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Valve-Regulated Lead Acid (VRLA) Battery Qualification Assessment

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PRODUCT DESCRIPTION

Valve-regulated lead acid (VRLA) batteries have been proposed as a prospective dc power source for Class 1E service in passive nuclear plants. However, they are not currently covered by IEEE Standard 535, which addresses qualification for this service. Furthermore, there are reports of significant failure modes or mechanisms beyond the predominant failure mode of grid corrosion of the positive plate associated with vented lead acid (VLA) batteries.

There have been a significant number of published technical papers on failure modes of VRLA batteries since their introduction over 40 years ago, with major improvements reported in the last 15 years. A representative sample of these technical papers was selected for use in assessing the suitability of VRLA batteries for Class 1E nuclear applications. This assessment provides an opportunity to determine the next steps needed to advance the use of VRLA batteries in existing and future nuclear plants.

VRLA batteries currently make up over 90% of the total standby battery market. Significant improvements have been made in eliminating or mitigating the consequences of the failure modes reported in the earlier technical papers. However, there are several failure modes and underlying mechanisms that have not been fully eliminated. Therefore, more work will be needed before VRLA batteries are ready for Class 1E, safety-related service in nuclear plants.

Results and Findings

VRLA batteries have significant failure mechanisms beyond those of VLA batteries currently included in the scope of IEEE Standard 535 for Qualification. A revision to the standard will be required to address VRLA failure mechanisms, and appropriate condition monitoring must be selected in concert with the revised methodology of the standard.

This report can serve as a decision point to plan for future research and testing activities to close the gaps identified and to work with battery manufacturers and users to drive the maturity of the VRLA products available for future deployment in nuclear plants.

Challenges and Objectives

This report is intended for nuclear utility managers and lead engineers who are interested in battery systems that provide a smaller footprint and eliminate liquid electrolyte maintenance and control associated with the current vented lead acid (flooded) batteries.

Applications, Value, and Use

The current state of VRLA battery technology does not meet the requirements for safety-related battery applications in nuclear plants; however, there are many non-safety-related applications where they can be used, and are being used now.

VRLA batteries offer several advantages over the traditional VLA batteries. These advantages include higher energy density in a smaller footprint, sealed (valve-regulated) containers with immobilized electrolyte, and normally lower gassing rates. The larger VRLA batteries are housed in steel containers with integral racking provisions, requiring no separate battery rack.

EPRI Perspective

VRLA cells by virtue of their market share have been established as a product in wide use in general industry. However, the requirements imposed on nuclear power plants exceed those of general industry, and products used in certain nuclear applications must meet strenuous requirements to provide assurance of their capabilities. There are existing standards that address known failure mechanisms for accepted battery technology, and this project is an attempt to extend that knowledge base to determine if VRLA can meet the challenge of nuclear safety-related service. This report provides a turning point in more clearly defining the steps needed to deliver a mature VRLA battery technology for use in existing and future nuclear plants.

Approach

The goals of the report were to identify any additional failure mechanisms of VRLA batteries that were not covered by the current qualification methodology in IEEE Standard 535 and to assess the suitability of VRLA batteries for safety-related applications in nuclear plants.

First a review of technical papers from the last 15 years was done to determine the state of the VRLA battery technology. A combination of highly technical papers dealing with battery electrochemistry as well as user and manufacturer reports on failures of VRLA cells was used to get an overview of the pertinent issues. In the period between 1995 and 1998 there were studies done on over 70,000 VRLA cells in Sweden and the United States. The overall failure rate reported was over 60% of the test population. One conclusion drawn was that VRLA cells at that time were only good for 2 years of service, not the 10 to 20 years advertised.

These early catastrophic failure reports led to very aggressive troubleshooting and development efforts by the battery manufacturers and others. The development efforts continue even now. During the last 10 years there has been a remarkable openness among some suppliers and even some shared technical papers addressing the failure modes and needed changes to the VRLA cell designs. The results from some of these developments are included in this report.

Finally, interviews were conducted with several battery manufacturers and one independent testing specialist to get their opinions about failure mechanisms, accelerated life testing, and whether they thought the current VRLA batteries were suitable for class 1E use in nuclear plants, both in existing plants and in the newer passive designs.

Keywords

VRLA
Valve-regulated lead acid batteries
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Failures
Failure mechanisms

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QUALIFICATION BACKGROUND

Class 1E Service

According to IEEE Standard 535-2006, the objective of qualification for Class 1E service is to demonstrate that the batteries and racks will perform their required Class 1E function throughout their qualified life [A.1.4]. Qualification testing, including aging of the test specimens to IEEE Standard 535, is required due to the significant aging mechanism identified as grid corrosion of the positive plates. This is also described in IEEE Standard 323, which is the basic qualification standard for all Class 1E equipment [A.1.5]. Currently, only vented lead acid (VLA) batteries are included in the scope of IEEE 535, but some of the principles can be applied to this assessment of valve-regulated lead acid (VRLA) batteries.

For example, the predominant aging failure mode for VLA batteries is grid corrosion of the positive plates, as noted above. Therefore, any other cell components with age-related failure mechanisms should be stressed to a life not less than the qualified life of the positive plates. The end of the expected service life for VLA batteries is defined as 80% of the manufacturer's rated capacity. This principle can be applied to VRLA batteries as well.

Significant aging mechanisms are those that progressively and appreciably render the equipment vulnerable to failure to perform its safety function(s) according to IEEE Standard 323 [A.1.5]. Therefore, if there are other significant failure mechanisms of VRLA batteries identified, then their effect upon qualification must be evaluated. More research will also be needed to identify the effect upon the current qualified condition of 80% of rated capacity. As a minimum, additional aging test methods may need to be added to IEEE 535. This is especially true if one or more of these additional failure mechanisms are shown to be dominant in VRLA batteries.

Because qualification testing is necessary to prove capability, it is important to identify all significant failure mechanisms of VRLA batteries. Once this has been done, plans can then be made for characterizing these mechanisms, mitigating their effects to the maximum degree possible, and adjusting the methods used for qualification accordingly. Additional condition monitoring may be required, depending upon the severity of the failure mechanisms.

Along with determining any new failure mechanisms, the appropriate condition monitoring techniques must be developed and proven by testing. The condition monitoring and trending of those conditions could be an evolving process, since trending implies more than one data point and those data points are typically collected over some time span.

Non-Class 1E Service

The requirements for non-Class 1E service are not as stringent as for Class 1E service. VRLA batteries are already being used in some nuclear plants in emergency lighting, engine cranking, and other applications. Since these applications do not require Class 1E qualified batteries, this investigation was limited to VRLA batteries for use in Class 1E service.

2
VRLA FAILURE MECHANISMS

Introduction

Before the details of any failure mechanisms are discussed, an illustration may be helpful to clarify the meaning of various terms. Almost all physical materials have some mechanism by which they degrade over time. For lead-acid batteries the grid structure of the positive plates corrodes due to the float current passing through it [A.2.1]. This failure mechanism is true for either VLA or VRLA batteries, and ultimately either type of battery will fail if this is the dominant failure mechanism. Hydrogen evolution at the negative plates is another failure mechanism in lead-acid batteries that results in water loss from the cell. For VLA batteries water loss is corrected by refilling as a part of normal maintenance. However, for VRLA batteries the cell containers are sealed, and refilling is not a normal maintenance activity. Therefore, if left uncorrected hydrogen evolution at the negative plates, which is a secondary electrochemical reaction, can cause water loss, which results in loss of electrolyte volume, additional internal heat production, increased acid concentration, and negative plate sulfation, which impacts both discharge capacity and service life [A.2.1]. Control of this type of electrochemical sequence is a challenging aspect of VRLA battery designs. There are many secondary reactions occurring in VRLA batteries, and a balanced approach must be used in internal electrochemical design and mitigation of the resulting external effects.

There are two methods used to immobilize the electrolyte inside VRLA cells. Some early VRLA designs introduced in the 1950s used a gelling process to immobilize the electrolyte. This type is sometimes called a VRLA-GEL design. In the more common type in use today, the electrolyte is absorbed in a glass mat between the plates, which also serves as the separator. This type is designated as a VRLA-AGM design. There are also some more recent hybrid designs that use both glass mats and gel to immobilize the electrolyte. The effects of the failure mechanisms are different between the designs, due to the immobilization methods used. The focus of this report is on the types of failure mechanisms rather than on the comparative susceptibility of the various types of VRLA cells.

There is a range of physical configurations, discharge rates, and sizes of VRLA batteries on the market. The focus of this report is on the large format, longer duration batteries with a design life of 20 years.

Failure Mechanisms Common to VLA and VRLA Batteries

Some failure mechanisms reported in the literature are common to both VLA and VRLA batteries [A.3.1, A.2.1]. These include grid corrosion of the positive plates, water loss, post-seal failures, and thermal runaway. However, the more mature designs of the VLA batteries and the ability to refill to correct for any water loss have practically eliminated these mechanisms from having a significant impact on the normally expected service life. Temperature remains a stressor for any lead-acid battery and must be mitigated properly to achieve full service life [A.1.2]. With

VRLA batteries the temperature effect is more pronounced. At low temperatures, self-discharge of the negative plates is most likely the cause of cell failures. Negative plate polarization decreases with temperature. Inadequate polarization leads to self-discharge and subsequent loss of capacity [A.2.8]. At higher temperatures the rates of hydrogen and oxygen evolution and corrosion are doubled for each 10°C increase in temperature. This has a compounding effect since the float current is also being increased and thus more heat is generated inside the cells [A.2.6]. If no corrective action is taken, the higher temperatures can lead to thermal runaway. These failure mechanisms are covered in the *NMAC Stationary Battery Guide* [A.3.1].

Failure Mechanisms Unique to VRLA Batteries

Reported failure mechanisms unique to VRLA batteries include negative lug corrosion and negative strap fracture leading to partial or total loss of the internal conduction path as well as negative plate discharge/sulfation with associated premature capacity loss [A.2.2, A.2.3, A.2.7, A.2.8, and A.2.9]. A description of each of these mechanisms is given below.

Negative Lug and Strap Failures

There were many reports of negative plate lug failures in the 1980s caused by corrosion of these elements. Dissimilar alloys in the plate lugs and group straps were used in the earlier VLA batteries, but the elements were immersed in electrolyte and thus protected from corrosion. With some VRLA batteries, these components were left exposed to corrosion and ultimately failed. This internal failure is difficult to detect externally with the conventional test equipment available. This mechanism results in a high-resistance connection between one or more of the plates and the connecting strap. If not detected, this mechanism can cause an open circuit in the cells/battery.

Another failure mechanism of the negative top lead components is strap corrosion. In the past there have been reports of sulfation corrosion of these components in VLA batteries when they were not submerged in electrolyte. The strap metal corrodes at a rapid rate until it ultimately fractures. This failure mechanism is due to a lack of cathodic protection of the strap, or to poor alloy selection and/or casting processes. Negative strap corrosion can result in the fracture and ultimately in an open circuit of one or more cells in a VRLA battery.

These internal negative top lead components conduct the discharge and charge currents between the internal plate elements and the external circuits and are critical to proper VRLA battery operation. Therefore, the complete elimination of these failure mechanisms is imperative.

Negative Plate Discharge (Hydrogen Balance) and Water Loss

Another failure mechanism of the negative element is negative plate discharge. According to one paper, “The negative plates on lead-acid cells have a natural tendency to self-discharge, in doing so, they release or ‘leak’ hydrogen into the cell.” It is through charging the cell that the hydrogen is replenished at the negative via hydrogen ions and electrons. Refer to Figure 2-1 for a simplified gas and ion flow diagram. Note: Electron flow, not conventional current flow, is used to show the electron path. Electrolysis of water furnishes some hydrogen ions and electrons in new VRLA cells, but is not available as a long term source. Therefore, electrolysis is not shown in Figure 2-1. In the normal oxygen cycle, oxygen is generated at the positive electrode during charging. This oxygen diffuses in the gaseous phase and is recombined with the hydrogen ions and electrons at the negative plate to reform water. This recombination process consumes almost all the hydrogen ions and electrons, so there are few left to charge the negative plate. The more efficient the internal oxygen cycle of mature cells, the more likely the negative plates are to be discharged.

The corrosion of the positive grid electrolyzes some water, with the oxygen being absorbed by the lead grid. This releases some hydrogen ions and electrons that are available to charge the negative plates. As one author expresses it, "Therefore, the long-life VRLA cell is totally dependent on the corrosion reaction of the positive grids to prevent discharge of its negative plates." The balancing of these two independent reactions is critical to the operation of VRLA cells. In one study, the grid corrosion furnished only 25% of the hydrogen ions plus electrons needed to keep the negatives charged. In addition, the negative plates in this study continued to discharge until they reached 25% capacity [A.2.5]. Obviously this is an unacceptable capacity level at which to achieve hydrogen balance.

In another study related to hydrogen balance, one pertinent observation was made [A.2.14]: "The self-discharge reaction rate of the negative plate determines the minimum hydrogen evolution that can be achieved for the fully charged lead-acid battery." (Berndt Law)

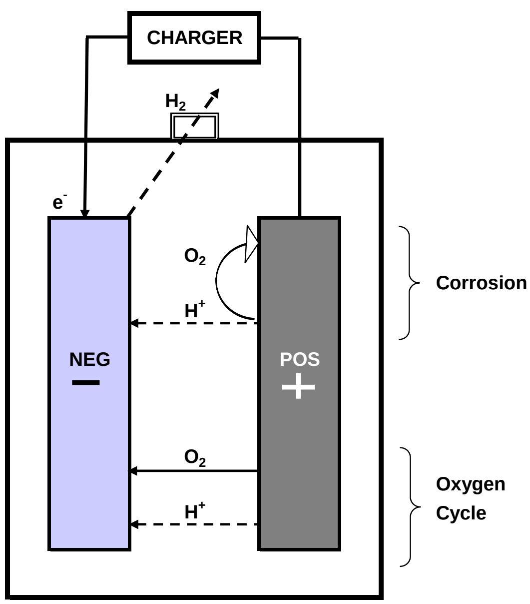

Figure 2-1
Simplified gas and ion flow inside VRLA cell

Water Loss Versus Loss of Compression (AGM)

There are still some reports of loss of compression instead of water loss, but the basic effects are very similar. Therefore, we have chosen to call the failure mechanism water loss for this report. If the saturation of the AGM fibers changes the compression as claimed, then there will be a loss of compression caused by the loss of water.

3
DEVELOPMENT OF MITIGATION STRATEGIES

Introduction

As noted in Section 2, VLA and VRLA batteries share some of the same failure mechanisms and to some degree some of the same mitigation strategies. However, due to the unique features of VRLA battery designs and their applications, careful attention must be given to fully addressing the failure mechanisms described in the previous section. This section discusses what has been and is being done, as reported in the literature. The more recent developments will be discussed briefly, recognizing that work remains to be done to fully demonstrate these fixes in actual service.

Cathodic Protection of the Negative Structures

The negative plate lugs and straps that are immersed in electrolyte in the VLA cells have been wrapped using an AGM separator wrap in VRLA cells to provide cathodic protection for these components. For the GEL cells, the negative elements are covered with gel. This approach has helped to reduce the corrosion of these negative elements.

Changes in Alloy Selection and Use of Cast-On Straps

Changes in alloy selection and manufacturing processes have been made to help in eliminating negative strap failures. In one study it was observed that the alloy crystalline orientation can be as important as casting porosity and the use of low corroding lead alloys when internal parts are subject to oxidation. Therefore, at least one manufacturer changed to cast-on type straps, with good results reported [A.2.4].

These first two mitigation strategies have been applied by some manufacturers for over 10 years, but no recent reports have confirmed that the associated failure mechanisms have been completely eliminated. This is an area where independent verification testing would be helpful.

Water Additions Followed by High Rate Charge

In the early 1990s there was an effort by at least one VRLA battery manufacturer and one independent research and testing company to offset the effect of water loss by simply adding a certain amount of water to the VRLA cells through the vent caps [A.2.13]. This turned out to be a short-term fix that only lasted for a few years. However, it did confirm some benefits for the use of internal ohmic measurements as a condition monitoring tool. Further development led to the use of a high rate charge to the battery after the water addition in certain cases. This process was then supplemented by the addition of a catalyst in the head space, as discussed below.

Use of Catalysts to Balance Hydrogen Evolution and Grid Corrosion

There were some material changes made to the cells during the 1990s, but there was a fundamental need to balance the secondary reactions of hydrogen evolution at the negative electrode and grid corrosion at the positive electrode. This led to the introduction of a catalyst to the vent cap assembly on several VRLA models [A.2.5, A.2.6, and A.2.13]. The catalyst recombines a portion of the oxygen before it can reach the negative plates. This necessitates a corresponding increase in the amount of hydrogen generated at the negative, which in turn brings the polarization back into a range ensuring full charge of the negative plates. On the positive plates, the polarization is reduced with a corresponding reduction in grid corrosion. The catalyst recombines the scavenged oxygen to form water, which remains in the cell. There are a few reports of service life for some VRLA-AGM type cells in the 10- to 14-year range with the use of the catalyst and other remedial actions [A.2.13]. The remaining questions with the catalyst are what contamination issues may be involved and what service life can be expected.

Another way of correcting the hydrogen imbalance in high-quality, long-life VRLA cells is to reduce the hydrogen evolution rates of the negative plates, which would involve greater purity of raw materials and perhaps variations in expanders [A.2.14]. There are questions about how successful these redesign efforts will be. These types of issues are especially pertinent for the longer-life batteries that would be required for nuclear plant applications.

Other Developments

There are several papers that reported on developments in plate alloys and hybrid combinations of AGM and GEL designs. One paper describes a hybrid AGM-GEL design to provide an increase in electrolyte in the cell and to improve retention of the plate-to-mat contact. Initial experimental test results showed some promise with this design [A.2.10]. Due to some other developments, this product line has now been retired. This and other developments offered little actual service life history and therefore are considered unproven at this time.

Proposed Future Research and Development

Areas for future research and development to prepare the way for the use of VRLA batteries in nuclear plants include the following:

- Develop/define the activation energy values for each failure mechanism based on previous basic EPRI work [A.3.3] and any other available data. The present Telcordia testing standard used by most battery manufacturers is based on positive grid corrosion alone.
- Condition monitoring methods need to be improved to address each failure mechanism. Various ohmic measurement methods are in use, with mixed results [A.3.2]. Float current monitoring and coup-de-fouet testing are two areas for further development.
- A proposed 80% service test method of trending battery capacity could eliminate performance testing for qualification and condition monitoring in the future. In addition, this method would minimize any recharging issues related to the 72-hour duty cycles on the passive design plants. This method will need to be fully proven before implementation.

4
ASSESSMENT FOR CLASS 1E NUCLEAR SERVICE

Introduction

The goals of this assessment were to identify any additional failure mechanisms of VRLA batteries that were not covered by the current qualification methodology in IEEE Standard 535 and to assess the suitability of VRLA batteries for safety-related applications in nuclear plants.

Additional failure mechanisms were addressed in Section 2.

This assessment is based on a review of the technical papers and interviews with representatives from several battery manufacturers and an independent battery research and testing specialist. One battery manufacturer has done some testing of a VRLA battery as reported in a technical paper, but there were no reports of its use in an actual safety-related application [A.2.12].

Technical Paper Review Summary

The paper review identified several additional failure mechanisms, as described in Section 2. The results can be submitted for a possible revision to IEEE 535 to qualify VRLA cells for Class IE service. This would include any additional aging/life testing required as well as proven methods of condition monitoring to address these failure mechanisms.

Interview Summary

Over the course of several months several battery manufacturers and one independent research and testing specialist were interviewed to get their perspectives for this assessment. The topics included significant aging mechanisms, accelerated life testing, activation energy values, and their opinions on the use of VRLA batteries in Class 1E service at nuclear plants.

There was general agreement on having more than one significant aging mechanism for VRLA batteries. As expected, there was some disparity on reported occurrences in AGM versus GEL types. The consensus was that changes were needed to IEEE Standard 535 before it should be used for VRLA battery qualification. One company has already used IEEE 535 for some “qualification” testing of VRLA batteries but reported no actual use [A.2.12].

Most manufacturers said the Telcordia standards were what they used for accelerated life testing since the major uses are in telecommunication applications. Several interviewees acknowledged that accelerated life testing missed some failure modes such as negative strap corrosion that occur at room temperatures but not at the higher test temperatures [A.2.4]. It was also acknowledged that the activation energy values used can vary significantly with the alloys used in the grid materials and the failure mechanisms under test [A.2.12]. This discussion reinforces the need for a thorough review of the accelerating aging methodology in IEEE 535 before it can be used for VRLA battery qualification.

The following questions were asked and answers provided:

- When asked if they would recommend VRLA batteries for Class 1E service in the passive plants having 72-hour duty cycles, all but one manufacturer said no.
- When asked if they would recommend VRLA batteries for Class 1E service in the existing nuclear plants, the response was no, not immediately, but perhaps after all the failure mechanisms have been fully addressed. Several mentioned the need for further development and deployment of condition monitoring systems to adequately surveil the state of health of the batteries.

The testing specialist gave an overall user perspective as one who has been involved in the testing of many VRLA batteries and pioneered a recovery process for cells/batteries that were previously being replaced. He questioned the use of the existing accelerated aging tests to really identify all failure mechanisms. He surfaced one concern with IEEE 535 related to more guidance on what components of the cells are allowed to be replaced or repaired during accelerated aging. For example, for the VLA cells, water additions are a normal maintenance activity, and therefore, refilling during the test is acceptable. However, water loss for the VRLA cells is a failure mechanism due to the sealed nature of the container. Therefore, it would not be appropriate to refill during the aging process, since the VRLA design is based on a fixed amount of electrolyte throughout its service life. Finally, he expressed concern that the users should be thoroughly trained on the operation and maintenance of VRLA batteries and the use of internal ohmic measurements as well as float charging current and temperature measurements as a part of their condition monitoring. In other words, VRLA batteries may require somewhat less maintenance than VLA batteries, but the condition monitoring is much more critical for VRLA batteries.

Conclusions

1. VRLA batteries are not currently suitable for Class 1E service.
2. The qualification methodology in IEEE 535 will need to be revised.
3. Accelerated aging methods need to be reviewed for all VRLA failure mechanisms.
4. Condition monitoring methods for all VRLA failure mechanisms need to be proven.

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