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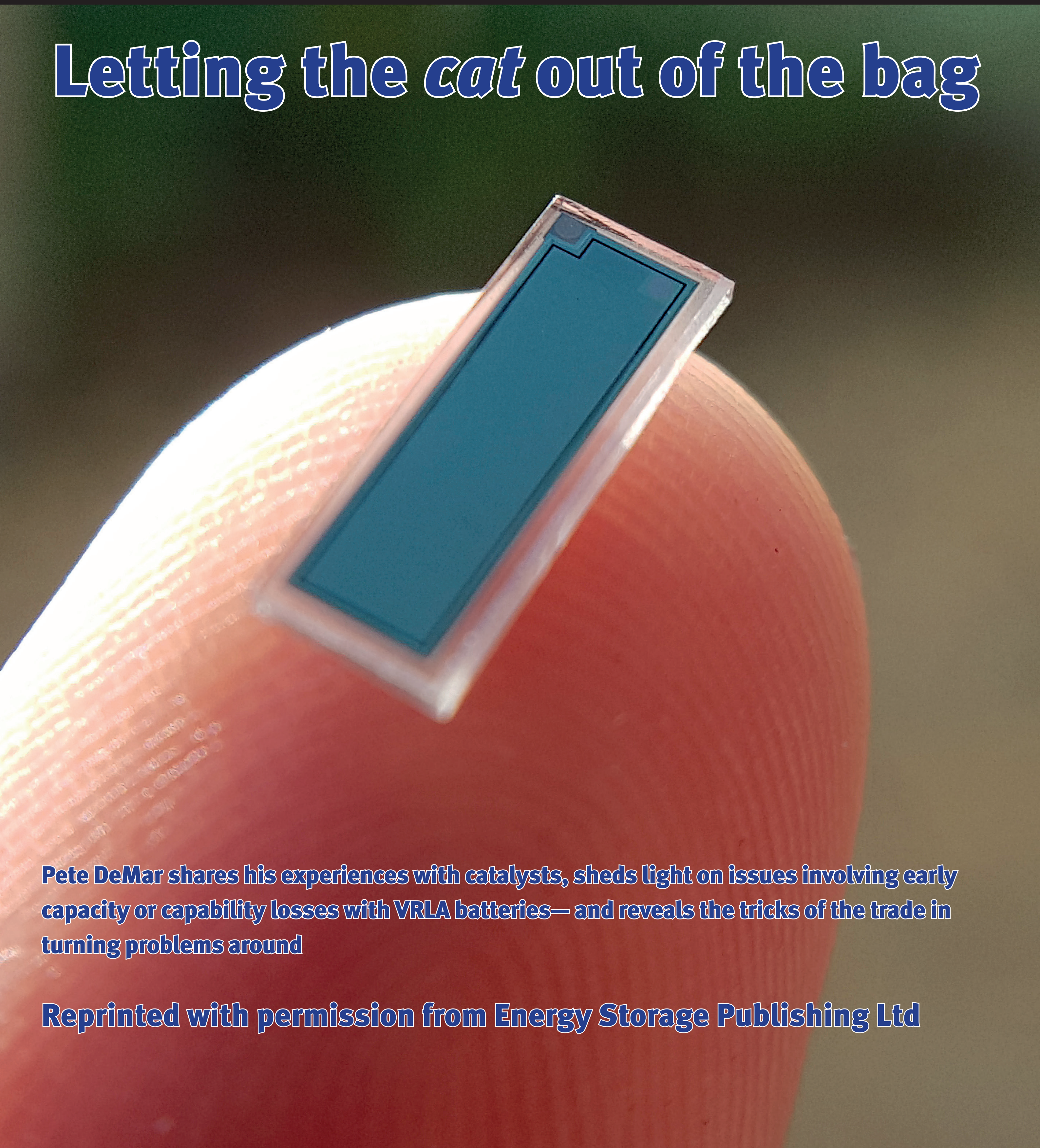
Letting the *cat* out of the bag



Pete DeMar shares his experiences with catalysts, sheds light on issues involving early capacity or capability losses with VRLA batteries— and reveals the tricks of the trade in turning problems around

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Letting the *cat* out of the bag

Pete DeMar, an independent battery testing expert and founder of Battery Research and Testing Inc, shares his experiences with catalysts, sheds light on issues involving early capacity or capability losses with VRLA batteries— and reveals the tricks of the trade in turning problems around. Inducted into the Battcon Hall of Fame, Pete is the inventor of the internal ohmic value recovery (IOVR+™) process.

Our introduction into, education on, and experience with understanding the benefits of catalysts with VRLA stationary batteries goes back more than 20 years, and it all started in 1994 with our trying to help United Telephone in Florida recover lost capacity in a number of very young VRLA battery strings.

While the general concept of how a catalyst works by re-combining hydrogen and oxygen back into water is the same with all battery catalysts/ re-combiners, the benefits vary from vented cells of either lead-acid or nickel-cadmium designs to the VRLA models. With vented cells it is easy to understand that there are labour savings from the reduction in time required for maintaining the electrolyte levels.

With VRLA cells, the benefit from using a catalyst is much greater than in any vented cell. In vented cells, the electrolyte levels can normally be observed and water easily added even though that can be time consuming. However no VRLA cell can function properly when undersaturated. For them to function properly, and not go into a thermal runaway, they must be saturated. By recombining the hydrogen and oxygen inside of the cell, the plates and AGM stay saturated and in contact with each other. Also, by the catalyst preventing some of the oxygen from getting to the negatives, it helps keep them properly charged.

In 1995, we performed capacity testing across the state of Florida for United Telephone on sites that had GNB Absolyte strings. Most were remote sites and had one or two 24-cell strings. All were the individual 2V cells, and were 4-6 years old. The results were dismal, with massive failure to meet their 80% ratings. All sites were climate controlled with telecom quality rectifiers. As part of our pre-discharge test inspections, we were measuring the individual cell impedance values, but not float current back then. It was not until quite a few years later, that we learned how important the float current measurement is to performing predictive maintenance.

Based upon the results, United contacted GNB to address the situation. GNB was fully aware of the issue of PCL (premature capacity loss) in the Absolyte cells and had developed a process called the FAR (field adjustment repair). The basis behind this was that the cells manufactured at that time had not been banded together, and were losing compression. They did not believe that the cells were drying out, but they needed to re-establish contact between the matt and the plates, so they added water to the cells. They had different amounts of water for each different model cell. United had the FAR process performed on all of the strings in their system that we were aware of.

Within a few weeks following the performance of the FAR program, United had us return and perform follow-up discharge tests on all of the systems that we had previously tested. Every string and every cell made improvements and there were no strings that failed their load test.

It is important to understand that the cell impedance readings did not correlate to their capacity. One would expect that the worst impedance would be the weakest cell, or the best would be the best cell. This was not true with the initial testing, or the follow-up. It is true that an improved impedance after the watering, did result in an improved capacity. It also is true that the cells that had the worst impedance's were often the weakest ones but not always.

What was puzzling to us was that often there was still a widespread in the impedances and individual cell capacities. We wanted to understand this better, so we approached United about letting us try an experiment of adding water based upon the impedance values. We learned that we could make improvement in most of the cells that had lower values, and additional follow-up load tests confirmed that the cells in those string were indeed closer to each other. We felt pretty proud of ourselves, and continued to experiment with individual cell impedances as a guide to how much water to add to individual cells. We thought that had found a cure for PCL.

However, it did not take long for our bubble to be burst. In 1996, United had us return for follow-up testing, and we found that the impedances were degrading as were the capacities. They were still better than before the water additions, but were declining. The results of this programme was presented at Battcon 1997. This taught us that the addition of water alone to cells suffering from PCL, will not produce a long term result. Again, we were not measuring float current, and the root cause of PCL was still unknown.

> “Premature capacity loss was occurring everywhere, with all different manufacturers' products...”

It was not until the discovery that most PCL in VRLA batteries was due to negative plate discharge, which leads to an increase in float current that increases off gassing, which increases the rate of dry-out, and so on, that we were able to provide a long term solution.

Back in the 1990s there was plenty of research going on in trying to determine just why there was such substantial failure, and what was the root cause, as dry-out by itself was not the whole story. PCL was occurring everywhere, with all different manufacturers' products, so it was not due to any one specific manufacturer or process, or QC (quality control). Yes, the purer the materials and the better the QC, the better the odds that the cells would last longer, but PCL was rampant, and the only way to determine the batteries capacity/capability was to load test. Internal ohmic measurements would not prove capacity or capability.

The breakthrough research into the root cause of this early life failure phenomena was led by Will Jones, in collaboration with Dr David Feder and Dr Dietrich Berndt and others. They published numerous papers on their research performed in the early 1990s (91-97 I believe), and proved their theories to the world. From their results Will Jones then introduced through Philadelphia Scientific a catalyst for VRLA cells, which addressed that root cause. The catalyst simply sits in the head space of a VRLA cell, scavenges some of the oxygen before it gets to the negative plates, and re-combines the hydrogen and oxygen gases back into water. By this simple process it helps prevent dry-out, and helps keep the negatives from becoming undercharged. And as everyone understands, if the negative plate group is being under charged the positive plate group must be being over charged and forced into abnormal growth, which leads to early life failure.

While we clearly understood by 1997 that adding water alone was not a long term solution for the PCL. We knew that it was a means to help users get out of an emergency and buy them time to make well thought-out decisions. By 1999 we started adding catalysts when we re-saturated the cells and named it the IOVR process. We used those letters because the first thing that was observed was an improvement in the internal ohmic values of the cells, so it became the IOVR (internal ohmic value recovery) process.

We found that sometimes the improvement from before the IOVR process was quite substantial, with some returning to 100% or near that, and some to substantially less than 80%. It did not seem to be manufacturer, model, age, or application dependent. One thing that always held true was that if the internal ohmic values were degraded from what we considered a reasonable baseline for the model cell, there would always be improvements.

Surprisingly, it did not seem to make any real difference in how advanced the positive plate growths were when the process was performed. Often the positive posts had stretched the covers so far that it would seem that they would rip through the covers at any time, but as long as they would hold pressure, we would add water and there would be an improvement. ***Fig 1*** is a good example of a battery with very advanced positive plate growth but which recovered very well, and was kept in service for many more years.

This battery was a 24V string, date code 3/92, and located in a microwave site. It was to be replaced based upon its capacity test result on 18 May 2000 of 32% of its 3-hour rating (58 minutes). This equated to a site support time of 4.7 hours. That site required 8 hours of battery run time. We were then brought into this as a demonstration project for this user, and performed our initial inspection and IOVR process on 14 July 2000. As can be seen in ***Fig 1***, these cells were in the vertical position, and not what is normal in the US where the cells are typically installed horizontally.

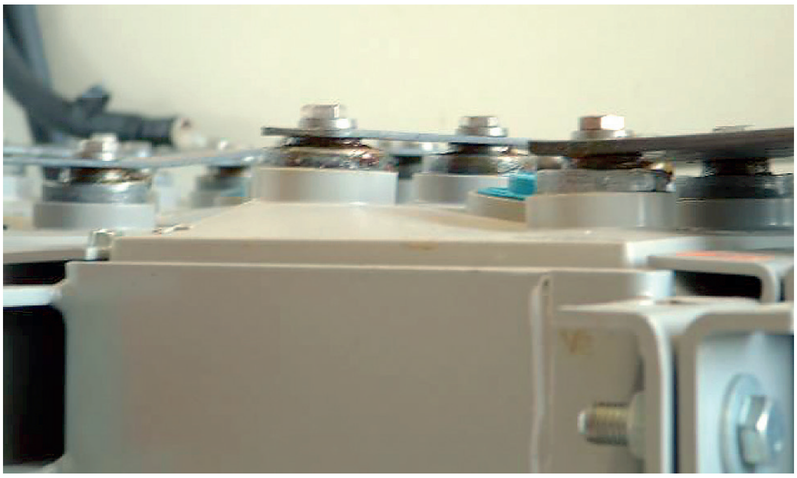


Fig 1: Extensive positive plate growth pushing cover upward around positive post.

Five days later we returned to the site with a temporary battery, charger, and load test equipment and performed a capacity test at the same rate as was previously performed. During the pre-test inspection we noted (as expected) that all of the cells' impedance values had improved. The battery lasted 118 minutes, and the test was terminated at 21V (66% capacity). There were three cells that dropped much faster than the rest. Even though the battery had improved substantially, we felt that it could do better still. So prior to recharging the battery and placing it back into service, we added some more water to those three weakest cells. The recharging was performed at a very elevated voltage.

Fig 2: Capacity changes over time.

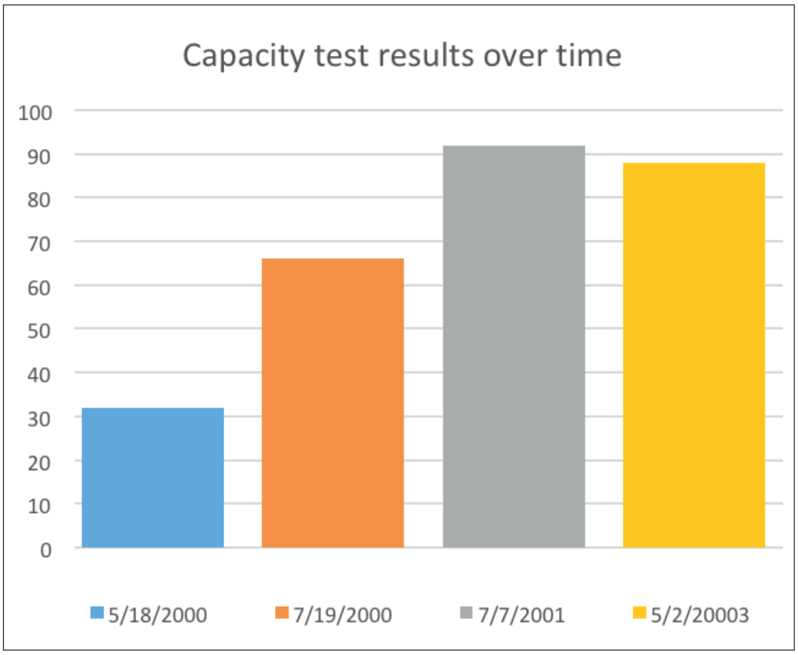


Fig 3: VRLA Negative bus breaking down observed with borescope. Battery on float.

One year later we returned to the site and repeated the capacity test, which lasted 165 minutes before reaching the 21V cut off, which was 92%.

Two years later the user had their original testing company return to the site and perform another test, to confirm our results. The battery tested at 88%. This was three years from when they found it at 32%.

Also of note is that the float current as measured during their original site visit and test was 2.4A and on 2 May 2003 it had been lowered to 0.8A. The float current is a huge indicator of internal issues with these batteries. ***Fig 2*** shows the capacity changes over time.

One more piece to the recovery puzzle we noticed, is that once we had restored a good saturation to the cells, a very high-rate charge often provided a marked increase in the capacity recovery. This was beyond the gains from re-saturation and adding a catalyst. This eventually became known as the IOVR+ process.

In order to prove to ourselves that the very high rate charge was indeed a key beneficial component, we needed to find a good way of verifying the benefits of the different steps. As luck would have it, we gained possession of a 1998 48V, 4,800Ah battery which is actually a model that was assembled as three 1,600Ah cells in parallel. The user had tested the capacity, found it to be less than 30%, and had it replaced. We were not given a copy of the discharge test results, so we did not know the exact capacity, only what we had been told.

We reconfigured this battery into three individual strings of 24 cells (1,600Ah strings). We then performed our standard initial process of adding water of varying amounts, based upon each cell's internal ohmic value, and placed the strings on float on a common bus at 54V. The impedances all showed improvements. Following three weeks on float we tested all three strings, one at a time, and all performed at 60-66%. While that was about a 100% improvement from where they had been, we knew that there was more to be recovered.
We then added more water to string 3; performed a very high rate charge on string 2; added more water, performed a very

Fig 4: Severe negative tab failure, found upon dissection after initial alert with borescope. You can see the negative post/pillar also is decaying.

What have we learned over the years?

1. That PCL can occur with any manufacturer's cells.
2. That dry-out with any VRLA battery is the kiss of death.
3. Hotter-than-standard environments accelerate dry-out.
4. Negative plate self-discharge and under polarisation/charging causes over charging of the positive plates and reduces capacity and life.
5. PCL caused by dry-out or negative plate discharge can be reduced/corrected with any structurally-intact cell, once proper saturation has been established.
6. All manufacturers have made improvements to their products over the years.
7. There is a wide variance in the quality of products from around the globe.
8. All 'pure' lead is not equal.
9. Plate orientation vertical or horizontal (pancake) does not yield any substantial difference in the ability of the cells to recover from PCL.
10. With all things being equal, cells that come with catalysts installed, either from the factory, or early on in their lives before the dry-out begins, will typically provide a longer service life.
11. Cells that have off-gassed to the point where they needed to be re-saturated and high-rate charged, benefit substantially by the addition of catalysts by maintaining their improvement.
12. Catalysts installed on any vented cells severely reduces labour hours for water additions.
13. Float current requirements can vary widely, and float current is one of the very first indicators of an internal issue and is usually the first 'canary in the mine' alert.
14. Temperature differential between the cells and the normal ambient is the second 'canary in the mine' alert.
15. Internal ohmic measurements are not a substitute for a capacity test. Though we have run thousands of capacity tests, we have found no instrument that can prove the capacity of a cell or string. They can show that there are issues that are causing abnormalities in the cells, which will require you to investigate further, but will not provide a capacity or capability answer.
16. Thermal runaway is still a substantial failure issue, both as expected with VRLA batteries, but also with VLA ones.
17. Thermal runaway issues can be detected many months, or in some cases, years in advance.
18. Thermal runaway prevention requires just four measurements on the battery string, which takes less than 5 minutes, but most users do not perform those four measurements correctly, or they do not know what is good or bad, or track the readings. There is a free programme that all the user needs to do is to enter the model of the cell, and a little other data, and then when they enter the four readings needed will provide alerts as appropriate. It takes the guess work out of thermal runaway prevention.
19. That there are known 'good' values for every battery model out there, means that 'questionable/bad' values are also known.
20. With VRLA batteries the predominant failure issues revolve around the negative elements.
21. With VLA batteries the predominant failure modes revolve around the positive elements.
22. With VRLA cells a borescope is an invaluable tool to diagnose abnormal issues. See ***Fig 3***.
23. With VLA cells, the naked eye, a good flashlight, and a borescope are the most valuable tools for detecting bad things, and a recurring failure point is the internal positive post seal and nodular corrosion, with its resulting problems. ***Fig 5*** shows an issue detected this way.

high rate charge and added catalysts to string 1.

We waited another three weeks and repeated the testing. String 1 made 94%, string 2 was at 88%, and string 3 was at 69%.

We then added more water, performed a very high rate charge and added catalysts to string 2. We performed a very high rate charge and added catalysts to string 3. After a three-week wait, string 2 tested at 95% and string 3 at 100.6%.

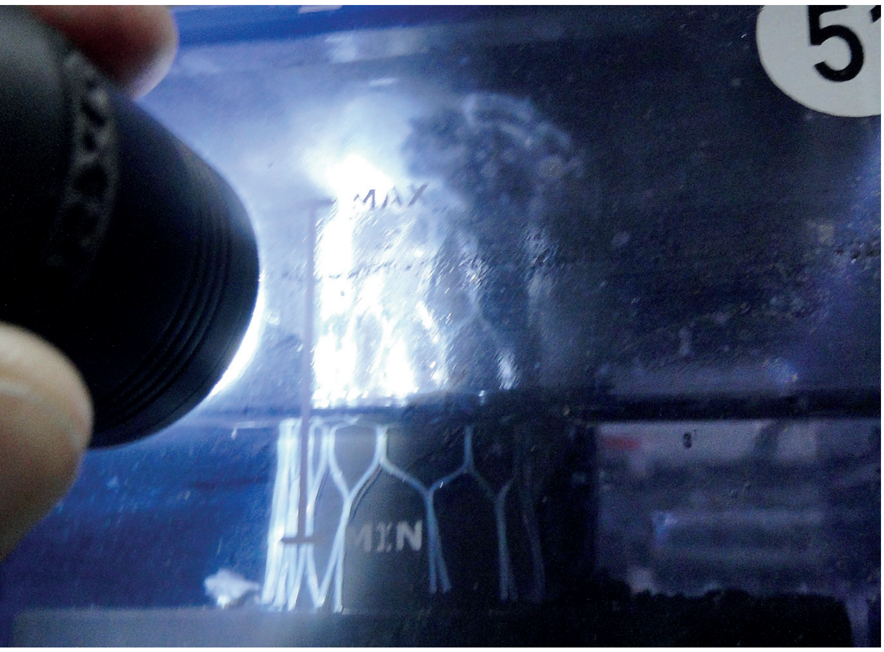
So far in our quest to understand why VRLA cells were failing from PCL, we had utilised reference electrodes to verify Will Jones' findings as to the negative plates becoming undercharged while under normal float. We also took into account Bruce Dick's (C&D) findings on the voltage needed to get the negatives recharged when they are sulfated. We utilised prismatic hydrometers to verify that the acid density as found was substantially elevated— which proved that water had been lost from the cells. The improvements in the internal ohmic values, reductions in the required float currents, and extended run times (capacity) before and after the IOVR+ process, showed us that we had finally figured out a means to recover strings and make that a long-term recovery.

It took many years to accomplish but we were eventually able to obtain letters from all four of the big US manufacturers stating that BR&T replacing their standard vents with catalyst equipped ones would not void their warranty. Additionally we offered a 100% money back guarantee that if we performed the IOVR+ process on structurally-intact cells and did not make improvements to the internal ohmic values, we would not charge for our work. There has been one single battery string (out of thousands) that we ended up not charging for our work... Still trying to understand that one!

By repeated demonstrations that the process was beneficial for users of VRLA batteries, the IEEE battery standards group (as know then) created and published the IEEE 1188a2014 document. That document called the process the "Special Recover Process", and was written following many years of proof of the methods that BR&T had developed. The IEEE1188a2014 document addressed batteries that were already suffering from PCL and was a re-active approach to the problem. What it did not address was the utilisation of the process pro-actively as a way to stop the degradation before it ever occured.

Figs 5-7 show the internal post seal failure from a number of cells in one particular battery string. This is an OPzS battery, that is less than 6 years old and on float service at a power plant. It was well maintained and just a little over a year prior to our inspection (May 2019) the battery had passed its load test.

The goal of the internal post



Figs 5 & 6: VLA positive internal post seal failure discovered with a flashlight.

seal (either positive or negative) is that it keeps electrolyte from migrating up into the area between the inner post seal and the outer post seal. In some cases you will see electrolyte on the cover, around the external positive post seal. However, in these cells there was no electrolyte on the cover and the external post seals did not show any signs of anything abnormal.

However, in some cases, as in these, the electrolyte gets past the internal positive post seal and then causes the post/pillar inside that space to be attacked. The post/pillar starts to corrode/degrade and it expands. When it expands it puts more pressure on that plastic post seal and the plastic cracks.

As the problem continues to degrade, more plastic ruptures and it goes on and on. While this degradation is occurring, the resistance of that post/pillar increases and becomes more of a voltage dropper.

We were called to this because the unit had tripped, which should not have been a problem, but one cell in the battery failed open, and the lube oil pump stopped pumping oil to the bearings, so the generator came to a grinding halt. No one had any idea of why that occurred, after all, all of the inspections and the capacity test showed that the battery was in good condition.

As the cause of failure was unknown and could happen again, the insurance company recommended that the plant contact us to see if we could determine what caused that failure, and to determine if they had other cells that could fail this way. We found a total of five more cells experiencing various stages of failure.

We found the first two cells with just a flashlight, then the other three with a borescope. The insurer told me that when all was said and done it would be just a little under $10M in losses.

In summation, we know of no downsides to the usage of catalysts in any VLA or VRLA cell. They cannot do any damage, but do provide substantial benefits. Until recently, the availability of catalyst equipped vent assemblies for vented cells was limited, but with the introduction of new recombiner designs, pretty much all manufactures' cells can benefit.

We once kept all of our research information such as expected 'good' internal ohmic values, float currents, model specific re-saturation volumes, and procedures to ourselves. However, we now share that information with any users, or battery service companies that sign an IOVR+ confidentiality agreement. In addition we will provide hands-on, onsite training for those companies

Over the years, as we serviced new manufacturers' products from around the world, we benefitted substantially because we had to create catalyst-equipped assemblies for those models. We presently have catalyst-equipped vent assemblies that fit what we believe are more than 80% of the 2V VRLA battery models produced anywhere. In addition, we now have catalysts specifically designed for applications where the expected ambient is going to be substantially above the manufacturer-recommended ranges, or where the float currents are higher than normal.

Hopefully this information sheds some light on our experiences with catalysts, and is beneficial to the readers of *BEST magazine*.

Fig 7: VLA internal positive post seal failure observed with borescope