# INDIVIDUAL CELL FLOAT VOLTAGE VARIATIONS AND INTERNAL CATALYST TECHNOLOGY FOR VRLA BATTERIES

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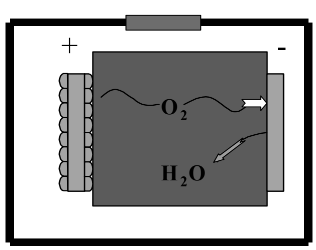
**Introduction**
Based on inspection of cells in operation and reports from the users we have reason to believe that individual cell float voltages in VRLA (valve regulated lead acid) battery product produced with internal catalysts now vary to a greater degree than previously observed or believed. This issue has been identified primarily in cells manufactured since 1999. Individual cell voltages have been recorded as high as 2.35 volts and greater. A majority of these cells have been installed in 12 and 24 cell strings being floated at 27.12 vdc and 54.24 vdc, respectively (2.26 vpc average).

**To understand why this is happening and what it means to the health of the battery system, we need to re-look at the basics of VRLA operation.**

**Typical VRLA cell recombination:**
Water ($H_2O$) is electrolyzed at the positive plates generating oxygen. The oxygen is diffused through the glass mat separator where it then reacts with the spongy lead (Pb) of the negative plate forming lead-oxide (PbO). The lead-oxide reacts with the sulfuric acid in the electrolyte ($H_2SO_4$) forming lead sulfate ($PbSO_4$) and water ($H_2O$). This recombination reaction has the undesired effect of discharging the negative plate *(increasing required float current)* and producing heat. The reactions are shown in Chart 1 below.

**Chart 1**

VRLA Oxygen Recombination




- $O_2$ and $H^-$ generated during reaction recombines into water
- Recombination rate ~ 98%

Reactions of Interest

At the Positive Plate

$$2H_2O \rightarrow O_2 + H^+ + 4e^-$$

At the Negative Plate

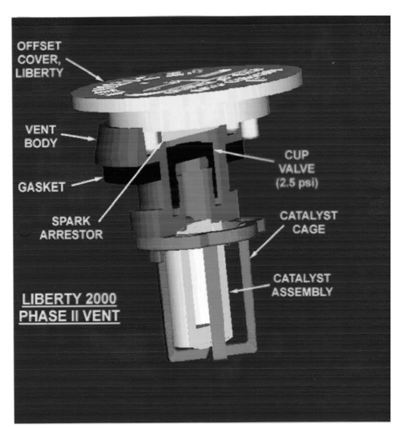
$$2Pb + O_2 \rightarrow 2PbO$$

$$2PbO + 2H_2SO_4 \rightarrow 2PbSO_4$$

$$2PbSO_4 + 4H^+ 4e^- \rightarrow 2Pb + 2H_2SO_4$$

At the Catalyst

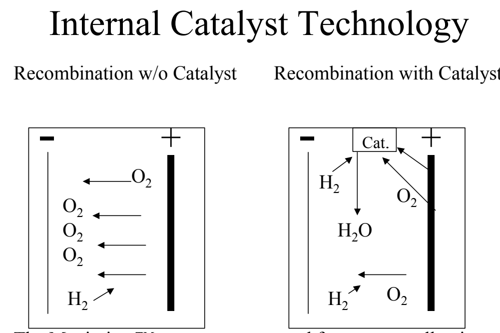
$$H_2 + \tfrac{1}{2} O_2 \rightarrow H_2O$$




**VRLA cell recombination with an internal Catalyst:**
To address the depolarization of the negative plates and slow the rate of corrosion of the positive plates, C&D utilizes an internal catalyst technology. See picture to the right. The catalyst is provided as part of a one-way pressure relief valve with a catalyst enclosed in a high temperature plastic cage. Recombination takes place at the catalyst, which reduces the traditional recombination reaction at the negative plates. This allows the negative plate to become charged and reduces the over-voltage on the

positive plates. Some of the advantages are reduced float current and heat generation and a slower rate of positive grid corrosion. A key benefit of the hydrogen-oxygen recombination at the catalyst is the significant reduction of water loss, when compared to a non-catalyst equipped VRLA cell. See Chart 2.

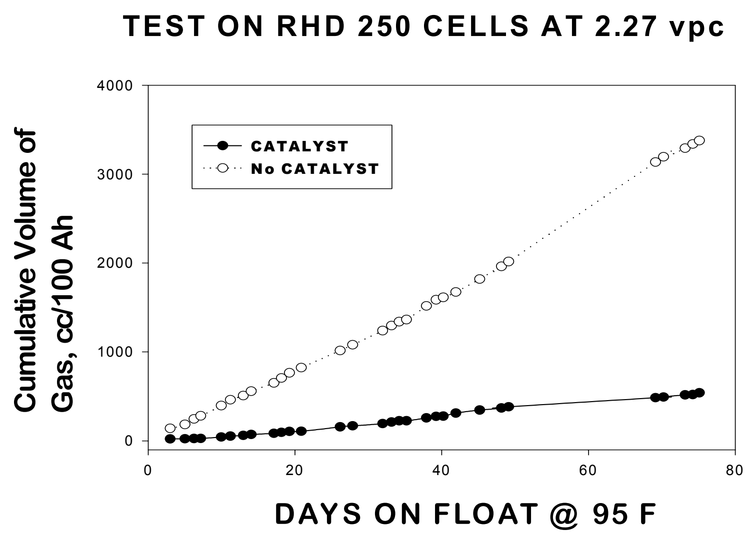
**Chart 2**



The Maximizer™ attracts oxygen and forms water allowing the negative to become fully charged at a lower float current.

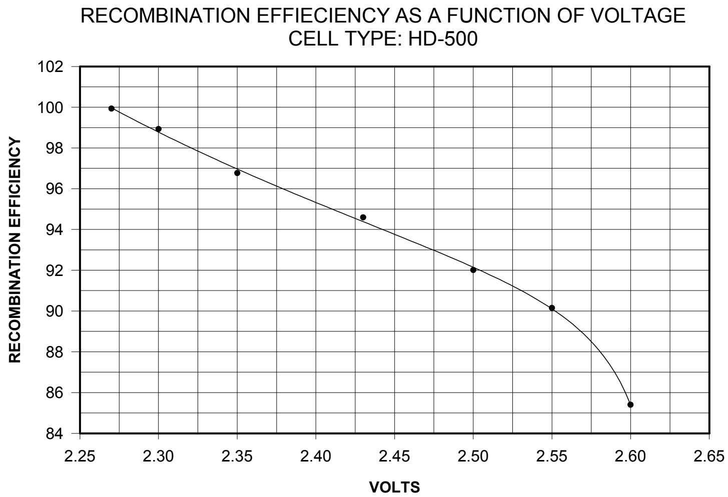
Reducing water loss does have a temporary negative affect. Not all cells within a new string of cells will be at the same state of recombination and will therefore require different amounts of float current to maintain a given voltage. This is the same situation as with newly manufactured cells. The cells in a more saturated state require less current than those cells in a higher state of recombination. If the majority of cells within a string are in a high state of recombination, any cells that are in a higher state of saturation will be driven to a higher voltage by the charge current required by the dominant cells. The higher voltages partly reflect the higher polarization on the negative plates, which is not harmful to the cells. When enough gasses are released, the cell will reach a higher state of recombination and the cell voltage will fall in line. This 'self-correcting' process normally happens rather quickly in a VRLA cell without a catalyst often occurring before the time the first preventative maintenance inspection is performed. However, in cells equipped with the internal catalyst, the time to reach a high state of recombination may exceed twenty-four months.

**Chart 3**




The reason for this delay is due to the catalytic recombination of Oxygen and Hydrogen, which maintains a higher level of saturation for a longer period than in cells without the catalyst. The catalyst keeps the negative plates fully charged and recombines gases within the cell maintaining an internal cell pressure below the 1.5-psi required to open the vent. **The result is a reduction in dry out and improved long term cell performance although with greater cell to cell voltage variations for longer periods than traditionally seen in cells without a catalyst.** See Chart 3 above.

**Chart 4**




Note: we have seen the same effect in cells without the catalyst but the higher voltages result in a higher level of out gassing with the cells getting into a high level of recombination in a relatively short period of time. Typically six months to one year depending on the state of recombination the cells were in at the time of shipment. A typical plot of recombination rate vs. charging voltage is shown in chart 4 above. Note that this is for cells without internal catalysts. You can see that recombination remains very high even at moderately high levels of charge.

A better way to look at this is by understanding the Tafel diagram for VRLA cells and then looking at the Tafel of some particular cells. The chart 5 below was shown at Battcon 2000 to show the effect of the catalyst in VRLA batteries. However, it is also an oversimplification of what happens to individual cells. In reality, the catalyst will effect individual cells between the extremes shown below.

**Chart 5**

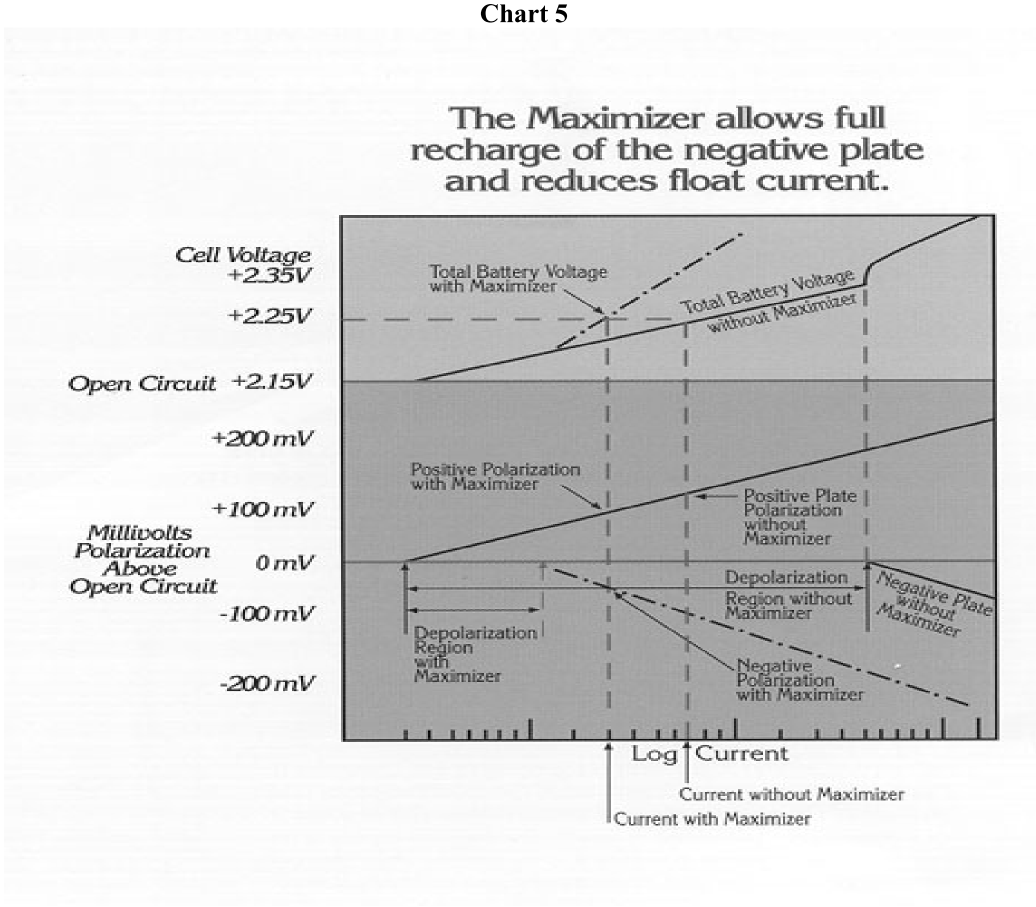
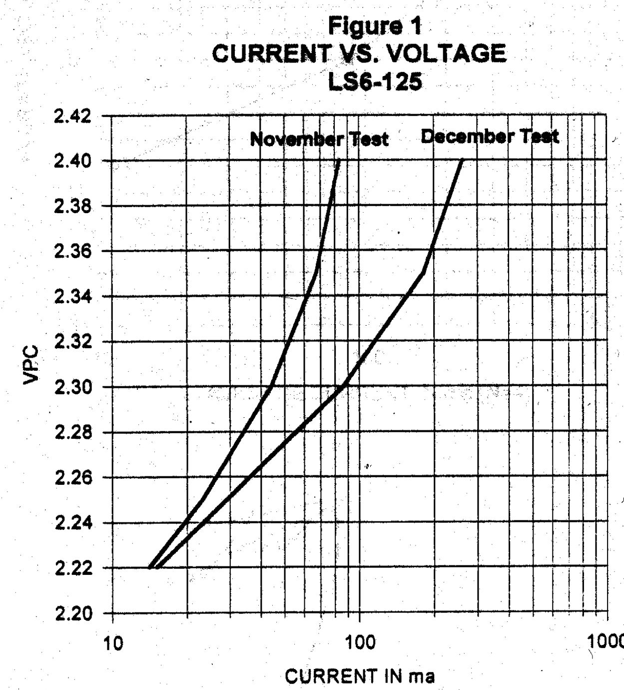


**Chart 6**




The Tafel will shift depending on the degree of saturation in the individual cells. I.E. the negative depolarization region is shifting further to the right as the cells become more highly recombinant. Looking at the Tafel for a new string of batteries and then cycling that string a number of times to degas the cells show a substantial change in the current required to maintain the cells at any given voltage. This increase in the current is due to the higher state of recombination. See chart 6 to the right.

The issue is that when the catalyst is added to the cells the cells do not outgas / vent out any surplus water to increase the recombination rate of the cells. Therefore if cells in the same string of a battery are in a different state of recombination, they will tend to float at a different voltage for any given current. This issue is the result of one of the major benefits of the catalysts, reduction of water loss by approximately 80%. Although the cell voltages may have a temporary wider range, the variation can be seen from the Tafel to be a function of the negative plate polarizations, which will not affect the long-term performance, or life of the product.

The typical expected individual cell voltage variation in operation has been +/-0.05 volts of the average cell voltage (this range is 2.21-2.31 vpc for cells floating at 2.26 average vpc- @ 77°F). If a cell(s) with catalyst exhibits a higher voltage, one of two options can be exercised.

1. Wait. The internal catalyst delays the process of reaching a state of equilibrium, but it will come into line in time. It is not uncommon to experience twelve to twenty-four months of service before the voltages begin to come into range. **Individual cell voltages in excess of 2.31 vpc, for this period of time, are not detrimental to the cell's performance capabilities or expected service life.**

2. The second option is to remove the catalyst valve and replace it with a 'standard' non-catalyst valve. Field results have shown the affected cell voltages to come in range in as short a time as thirty days after being retrofitted with a 'standard' pressure relief valve. Once the voltages drop, the vent (with catalyst) is reinstalled. If this option is exercised, it is important that the original catalyst-valve be reinstalled once the cell voltage is lowered to obtain the full benefit of the catalyst technology. **To date we have had a 100% success rate in bring down cell voltages with this procedure.**

The question we are being asked and I'm sure you would also ask is; what can be done to prevent this variation in production? One way we will show is better control of the electrolyte volumes to assure cells are in a high state of recombination at the time of shipment. This is not as easy as it sounds but with a controlled group of cells we can see that over a reasonable float period of 400 hours, almost three weeks, cells with the catalyst actually float tighter that cells with out the catalyst. See charts 7, 8 and 9 below.

**Chart 7**

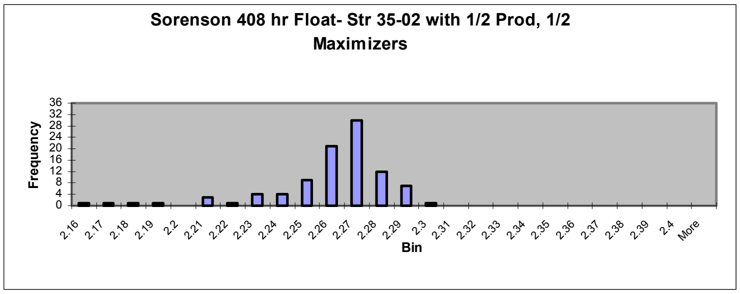



**Chart 8**

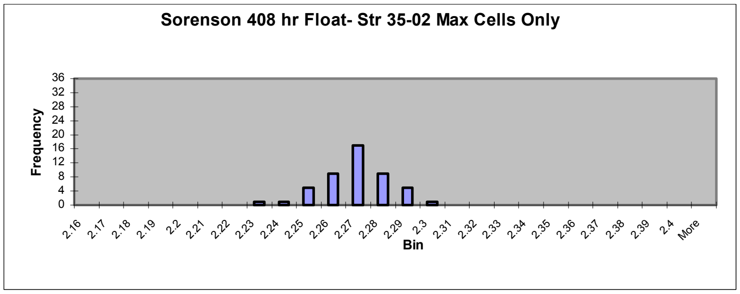
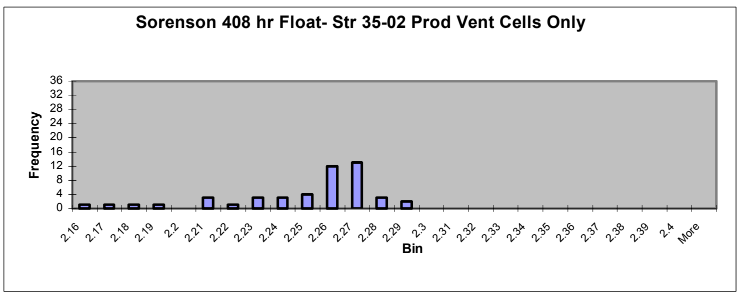



**Chart 9**




A second way we have always used was to try to float match cells during the constant current finish charge. We are now looking at constant voltage matching. I expect to report on this test during the conference.

**Lower current draw** is another related benefit of the catalyst that affects how fast and to what degree the voltage per cell will change. As shown earlier in chart 6, a new string of cells will draw lower current on float as the cells are not as yet in a very high (> 98% level of recombination). I.E. the negative plates are reaching a full state of charge and some albeit small level of hydrogen is coming off the negative plates. The hydrogen is recombined at the catalyst which is why the cells with catalysts could take years before enough water is lost from the high float cells to shift the individual cell Tafel to where the cell voltages drop within the desired range, below 2.31 volts.

The addition of catalysts into cells that are already in a high degree of recombination also results in a lower string current than cells without a catalyst. As mentioned earlier, the recombination at the catalyst reduces the level of recombination at the negative plates. Current draw in VRLA batteries without catalysts is typically in the order of 75 mA per 100 AH of capacity (8 hour rate). Current draw with the catalyst is the order of 50 mA per 100 AH. E.G. HD-1300 cells in operation for three years that used to draw 0.9 to 1 amp on float are now floating at less than 500 mA.

**Conclusions:**

**When the overall string of cells equipped with catalysts is adjusted to the recommended float voltage, individual cell voltages in excess of 2.31 vpc are not detrimental to the cell's performance capabilities or expected service life.**

- High voltages occur for cells that are in lower states of recombination since they receive higher current than those individual cells require. The higher voltage will be on the negative plates. This is self-correcting over time, as the recombination rate will increase as these cells age depressing the negative plate potentials.
- The higher voltage will not have a detrimental effect on either performance or expected life and the warranty is will not be effected as long as the cells are maintained and operated in accordance with the products operating procedures.
- String float voltage is distributive in nature and when one cell drifts high it minimally impacts the remaining cells in the string.  The standard low voltage range requirement should remain the same. Any cell with a float voltage less than 2.20 vpc (or lower than -.05 volts of average) warrants closer examination to be sure they are not being forced into a discharged state.