MONOBLOC BATTERIES: HIGH TEMPERATURES, LIFE AND CATALYSTS

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INTRODUCTION

12-Volt Monobloc batteries have become very popular in recent years due to their high power density and compact form. With the advent of the front terminal design, this battery has become easy to install and support and its compact form allows it to be used in a wide variety of space constrained applications where larger 2-volt VRLA cells will not fit. The Monobloc VRLA battery, while not new, has become the preferred battery to be used in outside plant (OSP) applications due to the features just outlined. As is being discovered, the high temperatures of the outside plant environment are not conducive to the life of these batteries. This paper will review the life expectations of Monobloc VRLA batteries, explore the effects of high temperatures on these batteries and explain why high temperature can drastically shorten the life of VRLA batteries. Finally the paper will present a possible application of catalysts to 12-volt Monobloc batteries in order to mitigate the effects of high temperature.

WHAT OTHERS HAVE SAID

In reviewing the published proceedings of Intelec and Battcon over the last 8 years the subject of VRLA life has been extensively written upon and hotly debated. Dr. Dave Feder and Will Jones led the charge through the mid and late 1990's at Intelec with their papers that described the early failures of 2-Volt VRLA cells and the electrochemical imbalances that can occur in VRLA cells and lead to the shortened life. These papers focused on so called "20-year" 2-volt VRLA cells and the newly discovered failure mode of negative plate self discharge. Dr Feder presented the results of a large study of 24,000 cells that clearly showed that the majority of these cells would deliver nowhere near the design life of the product. Over time various solutions to the problem of negative plate self discharge were presented: increased purity of lead and acid used to construct the cell, allow for positive grid corrosion and shortened life expectation, or use of a catalyst to balance the internal reactions. At the time, very little was written on 12-volt monobloc VRLA batteries. Their design life was significantly shorter, 5 to 10 years, than 2-volt cells. But over time the industry started to realize that 12-volt monobloc VRLA batteries were also delivering less than the design life. At past Battcon conferences, a specific problem, the ill effects of high temperatures on VRLA monobloc batteries, was addressed by authors such as Frank Vacarro and Steve McCluer, to name just a few. In these papers, both battery dry out and positive plate corrosion & growth have been cited as failure modes of VRLA batteries when exposed to high temperatures. Regardless of the exact failure mode it is now a known fact that high temperatures will drastically shorten the life of VRLA batteries. This is especially troubling given the fact that many VRLA 12-volt monobloc batteries are in use throughout North America in Outside Plant (OSP) applications with little to no cooling equipment. [1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13]

LIFE EXPECTATIONS

When speaking about batteries and life expectations two terms must be considered:
- Design Life: The life of the battery *as expected* by the designers and manufacturers of the battery.
- Actual Life: The life of the battery *as experienced* by the users and owners of the battery.

As with all products, it is when the actual life of the product does not live up to the design life of the product that trouble erupts between the end user of the product and the battery manufacturer. The battery manufacturer has advertised and sold the product based on the design life and the end user uses the battery based on the actual life. This mismatch in design life and actual life is an age-old debate that stretches back to flooded battery technology, but has become more dramatic and mismatched with VRLA technology. To understand the mismatch a short history lesson is in order.

For flooded stationary lead acid batteries, the design life of the cell is based on the corrosion of the positive grid material. The stationary flooded battery design has been refined over many years so that the weakest link is the positive plate. The other factors that used to cause these batteries to fail have been improved so that the positive plate is the first to go. Much of the reason that flooded lead acid cells last so long today (generally around 20 years) is that a huge amount of effort went into selecting and designing a positive grid that minimizes corrosion. Pure lead and thick grid elements were selected to obtain the 20-year design life. The test methods that were developed to prove out the design and to show that corrosion had been minimized were also used to determine the life expectations of the products themselves. This worked very well in flooded lead acid cells as history has proven. The life of these batteries could accurately be predicted by the corrosion rate of the positive grid so battery manufacturers could determine the life without having to wait 20 years. End users could reasonably expect their flooded stationary lead acid cells to last as long as they were being told because these cells were being used in an environment that matched the conditions tested for; namely life at room temperature in a controlled central office facility. Life was good.

The problem developed when this life prediction and testing was expanded to VRLA cells. VRLA cells do not behave like flooded stationary lead acid cells and the design has not had as much time to mature. While positive grid corrosion is a big concern there are other things that must be considered when the electrolyte is minimized. The health of the negative plate must also be considered, but this was not known at first. In the early days of VRLA technology the same life prediction equations were used because the thinking at the time was that the limiting life factor would be the positive grid as it was in flooded stationary lead acid. Time has proven that this is not entirely correct. There is more than one factor at work in VRLA cells to reduce the life of the battery, especially in high temperature applications. Many of the failure modes that have impacted VRLA batteries in the past have been greatly reduced by improvements in the design by battery manufacturers. These include: Post seal leaks, vent design, plate compression, alloy modifications, lead purity, and others. The goal of the industry is to maximize the life span of the positive plate and make sure no other cause causes battery failure prior to that point in time.

Unlike 2-volt VRLA cells, 12-volt monobloc VRLA batteries have shorter life expectations. The design life for 12-volt monobloc batteries is generally 5 to 10 years depending on the design of the battery and the price paid for the product. The shorter projected life is primarily due to the fact that these batteries have thinner positive plates. The thinner plates allow these batteries to take up less room and cost less for the same capacity as a thicker plate design would. Essentially the user gets higher energy density and higher capacity at a lower cost, but at the expense of a shorter life of the battery. In room temperature applications, the actual life is acceptable for 12-volt monoblocs. The problem arises when these batteries are placed in high temperature applications. In these instances there is a large mismatch between the design life and the actual life. In a previous Battcon paper it was found that at high temperatures the primary failure mode of 12-volt monobloc VRLA batteries at 65°C was positive plate corrosion and growth and that water loss was also seen.[12] Another paper found that the primary failure mode was dry out.[13] It is clear that sustainability of the 12-volt monobloc VRLA design is at risk in high temperature applications. The costs of replacing these batteries at remote, outside plant applications every year quickly surpasses the cost of the battery product itself and makes the economic viability of using this product in these high temperature applications questionable.

TEMPERATURE IMPACT ON LIFE

Batteries, unlike other components in the power plant, degrade over time. Unlike mechanical components that wear out, there is no visible sign of the degradation. Also the process is always progressing and can't be stopped. But there are many factors that can affect the rate of the degradation. There are design factors such as the purity of the alloys, the thickness of the plates, etc. There are also environmental or application specific factors that have an impact. The two sets of factors are inter-related, because the design must be done taking into account the environmental factors that are likely to be encountered. Temperature is perhaps the environmental variable that has the biggest impact on the actual life of the battery. This factor has become a much bigger issue because of the increase in distributed requirements for battery power. There are more applications for batteries in the outside plant environments where there is no air conditioning. In the past flooded batteries were tested at high temperatures to accelerate the testing with no expectation that batteries would actually be operated at those temperatures. Now, the elevated temperatures actually represent the operating environment the battery will see. How long a battery will last in these high temperature environments is becoming a major concern for end users.

Temperature impacts the battery life because higher temperatures cause all chemical reactions to speed up. Battery engineers are all familiar with the Arrhenius equation that quantifies the impact of a temperature rise on the rate of the chemical reactions. This equation is based on the concept developed in the late 1800's by Dr. Svante Arrhenius, a Swedish scientist who won the Nobel Prize for chemistry in 1903. Generally speaking, for every 10°C rise in temperature the speed of the reactions double and the life is reduced by half. It should be noted that not all chemical reactions will respond to temperature at the same rate.

When a VRLA battery is exposed to high temperature there is an increase in the current draw of the cell, an increase in water loss and an increase in the rate of corrosion of the positive grid material. High temperature causes an increased current draw because all of the reactions in the cell that govern the charge profile are increased. Increased water loss occurs because it is a direct result of the increase in current. The scientist Michael Faraday, in the 1830's, found that water is broken down into its components of oxygen gas and hydrogen gas when an electrical current is passed through it. The rate of decomposition is directly proportional to the amount of current passed through the water. Since water forms a part of the battery's electrolyte the more current that is passed through the battery the more the water portion of the electrolyte will be broken down into oxygen and hydrogen gas. This gas is then free to vent out of the battery and lead to the dry out of the battery over time. Corrosion is increased with temperature on the positive grid because rates of corrosion are directly related to temperature and current.[14] The following table summarizes the impact of high temperature on a lead acid battery:

Summary Table: Impact of High Temperature on Batteries

Effect of high temperature on battery	Reason why
Increased current draw	Cell reactions increase with temperature. Arrhenius Equation
Increased water loss	Electrolysis of water is directly related to current. Faraday's Law.
Increased positive grid corrosion	Corrosion is directly related to temperature and current.

To quantify the impact of temperature on a battery we looked at some of our test data. The following table presents our data and serves as an illustration of a typical rise in float current with temperature that you would find with any VRLA battery.

Table of Temperature versus Float Current

Temperature	Current (mA/100 Ah)
30°C (86°F)	0.04
40°C (104°F)	0.15
50°C (122°F)	0.25

As the table shows, the current of the cell did increase with increased temperature, which should be no surprise.

While we did not measure the water loss of the cell ourselves there is enough evidence collected and written by others to prove this. One source[15] collected the following data:

Table of Water Loss with Temperature

Temperature	Water Loss Per Year (Grams/100 Ah)
25°C (77°F)	9
35°C (95°F)	18.3

The data shows that the water loss of the cell increases with increasing temperature, which is due to the increased current draw of the cell; the Arrhenius equation does hold true.

At this point we have shown that high temperature can lead to increased current, increased water loss and increased corrosion of the positive grid in the battery, but what does this mean to the life of the battery. In essence, a higher temperature leads to a shorter life of the battery, but what can be expected? The following table presents the effect of high temperature on battery life as predicted by applying the Arrhenius equation:
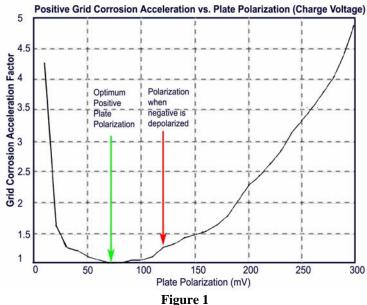
Expected Actual Life			
Temperature		5-Year	10-Year
°C	°F	Design	Design
25	77	5 Years	10 Years
35	95	2.5 Years	5 Years
45	113	1.25 Years	2.5 Years
55	131	7.5 Months	1.25 Years
65	149	3.75 Months	7.5 Months

As the table shows the design life is de-rated by half for each 10°C increase in temperature. As an example of how to use the table, assume that a battery user is getting 2.5 years of actual life from a battery with a design life of 5 years and that it is being run at 35°C. In this case, the battery user is getting exactly what they paid for and what the battery was designed for. The table clearly shows that high temperature can have a dramatic impact on the life of the battery. It is important to note that the highest temperatures on the table have actually been measured inside the battery compartment of an outside plant cabinet in the southern US in the summer.[13]

ACHIEVING DESIGN LIFE

The design of batteries is a complex matter. For an excellent discussion of the similarities and differences between flooded stationary lead acid and VRLA batteries, and a bit of history on the trials and tribulations involved in the design of both types of batteries, Dr. Dave Feder's 2001 Intelec paper is an excellent source.[16] With this background in mind, the question becomes are there steps that can be taken to ensure that the design life of a lead acid battery is achieved? For any lead acid battery corrosion of the positive grid is the main and first concern. Fortunately positive grid corrosion is well understood by battery engineers and has been quantified. The most widely used graph to describe how corrosion affects the positive plate was developed by J.J. Lander. The curve that bears his name shows us that there is a zone where corrosion is minimized in a lead acid battery and also that once out of that zone corrosion of the positive grid is accelerated.

As a general rule for all lead acid batteries, corrosion is a function of the charge voltage (polarization) applied to the positive plate. In all lead acid batteries there is a fixed amount of charge voltage that is supplied to the battery from the charger. This charge voltage is distributed to the negative and positive plates. The negative plate takes some of the charge voltage and the positive takes the rest. If too much oxygen/hydrogen recombination takes place on the negative plate, this plate becomes depolarized and then the positive plate will end up with all of the charge voltage. This can push the battery into the danger zone for increased positive grid corrosion (right side of the curve). This can be seen on the Lander curve in the Figure 1 below:

Figure 1

It must be noted that much of the information just presented on positive grid corrosion was based on flooded stationary lead acid cells and large 2-volt VRLA cells. Even though 12-volt monobloc VRLA cells employ thin positive plates the rates of corrosion as developed by Lander still apply. The difference between the designs boils down to how much material there is to work on, which is a question of plate thickness.

CATALYST REFRESHER

In our research on 20-year 2-volt VRLA cells, we have shown that we can shift the polarization into the optimal (minimized) corrosion zone by using a catalyst mounted inside the gas space of the VRLA cell. We know that this happens by measuring the float current of the VRLA cell. Generally we see a float current in a catalyst equipped cell that is half of what it is in an equivalent cell that is not equipped with a catalyst.[10] Since float current and positive plate polarization are directly linked and directly proportional we know that by reducing the float current we are reducing the positive plate polarization and therefore reducing the rate of corrosion on the positive grid. A catalyst, when placed inside a VRLA cell, provides many benefits to the cell through its primary role of keeping the negative plate polarized. The benefit of using a catalyst in a VRLA cell has become accepted as a practical way to ensure the health and life of the battery and because of this it is now included as an integral part of the battery by a number of leading battery manufacturers. For further information on this topic please refer to our previous Battcon papers.[10, 11]

HIGH TEMPERATURE TESTING

As we have already said much of the information presented was developed for larger 2-volt cells, but can these results translate to high temperature applications and 12-volt monobloc VRLA battery designs? It was thought at one time that the faster corrosion in the monobloc batteries would absorb enough oxygen to make the catalyst redundant. There has also been speculation that as temperature rises the subsequent polarization changes in the battery modify the effect of the catalyst. Our initial experiments do not support either of these theories.

To assess this impact of temperature on catalyst performance in 12-volt monobloc VRLA batteries we conducted a test of four 12-volt 100 Ah monobloc VRLA batteries. Two of the batteries were equipped with 6 catalysts each (one catalyst per cell) and two of the batteries were not equipped with catalysts – they were considered the control batteries in our test. All four batteries were float charged at 2.27 volts per cell and placed in an oven and exposed to temperatures of 30°C, 40°C and 50°C for periods of 14 days, 14 days and 46 days respectively. The following table presents the results of this test:

Table of Test Results: Float Current Measured at Temperature

Temperature		Current (mA/100 Ah)		Ratio
°C	°F	Catalyst Batteries	Non-Catalyst Batteries	
30	86	0.02	0.04	0.5
40	104	0.08	0.15	0.5
50	122	0.14	0.25	0.6

As can be seen from the test data, we found that at all temperatures the float current of the catalyst equipped batteries was half of that of the non-catalyst equipped batteries. In other words, the increased temperatures did not have an effect on the current reducing ability of the catalyst either to increase or decrease its effectiveness. This encouraging result led us to believe that a catalyst could bring some benefit to a 12-volt monobloc battery. The next step was to quantify that benefit.

The testing that yielded the results above was run for a total of 356 days at 50°C. At the end of the test a capacity test was conducted on all of the batteries. Figure 2 below shows the results of the capacity test.
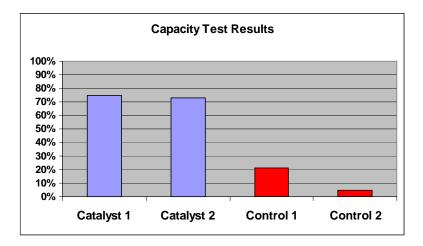

Figure 2

As can be seen from the graph (Figure 2) the capacity measurements from the two catalyst equipped batteries were very different from the controls. We then looked through the conductance readings that we had taken on these batteries throughout the test to see if we could determine or infer at what point in the test that the batteries had failed; we looked for a similar point of change for both groups. The following table presents the time to failure as inferred from our conductance measurements.

Time to Battery Failure Based on Conductance	
Catalyst Batteries	350 Days
Control Batteries	250 Days

As can be seen from the table, the catalyst equipped batteries were able to run an extra 100 days before reaching their point of failure. This is a 40% increase in life. After the capacity test, a tear down and inspection of the batteries was performed, which also yielded differences. The non-catalyst equipped batteries suffered from dry out, positive grid corrosion and growth that lead to internal shorting of the battery and had battery jar cracks. The catalyst equipped batteries were still sufficiently wet (not suffering from dry out) and had minimal positive grid corrosion and growth. In other words, the catalyst equipped batteries where in much better physical shape than the non-catalyst batteries. The results of the tear down test were in line with the capacity and life measurements.

As commentary on our test, it must be pointed out that the catalysts used in this test were our 1 amp Microcat® catalyst that is used in 2-volt VRLA cells. This catalyst design is physically too large to fit into each cell of a monobloc battery in a production mode. Also, it must be stressed that the results presented are from only one test and that they must be repeated on a large scale with an appropriately sized catalyst.

Our next steps are:
- Develop an appropriately sized catalyst for use in monobloc batteries that will fit in the space constrained environment.
- Conduct further testing on an expanded scale to measure the impact of the catalyst on:
  - Float current
  - Capacity
  - Life
  - Positive grid corrosion
  - Dry out
- In the course of our testing measure the polarization of the positive and negative plates of the batteries to determine the impact of the catalyst on the batteries reactions at high temperature.

CONCLUSION

12-volt monobloc VRLA batteries are being used in outside plant applications where they are being exposed to high operating temperatures. This is dramatically shortening the life of these batteries where the cost effectiveness of this battery type is being called into question. The relatively low cost of the battery is being outweighed by the higher cost of frequent replacement. The continued pressure to supply batteries to uncontrolled outside plants locations is causing the industry to look for solutions to the growing problem of shorter than expected battery life. Yes, there is an expectation management issue because the batteries are being exposed to temperatures beyond the design intent, but at the end of day battery users want cost effective, energy dense 12-volt monobloc VRLA batteries to deliver a reasonable life.

Our initial testing indicates that the use of a catalyst may allow 12-volt monobloc VRLA batteries to obtain a more reasonable service life in high temperature environments. More research is required, but the base work that has been accomplished combines the understanding of lead acid batteries gained over the last one hundred years with the latest thinking on ways to improve the technology. If our work is successful and a catalyst can allow monobloc batteries to achieve a longer actual life in high temperature applications, then the economic viability of the product will improve beyond today's level. Lead acid battery technology still remains a low cost and robust energy storage platform and the inclusion of a catalyst into 12-volt monobloc VRLA batteries may be an important component that allows the battery to achieve its maximum life.

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