpotential for the negative grid and to increase the corrosion resistance of the positive grid results in pure-lead being an ideal material for VRLA cells. Thinner plates can be used without reducing the service life on float and, in turn, these give better active-material utilization and high-rate performance. The addition of tin has beneficial effects for pure-lead grids in a similar way to lead–calcium alloy grids and provides better cycleability. The difficulty with pure lead is that it cannot be fabricated conventionally. Grid forms are punched into lead sheet in a continuous process which is then passed and made into plates for assembly. Beyond element assembly, battery construction is similar to cells using cast lead–tin–calcium grids.

2.3. Tubular cells with gelled electrolyte

Tubular VRLA cells with gelled electrolyte also use lead–calcium–tin alloys for both the positive spines and for the negative grids. The plates are manufactured in the same way as for flooded tubular cells. Microporous plastic separators are used and containers are moulded in flame-retardant ABS. A high integrity pillar seal is used with synthetic rubber grommets, specially lubricated and conforming to the lid and pillars. The pressure-relief valve operates through a Bunsen valve and incorporates a flame arrestor. The electrolyte is gelled with finely dispersed silica. The recombination reaction takes place by virtue of oxygen transfer from the positive to the negative plate in the gas phase through a network of microscopic fissures and passageways in the gelled electrolyte. The design of gelled electrolyte tubular cells is aimed at low-rate applications where the discharge rate is at least one hour. For higher-rate duties, cells with flat, pasted plates and AGM separators are specified.

3. Factors affecting durability in float service

In float service, the voltage is set to ensure full capacity is maintained and for efficient recharge after a discharge. Part of the current counters internal losses, part drives the recombination reaction, and part will corrode the positive grid. Pure-lead and lead alloys all corrode at low rates and failure will occur through grid corrosion at some stage. The design of the battery has to ensure that other time-, temperature- or voltage-induced failure modes will take place later than positive grid corrosion.

3.1. Negative group bar corrosion

Negative group bar corrosion (NGBC) has been a historic problem that has caused early failures for VRLA cells. For the majority of manufacturers, however, this problem was fully resolved some years ago. NGBC is unexpected in so far as the negative plate is normally protected against corrosion by virtue of its potential. It occurs uniquely in VRLA cells under the special conditions of gas composition and acid concentration that exist in the headspace of these cells, and with particular combinations of alloys and metallurgical processing. Localized corrosive attack occurs either at the group bar or at the plate lug adjacent to the group bar. This problem is now well understood, and by careful selection of the alloys for all components and control of metallurgical processing may be avoided. The use of cast-on-strap techniques has further improved the reliability of interconnections between plates.

3.2. Drying out

Drying out is not a failure mode under normal float service conditions. The recombination process is very efficient and tends to be self-regulating as the efficiency increases as the saturation of the AGM separators decreases or more paths for diffusion are created in the gelled electrolyte. The low level of hydrogen evolution at the negative phase and corrosion of the positive grid lead to water loss. Permeability of the container to water vapour transmission has been considered as a source of water loss, but it is low for practical wall thicknesses and moderate ambient relative humidity. Water vapour will also be lost from the cell along with vented hydrogen, but again the effect is very small.

3.3. Thermal runaway

VRLA cells are very sensitive to operating temperature such that service lives are reduced at elevated temperatures and, in extreme cases, an unstable thermal runaway can occur. As the temperature rises, higher currents are drawn from a constant float voltage. These, in turn, generate larger quantities of oxygen that recombine exothermically, generating more heat, and ultimately the current can rise to a level where the cell gases and begins to dry out. As the cell dries out, the internal impedance increases, more heat is generated, and failure may occur through softening of the case or, in extreme examples, as a result of melting lead components. These affects can, however, be readily avoided by good installation practice for cooling and venting, by the use of temperature compensation of the float voltage, and by limiting the available current.

3.4. Active material degradation

The cyclic requirements for standby applications are generally moderate and the positive active-material generally remains in good condition after long periods. Sulfation and capacity loss of the negative plates is a potential failure mode. The oxygen recombination reaction depolarizes the negative plate such that it never reaches the low potentials normal in flooded batteries, but the inefficiencies of the recombination reaction allow sufficient charge to be applied to the negative plate to keep it in good condition. In addition, cells are designed with additional negative active material to provide a further safeguard.

Acid stratification can occur in cells with AGM separators. During cycling, sulfuric acid with a higher specific gravity sinks to the bottom of the cell. This results in a concentration gradient. Discharge becomes acid limited at the top of the cell and occurs at the bottom. Separators with higher levels of finer fibres and higher levels of compression reduce the effects. Compression also helps retain the positive active-material. For standby applications, the separator is specified such that this is not a failure mechanism.

3.5. Shorting through the separator

In VRLA cells, it is possible for short-circuits to occur through the separator by leading-through if the electrolyte gravity reaches very low levels as a result of over-discharge. Under these conditions, high pH will allow lead species to become soluble and can lead to the formation of lead dendrites. The problem can be avoided by cell design to ensure adequate acid is provided, by special additives in the electrolyte, and by the use of a voltage cut-off during discharge.

3.6. Premature capacity loss

Premature capacity loss (PCL) affects all battery types using antimony-free alloys, but for standby batteries, where the cyclic duty is moderate, it is not a source of difficulty. Batteries can be designed to provide adequate cyclic life. The whole subject of PCL is an area of intensive worldwide research effort and success in this area will lead to VRLA batteries with cyclic performance equivalent to flooded lead/acid batteries.

3.7. Cell sealing and venting

The integrity of the lid/container weld is important and either a heat sealing process or an epoxy resin seal is used. Both processes are reliable and proven. Pillar seals use rubber grommets to seal against the container and pillar which are mechanically clamped into position and for some designs are embedded in epoxy resin. The venting arrangements are simple and reliable. All seals are tested by sensitive techniques in manufacture and in laboratory tests may be shown to be leak-tight to an order of magnitude greater than that required for satisfactory operation.

3.8. Manufacturing technology

VRLA cells require substantial improvements in the level of control and reproducibility in manufacture as compared with flooded batteries. This has been achieved in all areas of manufacture. Plate manufacture has been placed under very close control. The adoption of cast-on-strap has brought higher reliability and the inter-cell welds are all tested as they are being made. Seal integrity is tested in-line and the acid-filling techniques have a very high precision. Fully-charged batteries are tested for open-circuit voltage, discharge performance and capacity such that very high levels of reliability are well-established.

3.9. Grid corrosion

As summarized above, all of the other components in a VRLA cell may be designed such that their life is greater than the corrosion life of the positive grid. In a VRLA cell, the positive grid experiences conditions that are more corrosive than flooded cells. This is because the float current is higher because of the depolarizing effect of the recombination reaction on the negative electrode and because the rate of polarization is different. As a result, for the same applied voltage, the current is increased and the voltage supplied to the positive plate is increased. This, in turn, will influence the rate of corrosion.

Grid growth will also occur as the grid corrodes. The oxide corrosion product has a greater volume than the metal, and stress is applied to the grid. As corrosion proceeds and the grid metal becomes thinner, grid growth will tend to increase in the later stages of life. The rate of growth is determined by the creep rate of the alloy and the morphology of the corrosion product will also be affected by alloying elements. Grid growth will eventually lead to loss of contact between the grid and active material.

Some studies of the projected life of VRLA batteries are based on studies of grids in sulfuric acid at specified voltages. These studies often fail to recognize the impact of the environment in a VRLA cell. The effect of polarization of the negative electrode and grid growth can only be validated by cell testing.

Product life may only be effectively validated by accelerated life testing or by real-time testing of complete cells and monoblocs.

4. Life testing results

The test that has been adopted is based on an accelerated life test at 55 °C with a capacity check at ambient temperature after 40 day intervals. After a known numbers of intervals, cells are subjected to a teardown and the degree of corrosion of the positive grids are measured. This is correlated with a teardown of cells of identical construction after known times on float at room temperature to determine the corrosion of the positive grids.

This method was originally developed by Oldham France [3] in collaboration with Electricité de France (EDF) to validate the life of flooded lead–calcium tubular cells for electric utility installations. The 40 day testing interval was shown to be equivalent to 1.6 years at room temperature on the basis of the correlation with actual corrosion rates.

Figs. 2–4 show the results of the method applied to VRLA cells with lead–calcium–tin pasted plates and AGM separators. The test was conducted as described at 55 °C at 2.27 V/cell with discharges carried out at 1.5*C*/10 to 1.70 V/cell at 20 °C. A life to 80% capacity retention of 9.5 cycles was obtained. Correlation of the measured corrosion at 55 °C gave an acceleration factor

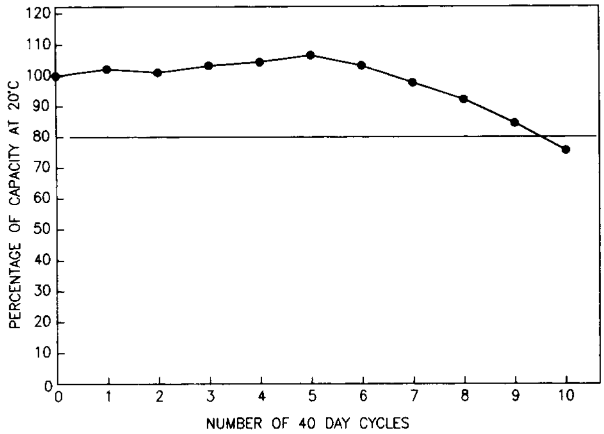

Fig. 2. Accelerated life tests of VRLA cells with lead–calcium–tin alloy grids and absorptive glass-mat separators at 55 °C.

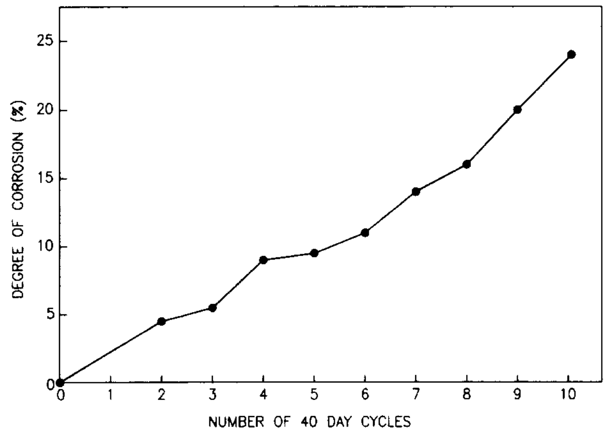

Fig. 3. Corrosion behaviour of lead–calcium–tin alloy grids in VRLA cells with absorptive glass-mat separators at 55 °C.

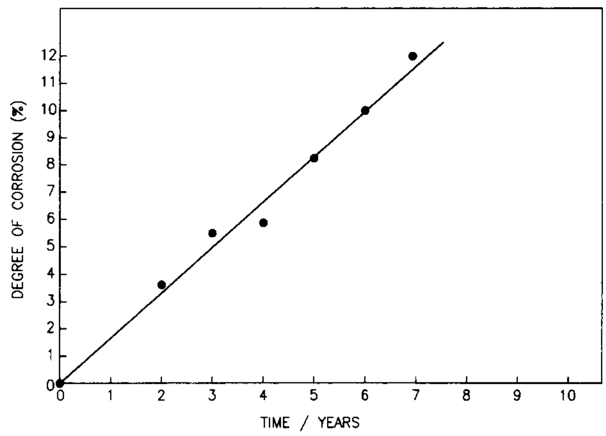

Fig. 4. Corrosion behaviour of lead–calcium–tin alloy grids in VRLA cells with absorptive glass-mat separators at room temperature.

of 1.14 and a room temperature service life of 11 years is predicted. These data were obtained with cells using grid alloys and grid profiles in use some years ago and recent data from improved products display a 40–50% improvement in life based on accelerated testing.

Figs. 5 and 6 show the same tests applied to tubular gel VRLA cells with lead–calcium–tin grids and spines. In this case, the cells were floated at 2.23 V/cell and discharged at 0.5*C*/10 to 1.80 V/cell at 20 °C. The same acceleration factor derived for tubular flooded cells may be used in this case to validate a room temperature life of 15 years.

Fig. 7 shows the *C*/10 capacity of cells using pure-lead grids and AGM separators (established by 55 °C accelerated life testing) given in equivalent years at 20 °C. Fig. 8 presents the same data for cells that had previously been exposed to five years float service at 2.27 V/cell and an average temperature of 26 °C. A lifetime of 17 years is indicated and is exceeded for the cells where only the latter part of the life has been accelerated.

These data demonstrate that VRLA batteries are capable of 15 years life on float at 20 °C, or 10 years of life at 25 °C. Service temperature is the key factor in determining corrosion life. A good guide is: for every 10 °C increase in temperature, service life is reduced by 50%. The importance of good installation practice is clearly evident. It should also be noted that life will be shorter at high discharge rates (5–30 min) than low

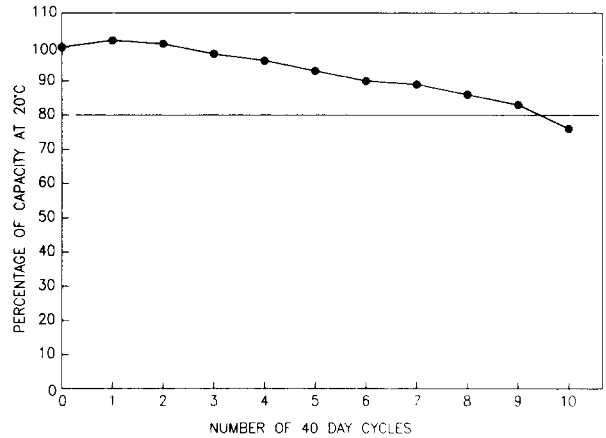

Fig. 5. Accelerated life tests for tubular gel VRLA cells at 55 °C.

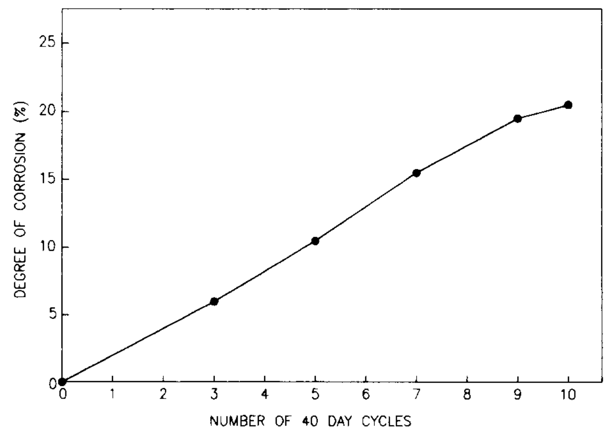

Fig. 6. Corrosion behaviour of spines in tubular gel VRLA cells at 55 °C.

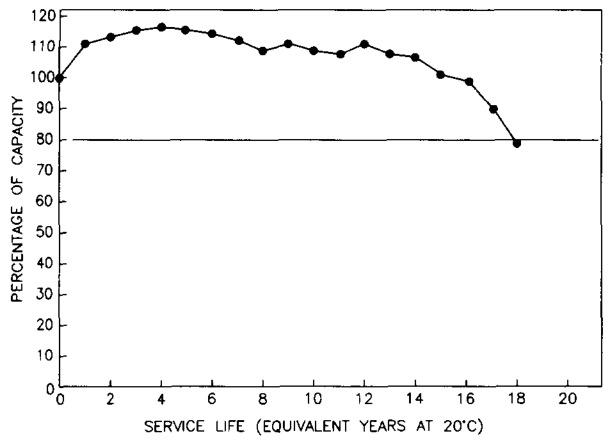

Fig. 7. Accelerated life test of cells with pure-lead spines and absorptive glass-mat separators at 55 °C.

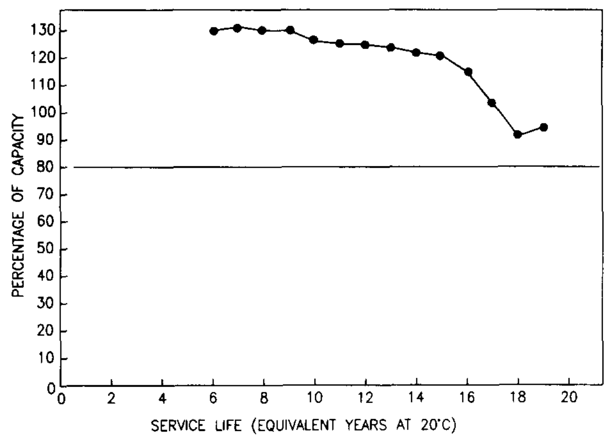

Fig. 8. Accelerated life test of cells with pure-lead spines and absorptive glass-mat separators at 55 °C. This test commenced with cells removed from ambient temperature service after five years.

discharge rates (>3 h) because more grid metal is required to sustain high-rate performance.

5. Monitoring and surveillance

The integrity of installed batteries can only be fully assessed by carrying out a measured discharge. For large populations of batteries, this may be done on a sampling basis by age, but other techniques are useful to indicate that end-of-life is approaching and to support replacement strategies. Continuous monitoring of voltage, current, temperature and time will result in identifying fault conditions prior to failure. Data-logging equipment will measure individual cell and monobloc voltages, both on float and during planned or unplanned discharges. Faulty batteries can be identified by reference to an acceptable voltage window and, on discharge, batteries with a higher rate of voltage decay can be identified. Charger faults and temperature can be recorded. Data can be interrogated to obtain a full operating history and alarms set to meet any local or remote requirement.

Conductance or impedance can be measured to give an indication of battery condition. This technique analyzes the battery as a small network of resistive and capacitive components. A.c. techniques give a measure of the resistive element and eliminate the capacitive elements expressed either as conductance or impedance. Impedance will increase as the cell ages and corrodes and will give some indication of battery condition. In practice, impedance measured by various techniques follows the reduction of capacity with life, but does not accurately indicate when the capacity has fallen to 80% of the original value. Impedance or conductance measurements can be used to identify when a battery requires further investigation and to detect conditions that will lead to rapid failure. A continuing record of impedance and temperature against time will give an indication of the security of the system.

6. Conclusions

VRLA batteries have been developed to a stage where they provide, safe, reliable, space-efficient and cost-effective power systems for virtually all applications. The product is significantly differentiated for various market sectors. Cells with plates cast in alloyed lead, or punched from pure-lead sheet with AGM separators or tubular gel cells are applied in different market sectors.

Reliability is assured by careful design and a full understanding of the factors that can contribute to failure. Cells are designed such that positive-grid corrosion is the normal end-of-life failure mode. All other potential failure modes are either eliminated or occur at a lower rate than grid corrosion.

Life testing is the only way to validate reliability. Accelerated life tests, correlated with corrosion studies, provide a good basis for ensuring actual service life is achieved. It has been shown that >15 years life at 20 °C or >10 years life at 25 °C can be obtained.

Monitoring and surveillance of in-service battery populations are important. Impedance or conductance measurements are useful as an aid to identifying incipient failures. Systems for continuous monitoring are widely used. All of these techniques enhance reliability, but it is vital to recognize that VRLA batteries do require maintenance checks from time to time to ensure the integrity of the system.

In many ways, sealed VRLA batteries are an enabling technology for a variety of industries, particularly telecommunications and information technology. They have become a key factor in facilitating the establishment of new networks. The battery industry has been the leader in this area and will continue to break new ground.

Acknowledgements

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