Developing Monobloc Batteries for High Temperature Applications

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History

There is an ever increasing need for Valve Regulated Lead Acid (VRLA) batteries that can last at high temperatures. The need is for uncontrolled temperature outside plant environments and temperature controlled environments. The main focus of this project was for the uncontrolled environment applications. However, it is logical to think that in controlled environments, if a battery can operate at slightly elevated temperatures, then the air conditioning loads can be decreased. This concept and the related cost savings have been the topics of many discussions.

It is commonly accepted that standard telecom design VRLA products last only a few years in uncontrolled environments.[1] Some users replace their batteries at intervals as frequent as every year. Unfortunately, due to the costs associated with conducting capacity tests in the field, there isn't a lot of actual capacity data available.

Most specifications in the United States reference a temperature of 25°C (77°F) as the recommended battery operating temperature. There is a penalty in product life as temperatures increase and a penalty in capacity when temperatures decrease. These penalties are mainly due to the fact that reaction rates double for approximately every 10°C increase in temperature.

The Beginning

The project started in 2009 with a blank sheet of paper and the task of developing a monobloc battery for high temperature applications. This immediately spurred several questions, such as: What is high temperature? What is the application and how often is it cycled? How long does it have to last? After reviewing historical data and talking with customers, the focus became developing a battery for continuous operation at 50°C while at the same time not compromising cycle life or discharge capacity.

To address product longevity, project goals were developed in the following three phases:

- Phase I - Develop a battery that would last twice as long as current products.
- Phase II - Review the results of the Phase I testing and develop a battery that would last three years at a continuous temperature of 50°C.
- Phase III - Evaluate the results of Phase II and develop a battery that would last five years at 50°C.

To put five years at 50°C in perspective with VRLA, (if you apply the Telcordia multiplier of 6.6 for 50°C), it is equivalent to a battery that would last 33 years at 25°C. This project was focused on enhancing the high temperature life of 12 volt monobloc batteries, not 2 volt cells that typically achieve longer high temp life as a result of thick grids.

Historically, the primary modes of failure in 50°C and 60°C tests of our products have been grid corrosion and dry out induced loss of compression/continuity. The following list was developed to show the majority of potential failure modes that could develop at high temperature:

1) Positive active material softening
2) Shorting
3) Leaks

4) Passivation PCL-1
5) Dry out
6) Loss of compression
7) Grid corrosion
8) Strap corrosion
9) Negative depolarization

As soon as one mode of failure is fixed, another mode of failure needs to be addressed. Therefore an attempt was made to address each mode of failure, even if it wasn't currently one of the main causes.

One of the primary focuses of the project became reducing float currents. Reducing float current in a properly balanced cell can combat most of the common failure modes encountered at high temperatures. After an extensive review of internal historical test data and published papers, it was determined that there were five items that were already proven and should be part of a high temperature battery.

Proven Items

Microcat Catalyst – Targeted Failure Modes (1,5,7,8,9)

It was obvious that a catalyst would be needed in a battery designed for high temperature. The Philadelphia Scientific Microcat catalyst is a precious metal based catalyst that utilizes a poison filter to prevent contamination from amines, stibines, arsines and more importantly hydrogen sulfide. The Microcat recombines hydrogen and oxygen produced within a cell back to water. This reduces water loss but more importantly, it maintains negative polarization by removing some of the excess oxygen that would typically oxidize and depolarize the negative plates. By maintaining negative polarization, negative plate walk down is prevented, float currents are reduced and therefore so is grid corrosion and water loss.[2,3,4] After more than a decade of testing the Microcat, one thing has become undisputable; the higher the operating temperature becomes, the more beneficial the Microcat catalyst becomes.

During initial testing, a catalyst that was designed for use in monobloc batteries was utilized. The test results showed only a minor change in float currents at elevated temperatures and no significant increase in life at 60°C. Several additional tests were conducted that utilized two of the monobloc catalysts per cell. Figure 1 shows the float current of three batteries while on charge at 13.5 volts at 60°C. Two monobloc catalysts were added to each cell of the battery with the highest float current and one monobloc catalyst was added to each cell of the battery with the second highest current. In this test, an immediate reduction in float current was seen in both variables. A discharge and recharge was conducted and after the recharge, the float current of the battery with two monobloc catalysts was obviously the lowest. The other interesting thing to note is that the current of the battery without monobloc catalysts was steadily increasing while the monobloc catalyst equipped cells remained stable. Several additional tests were conducted that produced very similar results, with tests showing up to a 50% decrease in current with two monobloc catalysts installed. Therefore, two monobloc catalysts were inserted into each cell of all of the high temperature test batteries. Based on these findings and numerous other tests, Philadelphia Scientific has modified their design to increase the recombination efficiency to align with our requirements.

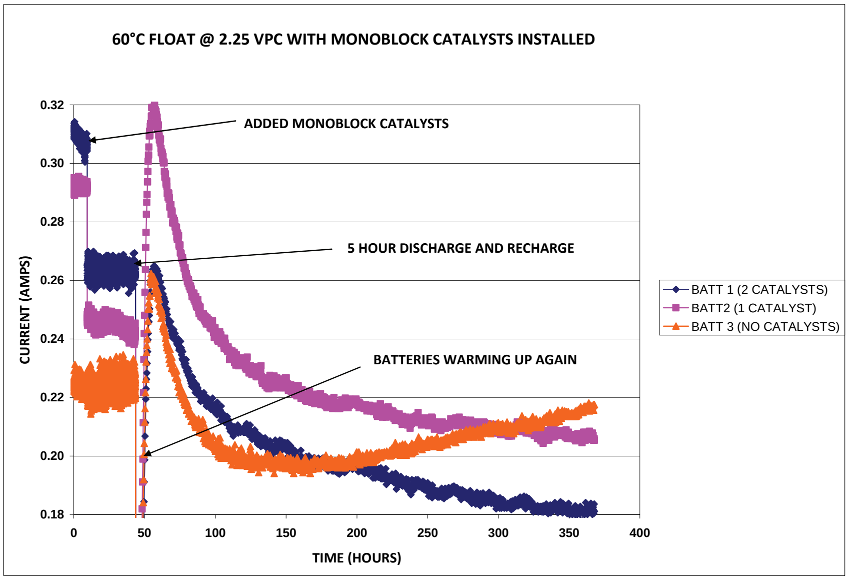

Figure 1 - Float Current

Negative Plate Additive - Targeted Failure Modes (1,5,7)

Previous high temperature tests on various paste additives showed one that caused a substantial decrease in high temperature float current. As shown in Figure 2, the additive reduced 60°C float current by almost 75%. It also caused a substantial increase in life at 60°C. Therefore, the additive was used in all of the test batteries.

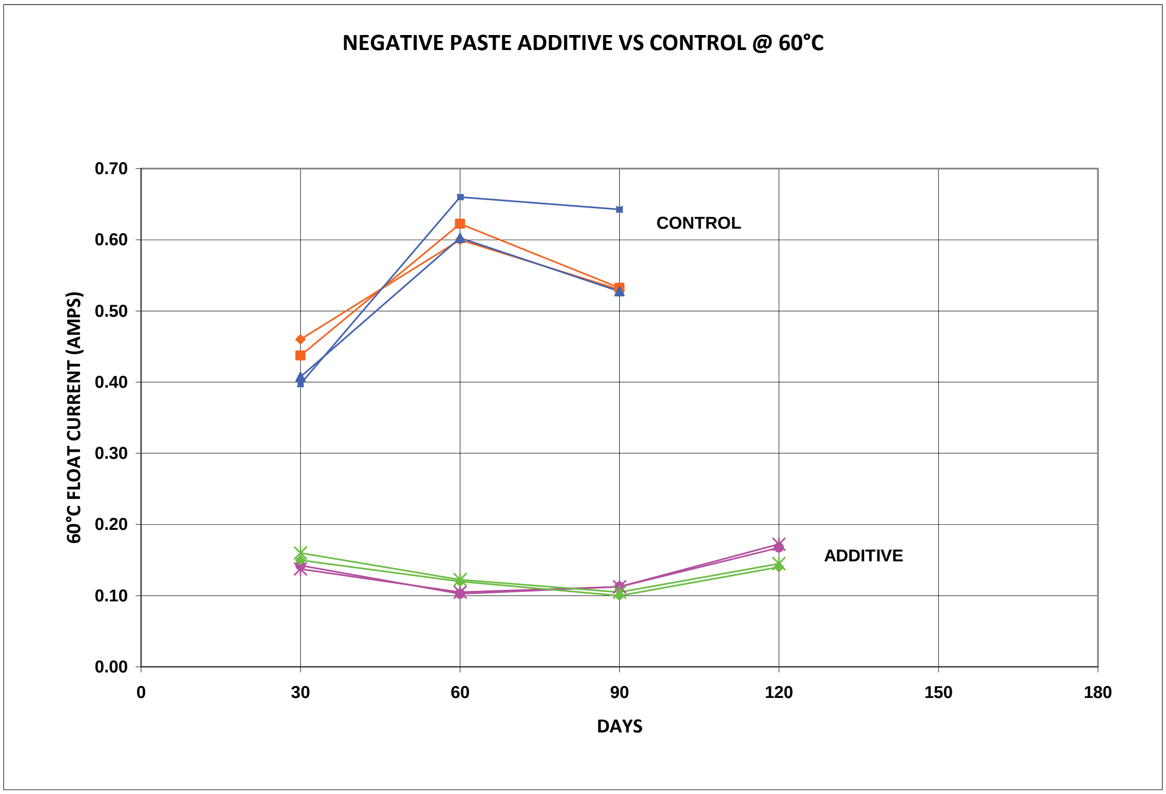

Figure 2 - Additives

Selenium in the Top Lead - Targeted Failure Modes (8)

Selenium is a grain refiner that is used in the top lead of a fair amount of commercially available VRLA batteries. Its benefit in preventing negative strap corrosion has been well documented.[5] Even though negative strap corrosion was not a typical failure mode of high temperature tested batteries, selenium was used as a preemptive solution.

Stiffer Case to Reduce Cell Bulging and Maintain Compression – Targeted Failure Mode (6)

As temperatures and internal pressures are increased, all plastics begin to yield. When this occurs in a battery container, it causes an increase in resistance and loss of continuity between plates. Testing has shown that by reducing the container bulge, high temperature life can be significantly increased. Plastics have a large number of measurable quantifiable aspects that can be compared. Comparing all of the aspects is only the beginning of choosing the right plastic for high temperature battery applications. In addition to requiring a high heat deflection temperature and low water vapor transmission, the plastic needed to lend itself to current molding and processing methods. The plastic selected for the test batteries met all of these parameters.

Positive Grid Alloy – Targeted Failure Mode (4,7)

Reducing grid corrosion is a significant factor in determining high temperature life. A substantial amount of grid corrosion/plate growth testing had already been completed that showed one alloy outperforming the rest (Figure 3). That alloy was chosen for all test batteries.

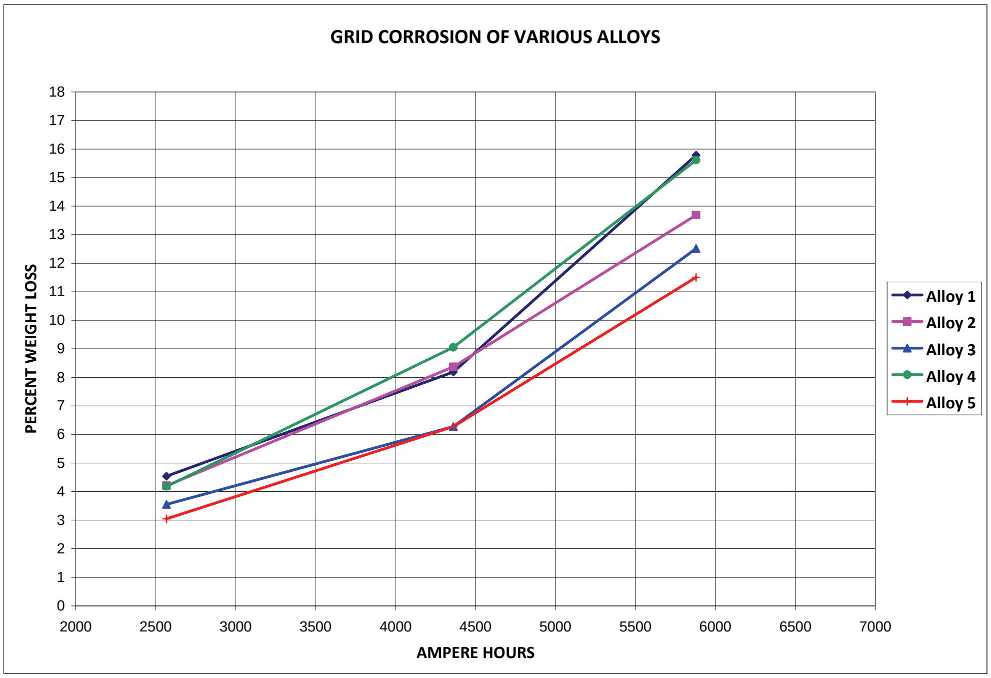

Figure 3 - Alloys

Unproven Items/Design of Experiment

A common approach to testing new ideas is to test one idea at a time, review the results, then try another idea and review the results. This method is very time consuming and adds many variables to the experiment because trials are run at different times. In between the test runs, equipment, operators, temperatures, humidity and many other parameters can change. Design of Experiment (DOE) is a method of testing several ideas at one time while being able to statistically determine which changes had the greatest impact on the results. It also typically facilitates a reduction in the number of samples required to gather reliable data.

After the historical data was reviewed and all of the proven items were agreed upon, a list of possible ideas that could enhance high temperature life was developed. In addition, component suppliers were contacted and asked to provide their best solution for the targeted applications and project goals. From the list and supplier input, five items were selected and incorporated into a five factor design of experiment. The items are listed in detail below.

No Lignin vs. High Temp Expander – Targeted Failure Mode (1,5,7,8,9)

Expanders, in general, are added to the negative paste in small amounts to prevent the contraction and solidification of the spongy lead and consequent loss of capacity and life. Expanders typically contain carbon, barium sulfate and an organic lignosulfonate (lignin). Lignin is extracted from soft woods and is strongly absorbed on the surface of the lead, therefore increasing surface area, high rate discharge performance and cycle life.[6] The use of lignin in lead acid batteries can be traced back to early cells that were built with wood sheet separators. When the wood separators were replaced with "wood free" separators, premature capacity decay of the negative electrode was encountered. As a result, sawdust was added to counteract the premature decay. Since that time there have been many lignins that have been developed and tested, including synthetics. Even though there has been published information that relates the addition of lignin to an increase in voltage (decrease in float current), our supplier had data indicating the opposite.[7] It was believed that removing the lignin from the expander would cause a decrease in current at high temperature. Even though a decrease in cycle life was expected, it was thought that the increase in high temperature life could be significant enough to outweigh the reduction. Therefore a no lignin variable was tested along with an expander that was recommended by the supplier for use in high temperature applications.

2psi vs. 4psi Pressure Relief Valve – Targeted Failure Mode (5)

Valve regulated products contain a pressure relief valve. The one way valve is designed to allow excess gas to exit the battery when a certain internal pressure is reached, while not allowing gasses to enter the cell.

Laboratory testing of valves from most prismatic VRLA batteries has shown typical opening pressures between .3 and 6.5 psi.

There have been two theories about the benefits of selecting high or low pressure valves. One theory is that by increasing the operating pressure of the valve, it forces more internal recombination and will not open as often as a lower pressure valve. The other theory is that a low pressure valve will not cause as much case bulging and even though it will open more often, it will not expel as much gas each time that it opens. To test out the two theories, two valve pressures were selected for testing, 2psi and 4psi.

Overpaste - Thick vs. Thin – Targeted Failure Mode (5)

In an effort to get more electrolyte into each cell, the thickness of the standard positive plate was reduced by .007". The .007" reduction in plate thickness resulted in a 1% increase in electrolyte volume. This was only a reduction in the thickness that each grid was overpasted. The grid thickness remained the same; therefore grid life due to corrosion was not compromised. Standard thickness plates and reduced thickness plates were selected for testing. Separators were selected to maintain the same cell compression in both cases.

Positive Active Material Density – Targeted Failure Mode (1)

An increase in the density of the positive active material results in reduced initial capacity. However, the benefit is typically a longer time before the material becomes soft/sulfated and inactive. The standard density paste was compared to a high density paste.

AGM/Gel Combination (Fringe Gel) – Targeted Failure Mode (5)

A Hollingsworth and Vose patent explains the benefits of using a “fringe gel” where the sulfuric acid is mixed with a never dried precipitated silica slurry.[8] The acid/silica slurry is added to an AGM cell. The silica forms agglomerates with an average size of approximately 15um. The active material in the battery has pore sizes that typically range from .1 to 2um and the separators have an average pore size of 5um. As the acid/silica slurry mixture is added to the battery, only the acid penetrates the separators and plates due to pore size. Therefore, the silica dioxide concentration in the acid around and on top of the cell increases to >12% and starts to form gel. The fringe gel increases the amount of electrolyte in each cell by approximately 6%. In theory, the gel should also benefit heat transfer and possibly force greater recombination. Batteries were built with and without fringe gel.

The Test

A group of 36 test batteries were constructed. All of the batteries contained the five items that were already proven to enhance high temperature life (two monobloc catalysts per cell, stiffer plastic, Se in the top lead, negative paste additive, and enhanced positive grid alloy). The five unproven items (expanders, valve pressure, paste density, plate thickness and fringe gel) were inserted into the 5 factor, 16 variable design of experiment matrix (Figure 4).

BATTERY #	VARIABLE	EXPANDER	VALVE PRESSURE (psi)	POS PLATE OVERPASTE THK. (in.)	GEL BLANKET	POSITIVE CUBE WEIGHT
1	V1B1	High Temp	2	0.008	None	High
2	V1B2	High Temp	2	0.008	None	High
3	V2B1	No Lignin	2	0.008	None	Standard
4	V2B2	No Lignin	2	0.008	None	Standard
5	V3B1	High Temp	4	0.008	None	Standard
6	V3B2	High Temp	4	0.008	None	Standard
7	V4B1	No Lignin	4	0.008	None	High
8	V4B2	No Lignin	4	0.008	None	High
9	V5B1	High Temp	2	0.015	None	Standard
10	V5B2	High Temp	2	0.015	None	Standard
11	V6B1	No Lignin	2	0.015	None	High
12	V6B2	No Lignin	2	0.015	None	High
13	V7B1	High Temp	4	0.015	None	High
14	V7B2	High Temp	4	0.015	None	High
15	V8B1	No Lignin	4	0.015	None	Standard
16	V8B2	No Lignin	4	0.015	None	Standard
17	V9B1	High Temp	2	0.008	Blanket	Standard
18	V9B2	High Temp	2	0.008	Blanket	Standard
19	V10B1	No Lignin	2	0.008	Blanket	High
20	V10V2	No Lignin	2	0.008	Blanket	High
21	V11B1	High Temp	4	0.008	Blanket	High
22	V11B2	High Temp	4	0.008	Blanket	High
23	V12B1	No Lignin	4	0.008	Blanket	Standard
24	V12B2	No Lignin	4	0.008	Blanket	Standard
25	V13B1	High Temp	2	0.015	Blanket	High
26	V13B2	High Temp	2	0.015	Blanket	High
27	V14B1	No Lignin	2	0.015	Blanket	Standard
28	V14B2	No Lignin	2	0.015	Blanket	Standard
29	V15B1	High Temp	4	0.015	Blanket	Standard
30	V15B2	High Temp	4	0.015	Blanket	Standard
31	V16B1	No Lignin	4	0.015	Blanket	High
32	V16B2	No Lignin	4	0.015	Blanket	High

Figure 4 - Experiment Matrix

Although the focus of the project was continuous 50°C, it was decided that the batteries should be tested at 60°C to reduce the testing time required to get results. An initial 5 hour discharge was conducted on all of the batteries. After a full recharge, the batteries were placed in an oven set at 60°C. Every 30 days, the batteries were returned to room temperature and a 5 hour discharge was conducted. The test continued until all batteries failed to make 80% of capacity.

Results

DOE/High temperature test

After 180 days at 60°C, the batteries divided into two distinct groups, all of which was associated with the expander. It was obvious that the no lignin batteries were failing much quicker than the high temperature expander batteries (Figure 5).

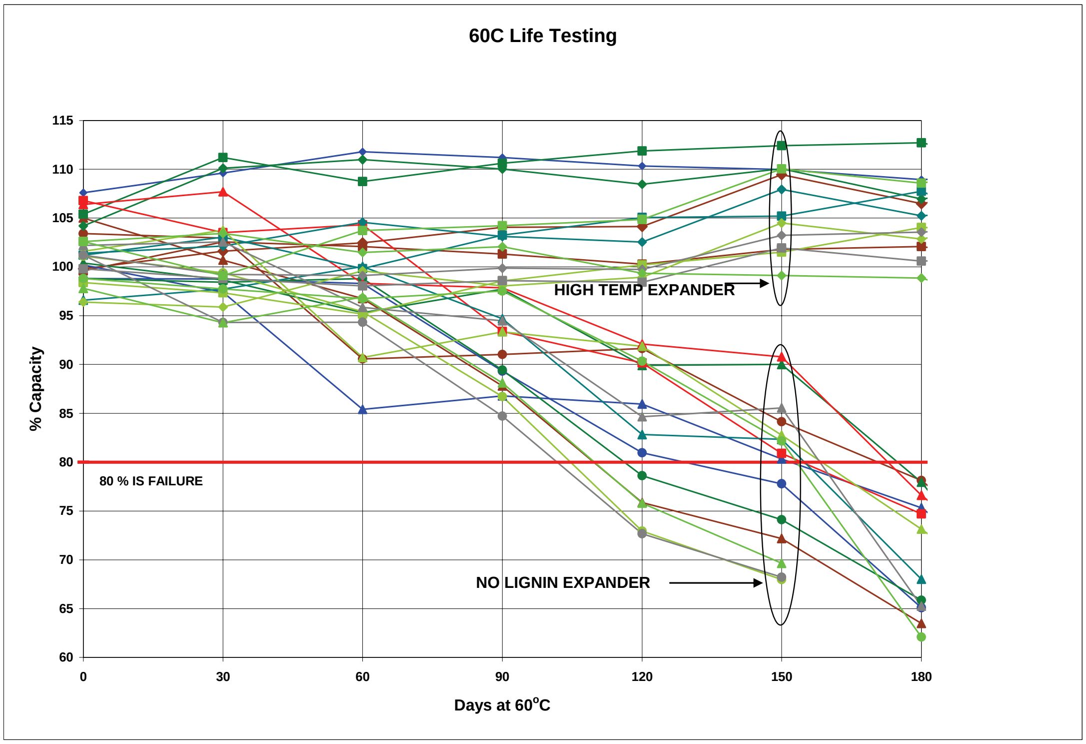

Figure 5 - Expander

Figure 6 is a main effects plot that shows the effect of each of the remaining factors of the DOE. A further analysis of the data showed that only the high temp expander caused a statistically significant increase in life.

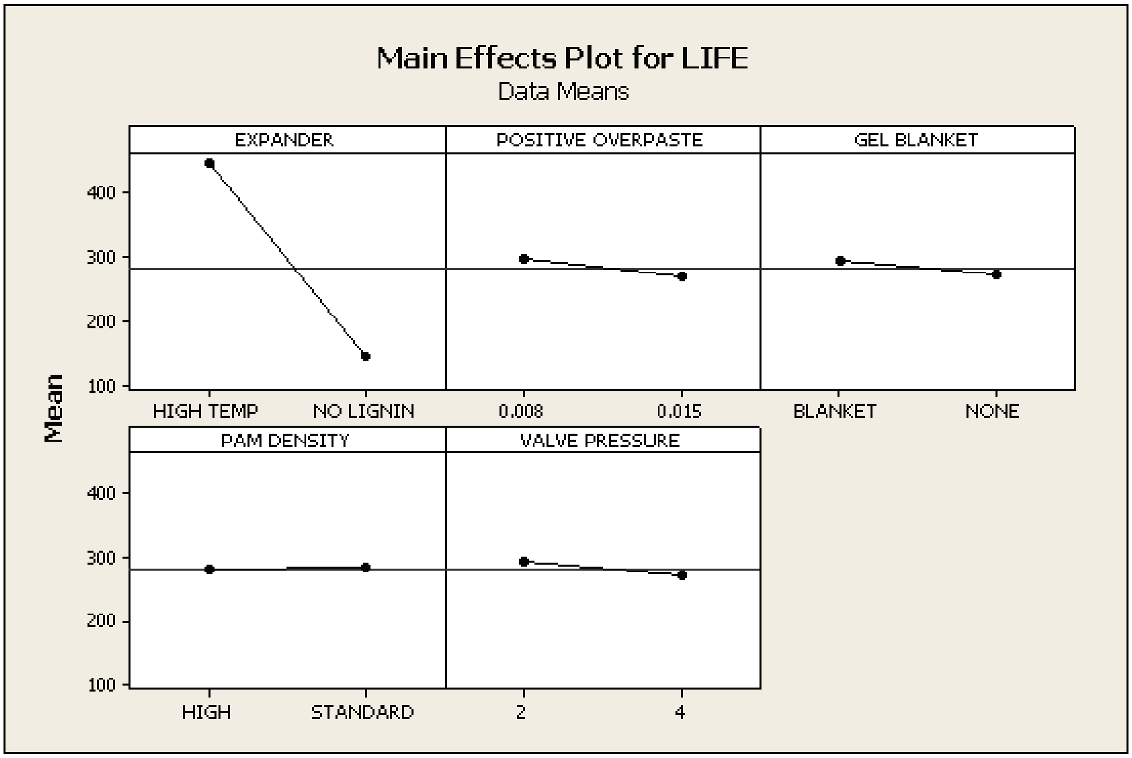

Figure 6 - Main Effects Plot

An analysis of valve opening pressure and closing pressure vs. water loss was also conducted, which showed neither making a statistical difference.

After 540 Days at 60° C, the test concluded with the results shown in Figure 7. One of the batteries failed early due to a case to cover seal leak and another battery failed early due to a short that was caused by shedding of strap material. It was found that lead straps that incorporate selenium do not crystallize and crack like non-selenium straps; however, it appears that the tighter grain structure results in more shedding. The two premature failure batteries were not included in any of the final analysis.

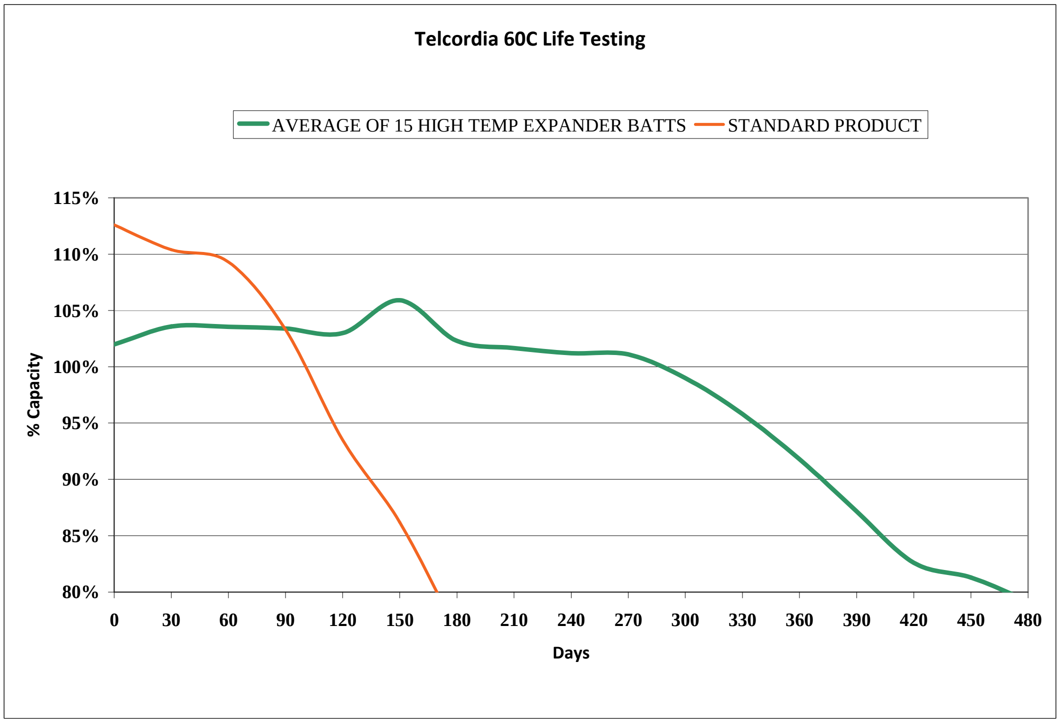

Figure 7 - Accelerated Life Testing

The main mode of failure was positive grid corrosion and positive paste softening. Knowing that, it is no surprise that items specifically incorporated to prevent dry out, such as valve pressure, paste thickness and the fringe gel did not increase life.

Conclusions

The Phase I goal of this project was to double the high temperature life of VRLA batteries. By reviewing historical internal test data, published technical reports and relying on the expertise of component suppliers, that goal has been met. The life of standard products at high temperature has almost tripled by combining proper design and testing.

Future Work

The next phase of testing is already in progress and will focus on enhancing grid corrosion resistance. A positive paste additive that has already been proven to prevent positive paste degradation during cycling, will also be tested at elevated temperatures. Short protectors will also be incorporated to prevent shorts as a result of strap mossing/shedding.

Temperature recorders were deployed in outside cabinets in some of the hottest areas in the United States. The data is being reviewed and methods of forecasting actual battery life in outside cabinets are being explored.

References

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