

# Float Life Verification of a VRLA Battery Utilizing a High Purity Electrochemical System

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**Abstract** - Claims made at recent INTELEC battery workshops suggest that VRLA batteries may have a reliable life limited to as little as 2 years in standby applications. Furthermore, several published papers propose that one of the inherent failure modes is loss of capacity of the negative electrode.

This paper examines float life verification of commercially available high purity VRLA batteries in light of this recent concern regarding negative electrode capacity loss and includes data from real-time room temperature float testing which has been ongoing well in excess of 10 years.

The condition of the negative electrode, from both new and real-time aged product, has been carefully examined by both electrochemical measurements of the product and also by analyzing the morphology and crystallography of the plates. The condition of the positive grid has also been examined to determine the extent of corrosion.

In conclusion, this paper demonstrates that by using a high purity VRLA technology, which has been commercially available for 25 years, it is possible to far exceed 2 years of reliable service. Properly designed batteries using this technology have been proven to deliver greater than 13 years in real-time float service.

## 1. Introduction

Recent INTELEC workshops have focused on the perceived shortfalls of VRLA batteries in telecommunication applications. In particular, the ability of the negative electrode to maintain a full state of charge throughout life has been questioned. Several papers have been published that elegantly postulate a mechanism for the decline in negative electrode capacity throughout the batteries float life<sup>(1)</sup>.

The following is a brief explanation of the negative plate run down mechanism whilst in a float application. Figure 1 depicts the flow of current into and out of a VRLA battery whilst under float charge conditions.

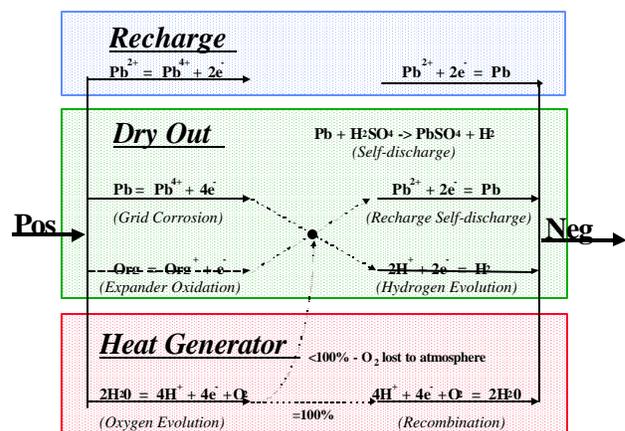


Figure 1 – VRLA Current Flow

There are three areas to consider, namely:

1. Recharge – immediately following a discharge the predominant mechanisms are the recharge of both electrodes. Due to the inefficiencies associated with these recharge processes, the two electrodes tend to recharge at different rates dependent upon, amongst other things, the state-of-charge of the individual electrode. For the purpose of this paper we assume that recharge has been completed.
2. Dry Out – the consumption of water through the corrosion of the positive grid material and the loss of hydrogen gas either via self-discharge (local action) or via hydrogen ion reduction. Other minor reactions can contribute to the current flow within this region such as oxidation of organic expanders that have

leached from the negative electrode or the loss of oxygen gas from the cell.

- Heat Generator – this describes the recombination process whereby oxygen generated at the positive is reduced to water at the negative electrode, with the subsequent generation of heat. If the recombination process is 100% efficient then the two partial currents perfectly balance one another.

If we make the assumptions during float operation that, a) the battery is fully recharged, b) that it is behaving in a 100% efficient recombination mode and, c) that side reactions such as organic expander oxidation at the positive electrode are minimized, then we need only consider the simplified ‘Dry Out’ portion as shown in Figure 2.

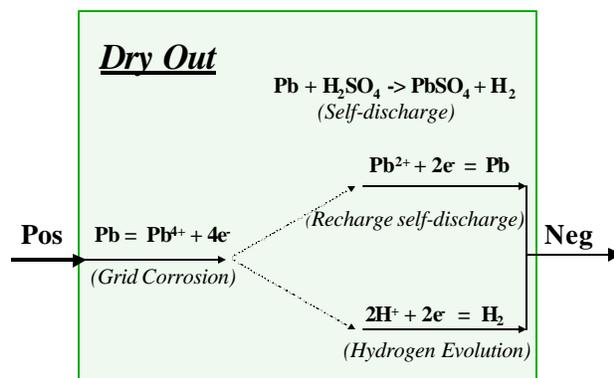


Figure 2 – VRLA Positive Grid Corrosion Partial Current Flow

As can be seen from Figure 2, the partial current responsible for positive grid corrosion offsets the self-discharge of the negative electrode and, if sufficient, can polarize the negative electrode with subsequent electrochemical generation of hydrogen gas.

If the partial current responsible for positive grid corrosion, i.e. the rate of positive grid corrosion, is greater than the partial current required to recharge the negative self-discharge then the negative electrode will maintain its capacity throughout its float life. If, however, the partial current responsible for positive grid corrosion is less than the partial current required to recharge the negative self-discharge then the negative electrode will progressively lose capacity.

There are two principal reasons for the self-discharge of the negative electrode:

- Oxygen ingress – if external oxygen is allowed into the VRLA system then the negative electrode will readily react with the oxygen resulting in a reduction of its SOC. It is imperative, therefore, that the VRLA manufacturer ensures the batteries are leak free and that the safety valve operates in a correct manner throughout the product’s life.

- Impurities – the purity of the raw materials that make up the battery is absolutely critical due to the deleterious local action of certain metallic impurities at the negative electrode resulting in self-discharge<sup>(2)</sup>. This is made even more critical with VRLA technology since, due to the depolarizing nature of the recombination reaction, the negative electrode has less ability to recharge any self-discharge resulting from local action, relying only upon the partial current from the positive grid corrosion reaction. (In a flooded design any partial current associated with oxygen evolution at the positive will recharge/polarize the negative electrode). Furthermore, in recent years, VRLA battery manufacturers have developed more and more corrosion resistant positive grid materials. This inadvertently has had the effect of reducing the amount of partial current available to offset any self-discharge of the negative electrode. Therefore, the concentration of impurities that the negative electrode can endure has decreased with the development of VRLA technology. **Indeed, the worst case scenario would involve a corrosion resistant positive grid and an impure system.**

Several researchers have since advocated the deployment of catalysts in the gas space of VRLA cells<sup>(3)</sup>. This action will undoubtedly polarize and offset the rundown of the negative electrode, indeed may well offer benefits in abusive situations, but is unnecessary if the VRLA cell/battery is manufactured with due consideration to the aforementioned run-down mechanisms.

The purpose of this paper is to demonstrate that even with the highest corrosion resistant grid material, i.e. pure lead or pure lead alloyed with a small amount of tin, the negative is not the limiting electrode, even after up to 13 years real-time float duty, provided that the VRLA cell/battery is manufactured to a high purity standard. Furthermore, that the use of catalysts is not required for normal float applications.

Commercially available Cyclon<sup>®</sup> and SBS pure lead and lead-tin VRLA batteries were used for this float life verification study. The manufacturers of these products take significant precautions to ensure that the entire system is free of contaminants. The grid lead of both electrodes, as well as the oxides used in both electrodes, are manufactured from primary lead from sources known to have low impurity levels. The electrolyte is manufactured from highest reagent grade acid and de-ionized water. The separator material is also of the highest possible purity. All raw materials and in-process materials are monitored to ensure that a high system purity is consistently maintained.

## II. Experimental

All the cells and batteries used in this study were taken from real-time float experiments, i.e. floated under ambient temperature conditions, and were not taken from

accelerated float life tests which can artificially alter the condition of the negative electrode. Capacity tests on the aged product were conducted immediately following the float duty without any boost charging, which also can artificially alter the condition of the negative electrode. In all cases, a mercury/mercurous sulphate reference electrode ( $\text{Hg}/\text{Hg}_2\text{SO}_4$ ) was inserted into the cell in order to determine the capacity-limiting electrode during the discharge. Finally, teardown analysis was carried out to determine the chemical and morphological condition of both the positive and negative active masses and also to quantify the degree of positive grid corrosion.

In the first part of the study, six batteries each containing three individual Cyclon<sup>®</sup> X-cells (5AH @  $C_{10}/10$ ), which had been undergoing real-time ambient float life testing, for up to 9 years, at Hawker Energy Products Inc. (HEPI), were analyzed. The cells had been floated at a potential of 2.30VPC with the ambient temperature in HEPI's electrical test laboratory carefully controlled @  $23\pm 2^\circ\text{C}$ . The float current was continuously recorded and periodic capacity tests conducted on a biannual basis.

Among the six Cyclon<sup>®</sup> battery groups only one group, 90083, was constructed using pure lead positive grids and the cells within this group had been on continuous float at room temperature for 8.9 years, Table 1. Four groups 90082, 92045, 94022 & 97185 all utilized lead-tin positive grids and had been on real-time ambient float for 8.9, 7, 5 & 2 years respectively. The final group, utilizing lead-tin positive grids, were fresh cells that had not been subjected to any float duty.

Test designation	Duration of time float	Positive material
90083	8.9	Pb/Sn
90082	8.9	Pb
92045	7	Pb/Sn
94022	5	Pb/Sn
97185	2	Pb/Sn
99033	Fresh	Pb/Sn

Table 1- List of sample cell specifications.

A  $C_8/8$  constant current discharge was performed on two cells from each group. In order to demonstrate that reference electrode insertion had no effect on the performance of the cells, one cell was fitted with, and the second cell without a reference electrode.

Teardown analysis was carried out on the third cell. Both plates were carefully detached from the separator and the three components weighed. The electrodes were soaked and rinsed with de-ionized water to extract the residual

sulphuric acid and were then dried in a vacuum oven. The electrodes were then stored in an inert atmosphere in order to prevent further chemical reaction, in particular oxidation of the negative active mass. Accurate analysis of the sulphate concentration on both electrodes was conducted employing wet chemistry techniques. X-ray diffraction (XRD) was employed to determine the crystallographic composition of both the positive and negative active masses (PAM & NAM). Mercury porosimetry was used to characterize the porosity of the electrodes and BET surface area analysis was conducted to measure the surface area evolution with float life.

In the second part of the study, further investigative work was performed on the commercially available SBS product manufactured by Hawker Energy Products Limited (HEPL). The SBS product utilises pure-lead positive grids and is manufactured to the same metallurgical and electrochemical standard as the Cyclon<sup>®</sup> cells but is a prismatic design. Comparison work was carried out on a freshly formed SBS110 and also on two 13-year old field returned SBS110 batteries (6V-110AH @  $C_{10}/10$ ). The 13-year old samples formed part of a large battery that had successfully completed 5-years in a customer application before being returned to HEPL. Since then the battery has been on continuous real-time float duty @ 2.27VPC and  $22\pm 2^\circ\text{C}$  in the electrical test laboratory for an additional 8 years.

Both samples were analyzed immediately following removal from real-time float service.

The first sample was discharged to verify its capacity. Prior to the  $C_8/8$  (13.6A) capacity test, a  $\text{Hg}/\text{Hg}_2\text{SO}_4$  reference electrode was inserted into one of the three cells in the battery and the positive and negative electrode potentials recorded.

The second sample was dismantled for internal examination. This evaluation, as well as covering the same analysis as conducted for the Cyclon<sup>®</sup> products, also included stratification (by extracting and carefully measuring the specific gravity of the electrolyte in the top, middle and bottom sections of the separator) and scanning electron microscopy (SEM) of the NAM.

### III. Results & Discussion

#### Cyclon<sup>®</sup> Capacity Test and Reference Electrode Work

Figure 3 shows the magnitude of the float current, expressed as mA/AH, during the real-time float test for both the 8.9-year pure lead and lead-tin test cells.

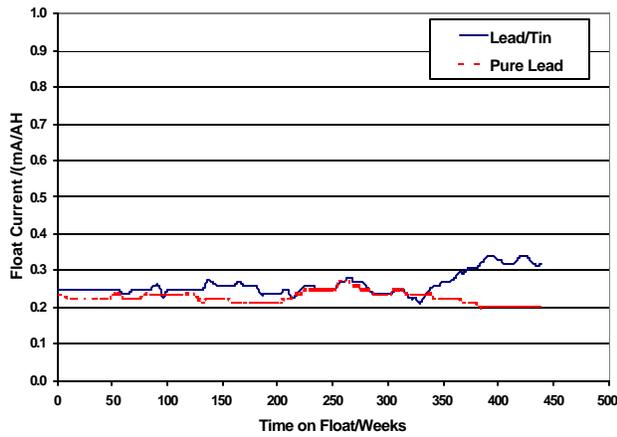


Figure 3 - Float Current V's Real-time Float for 8.9-Year Cyclon<sup>®</sup> Cells

The above figure shows that the float current has remained low for both variants over the test period. The magnitude of the float current is between 0.2-0.3 mA/AH (i.e. 1.0-1.5 mA for the cells under investigation) which is quite typical for this technology.

Table 2 summarizes the average float current and total charge input (excluding recharge following a capacity check) taken by the experimental cells over the 8.9 year test period.

Positive Grid Alloy	Pb	Pb/Sn
Average float current over 8.9 years /mA	1.154	1.269
Total charge over 8.9 years /AH	90.0	98.9

Table 2 - Average Float Current and Charge Input For the 8.9-Year Cyclon<sup>®</sup> Cells

The slightly higher average float current, and hence charge input, for the Pb/Sn product is consistent with the fact that the addition of tin to the pure lead positive grid increases the rate of positive grid corrosion<sup>(4)</sup>. As we will see later on in this paper knowing the total charge in and by determining the extent of positive grid corrosion we can estimate the proportion of float current involved in the grid corrosion process and the proportion involved in the recombination process.

Figure 4 shows the capacity of the 8.9-year-old cells as a function of float time.

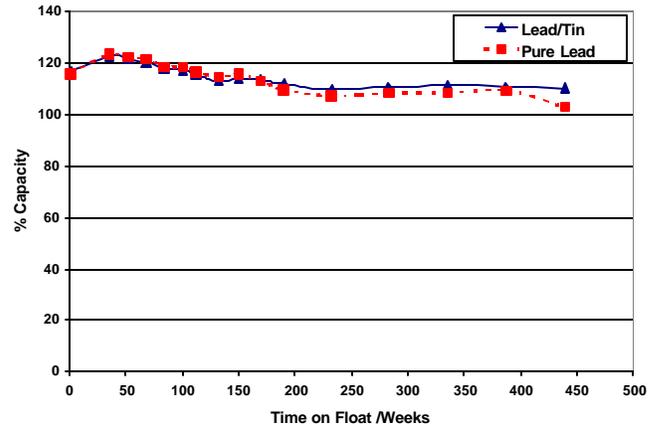


Figure 4 - Capacity V's Real-time Float for 8.9-Year Cyclon<sup>®</sup> Cells

The capacity of the Cyclon<sup>®</sup> cells remain in excess of 100% nominal even after up to 9 years.

The other groups, which had been on real-time float testing for shorter times, also exhibited similar float current and capacity behavior.

In order to determine the capacity-limiting component of the cell, a reference electrode was inserted to measure the individual electrode potential and its discharge profile. Figures 5, 6 and 7 show individual electrode potentials during a C<sub>8</sub>/8 discharge (0.62 A) of a new Pb/Sn X-cell, a 8.9-year-old Pb/Sn X-cell and a 8.9-year-old pure lead X-cell.

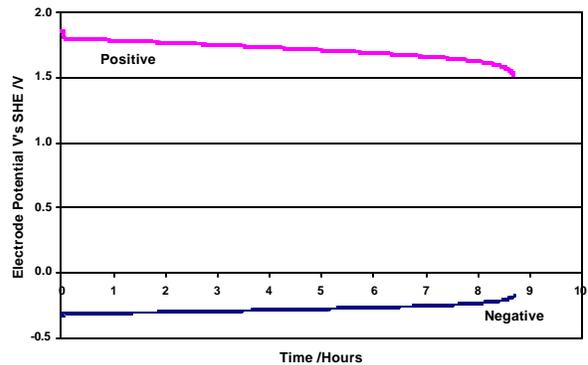


Figure 5 - Discharge Potential Profile for a new Pb/Sn Cyclon<sup>®</sup> Cell

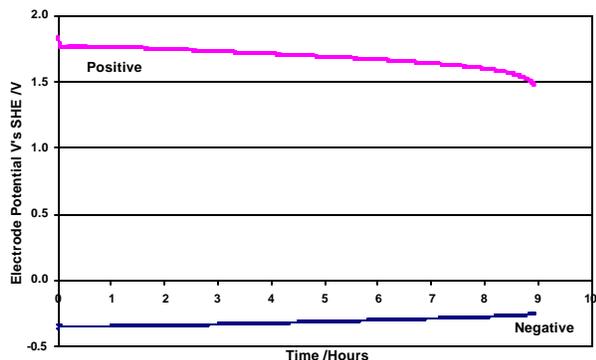


Figure 6 - Discharge Potential Profile for 8.9-Year Pb/Sn Cyclon® Cell

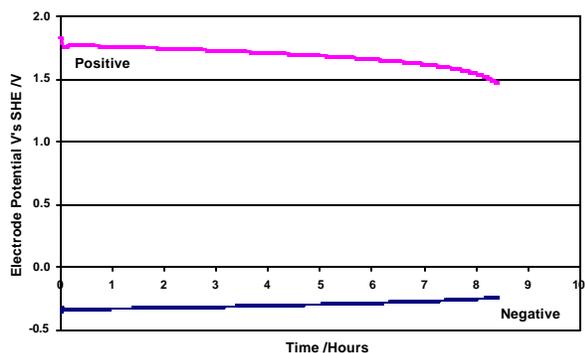


Figure 7 - Discharge Potential Profile for 8.9-Year Pure Pb Cyclon® Cell

Analysis of the above discharge profiles show that, in all cases, the positive was decaying more rapidly at the end-of-discharge than the negative electrode potential. *It is quite clear that the limiting component at the end of the discharge was not the negative electrode.*

### Cyclon® Morphological & Crystallographic Analysis

The concentration of lead sulphate present in the active masses of both electrodes from all test groups was evaluated by employing wet chemistry techniques and is graphically represented in Figures 8 and 9.

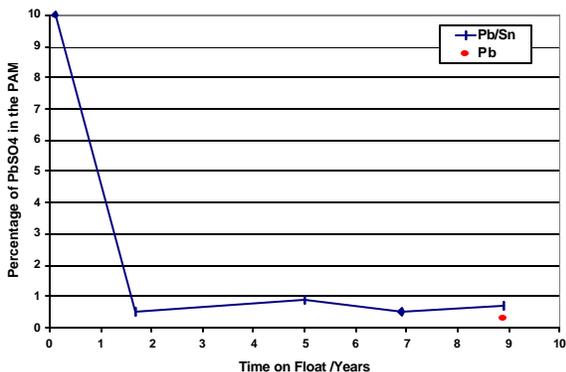


Figure 8 - Percentage of PbSO<sub>4</sub> at the positive electrode as a function of float time.

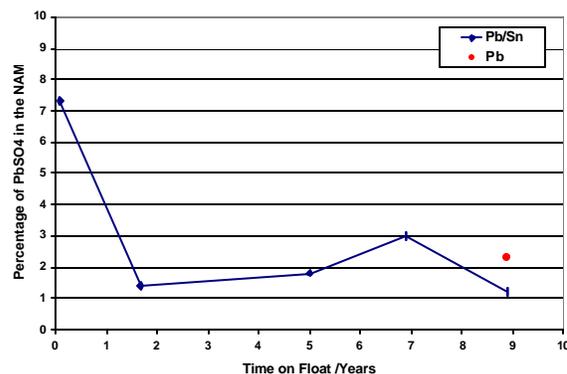


Figure 9 - Percentage of PbSO<sub>4</sub> at the negative electrode as a function of float time for the Cyclon® Cells

For both the active masses, the PbSO<sub>4</sub> concentration is relatively high immediately following formation but rapidly decreases during the initial period of float charge and then remains consistently low over the remaining 8-9 years of real-life float duty. For both the pure lead and the Pb/Sn variants there is no significant build up of sulphate concentration on the negative electrode indicating no negative run-down.

In order to ascertain the change in active mass surface area over the course of the real-time testing, BET analysis of the positive and negative active masses was carried out and the results are shown in Figure 10.

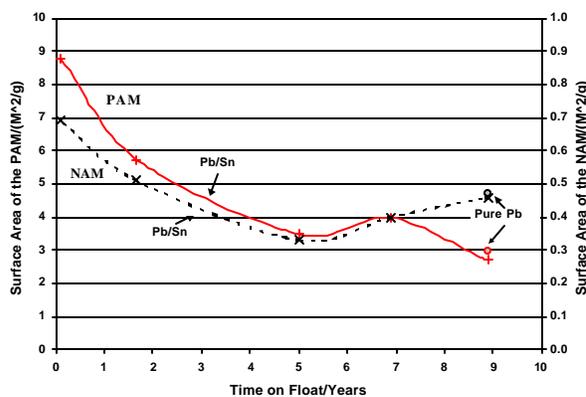


Figure 10 - Surface area analysis of both electrodes vs. float time for the Cyclon® Cells

The surface area of both electrodes has steadily decreased over the first 5 years and then has stabilized. For the negative active mass this behavior is possibly explained by the progressive reduced activity of the organic expanders. However, a surface area of 0.4 m<sup>2</sup>/g after 9 years of real-time float remains consistent with a healthy NAM.

The degree of positive grid corrosion in all samples was determined by wet chemistry techniques. Figure 11 shows that the extent of positive corrosion has risen up to 45% over the 8.9 years of float duty for the lead-tin samples.

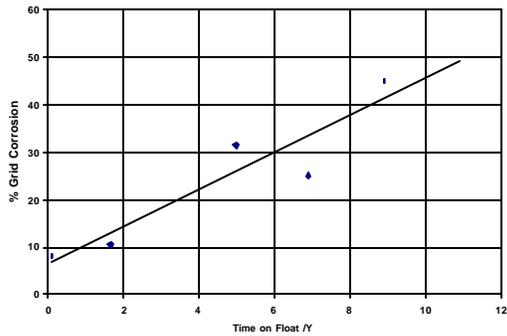


Figure 11 - Positive grid corrosion of the lead-tin Cyclon® Cells as a function of float time

For the pure lead product, however, only 25.3% positive grid corrosion was determined over the same period of float duty.

As mentioned previously, knowledge of both the total charge in and the extent of grid corrosion over the real-time float life will enable us to roughly estimate the proportion of float current involved in both the grid corrosion and the recombination processes, Table 3.

	Cyclon® Positive Grid Alloy	Pb	Pb/Sn
1	Measured degree of positive grid corrosion after 8.9 years	25.3%	45.0%
2	Charge required to corrode positive grid by above percentage	6.3AH	11.2AH
3	Recorded total charge in over 8.9 years	90.0AH	98.9AH
4	Therefore charge associated with recombination process (row 3 – row 2)	83.7AH	87.7AH
5	Recorded average float current over 8.9 years	1.153mA	1.269mA
6	Therefore, average corrosion current over 8.9 years (row 2 ÷ float-time)	0.089mA	0.144mA
7	Therefore, average recombination current over 8.9 years (row 5 – row 6)	1.064mA	1.125mA

\* Based on known positive grid weight (following formation) and assuming complete conversion to PbO<sub>2</sub>

Table 3 – Partial Current Analysis for the 8.9-Year Cyclon® Cells

It can be seen from Table 3 that the recombination partial current for both the pure lead and the Pb/Sn positive grid products is, within experimental error, effectively the same as might be expected. The corrosion partial current for the pure lead product is approximately 40% less than that for the Pb/Sn variant, which is in good accord with the high corrosion resistance of the pure lead positive grid material. However, because the negative electrode for the pure lead product has been shown not to run-down with life, then the equivalent partial current for the negative self-discharge reactions must be equal to or less than the

partial current for the positive grid corrosion reaction, i.e. < 0.089mA or expressed as a normalized factor < 17.8µA/AH.

### Pure Lead SBS Battery

Immediately prior to removal from real-time float duty the float current of the SBS110 battery string was measured and found to be 24mA (0.22mA/AH). This is in good agreement with the float currents measured for the aged Cyclon® products as discussed in an earlier section.

Figures 12 & 13, show the positive and negative electrode potentials during the C<sub>8</sub>/8 capacity discharge for both the fresh and the 13-year old product.

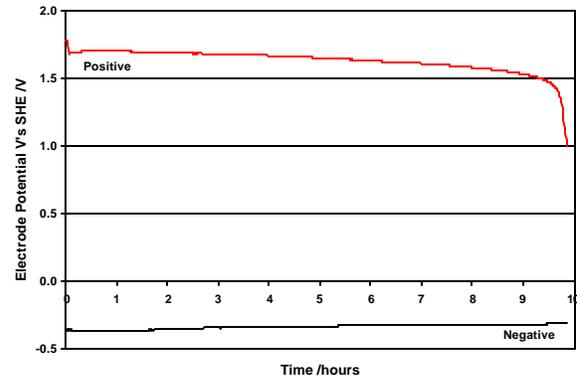


Figure 12 – Electrode potentials during C<sub>8</sub>/8 discharge for the new SBS110 product

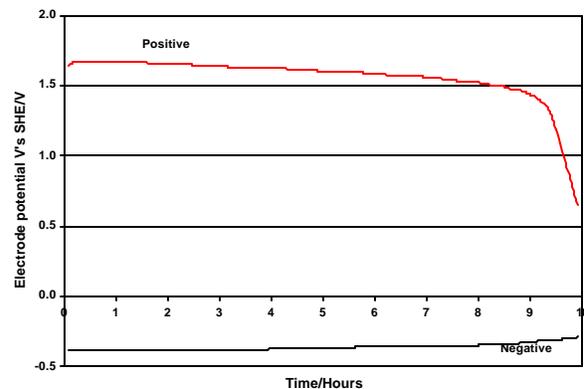


Figure 13 – Electrode potentials during C<sub>8</sub>/8 discharge for the 13-year old SBS110 product

Clearly, for both batteries, the capacity limiting component is once again the positive electrode as seen by its rapidly collapsing potential towards the end-of-discharge. Indeed, the 13-year old product has delivered in excess of 115% of its rated C<sub>8</sub> capacity down to 1.70VPC.

The following table lists the PbSO<sub>4</sub> concentrations and the surface areas of both the PAM & NAM for the new and aged batteries.

	Positive Active Mass		Negative Active Mass	
	% PbSO <sub>4</sub>	RFT <sub>2</sub> SA (M <sup>2</sup> /g)	% PbSO <sub>4</sub>	RFT <sub>2</sub> SA (M <sup>2</sup> /g)
New Product	N/A	7.7	2	0.87
13-Year Old Product	0	5.3	4	0.62

Table 4-PbSO<sub>4</sub> concentration and surface area analysis results of both electrodes for new and aged batteries.

Both the BET surface area and the concentration of lead sulphate for the SBS new and aged products are in good agreement with the Cyclon<sup>®</sup> analysis results. Once again the surface areas of both the PAM & NAM decrease as the battery ages. The low concentration of lead sulphate within the NAM for the 13-year old sample once again helps confirm that the negative electrode has maintained capacity throughout its life.

SEM pictures of the NAM from the fresh and aged monoblocs are shown in Figures 14 and 15.

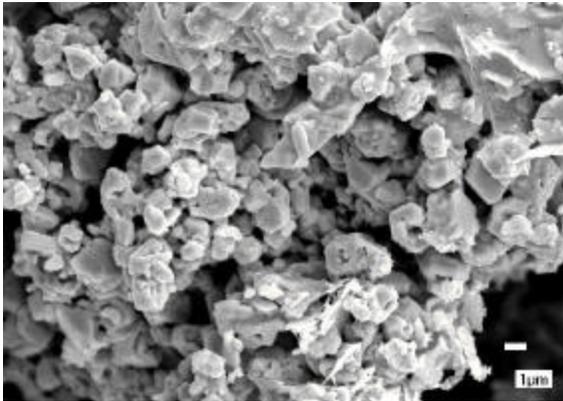
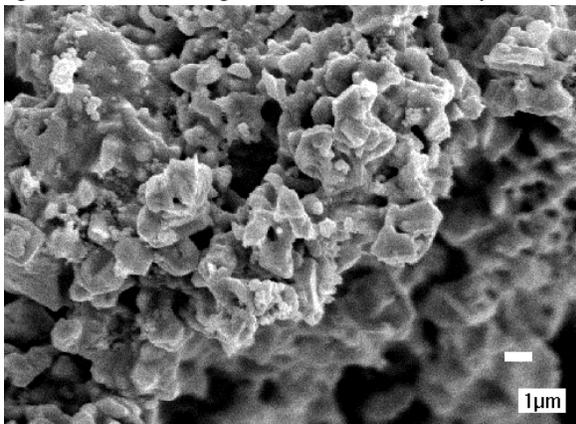


Figure 14 - SEM image of the freshly formed NAM.

Figure 15 - SEM image of NAM from the 13-year old



product

For both the fresh and aged NAM structure, the crystallites are small, less than one Micron, and are highly dispersed in accordance with the measured high surface area. For the aged NAM however, there is some evidence of conglomeration, presumably as a result of

organic expander deterioration over life. However the structural integrity is still largely retained. This observation is in good accord with the reduction in measured surface area for the aged product.

Analysis of the positive electrode revealed marginal grid growth of approximately 3% and grid corrosion of approximately 35%.

Specific gravity readings were taken from the top and bottom areas of the separator paper. No stratification was observed for the new battery and only a marginal difference (<0.005 g/cm<sup>3</sup>) was detected for the 13-year old product.

#### IV. Conclusions

In summary, a detailed and extensive study has been conducted on commercially available VRLA cells/batteries that have been on real-time float duty under ambient temperature conditions for up to 13 years. The findings are as follows:

- It has been demonstrated that the performance limiting component from commercially available VRLA Cyclon<sup>®</sup> cells and VRLA SBS batteries, even after up to 13 years under real-time float conditions, is not the negative electrode. In all cases the positive electrode was the capacity limiting component.
- It is hypothesized that the perceived run-down of the negative electrode is a function of the level of impurities found within a VRLA battery. This run-down is offset by the partial current responsible for positive grid corrosion. For the high purity batteries employed in this study the level of local action/self-discharge of the negative electrode is calculated to be equal to or less than 17.8µA/AH @ ambient temperatures. This being the partial current responsible for the corrosion of pure lead positive grids.
- Pb/Sn positive grids, in the same high purity VRLA designs, exhibit a higher positive grid corrosion rate which is clearly greater than the level of local action/self-discharge of the negative electrode.
- Recently it has been proposed that the use of catalysts in the gas space of VRLA cells will help to maintain the negative at a full state-of-charge. For the high purity VRLA products employed in this study the deployment of such catalysts is not required.

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