Additional Studies on the Degradation of VRLA Batteries and the use of the Catalyst or Alternative Charging Techniques to Reverse Degradation

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Introduction

For the last two years, we have been informing this august body about our testing and evaluation on the use of internal precious metal catalyst to enhance the performance and life of VRLA (Valve Regulated Lead-Acid) batteries. This year while we will bring everyone up to date with the latest results after two years as a production product. In addition I will report that, as a result of our testing, it is possible to improve many older VRLA product by retrofitting with an internal catalyst. We will also show that it is possible to reverse the negative plate sulfation that has caused performance degradation by boost charging.

Summary of past Presentations

As a quick refresher and to bring new attendees of the Battcon conference up to date, the following is a summary of the benefits of the internal catalyst[1]:

1. To ***maintain the charge level and therefore the performance of the negative plates and the battery*** while reducing the secondary evolution of Hydrogen due to chemical reactions at the negative plates.
2. The corresponding reduction of the polarization on the positive plates resulting in a ***lower rate of positive plate corrosion and therefore longer life***.
3. The recombination of Hydrogen that is normally vented and therefore a ***reduction in gassing and water loss.***
4. The reduction in float current due to the lower level of recombination occurring at the negative plates and therefore ***lower internal heat generation and reduced potential for thermal runaway.***

1999 – 2000 Update

This past year, with the cooperation of many of the end user customers as well as third party test and installation providers, we have completed additional work which we believe confirms our hypothesis for VRLA degradation over time. This was accomplished by taking impedance readings and float current readings on cells in service and open circuit readings on cells that have been taken out of service. While there is some level of correlation between a cells age and the impedance readings there is also a lot of variation in the field due to factors like ambient temperatures at the batteries. Examples for Liberty 2000 HD-700 (770 AH) cells are shown below. Details will be shown on the slides.

Table 1

HD-700 Cell Impedance Readings
New cells typically average 0.250 milli-ohms

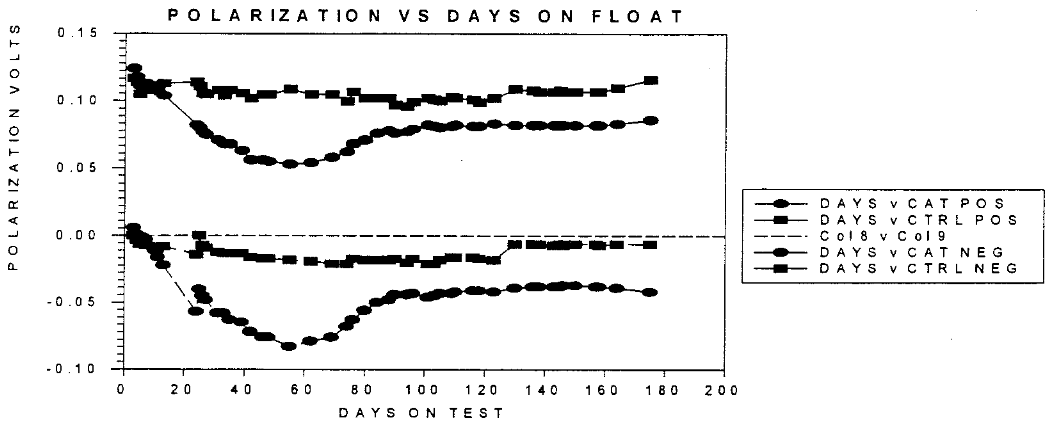
Site Name:	Ten Mile	Newport	Oregon	Barn - WA	Oak Creek
Batt. MFG. Date:	Aug-94	Jul-94	Oct-95	Oct-95	Apr-96
	Cell Impedance milli-ohms	Cell Impedance milli-ohms	Cell Impedance milli-ohms	Cell Impedance milli-ohms	Cell Impedance milli-ohms
Average	0.378	0.542	0.274	0.401	0.339

You will notice that the older strings typically have higher impedance. However, many factors such as site historical environmental conditions and variation in test equipment and the way the cells are measured can affect the readings.

I personally had the opportunity to check open circuit readings on cells that had recently been taken off line, many with the expectation that they would be reused in other sites. Note that a fully charged cell on open circuit should read between 2.14

and 2.15 volts. For VRLA cells it is not possible to obtain the specific gravity measurements that had been the main technique used in evaluating state of charge in a flooded battery. However, by looking at the open circuit readings, we can get an indication of the state of charge. I'm sure that most of this audience will be familiar with looking at open circuit readings for new cells that are on open circuit prior to installation. We do not like to see open circuit voltages below 2.10 volts per cell for 1.300 Specific Gravity VRLA product because it is indicative of cells building up heavy sulfate layers due to the local electrochemical action of self-discharge. For VRLA cells on float all the positives plates are fully charged and it is only the negatives plates that are discharging. The attached are the 3rd electrode readings shown at the last two Battcon conferences.

Chart 1



Typical of the open circuit voltages seen were:

1993 vintage 2.06 volts to 2.10 volts per cell
1994 vintage 2.08 volts to 2.12 volts per cell
1995 vintage 2.10 volts to 2.13 volts per cell
1996 vintage 2.12 volts to 2.14 volts per cell

We see similar readings on VRLA product from all manufacturers.

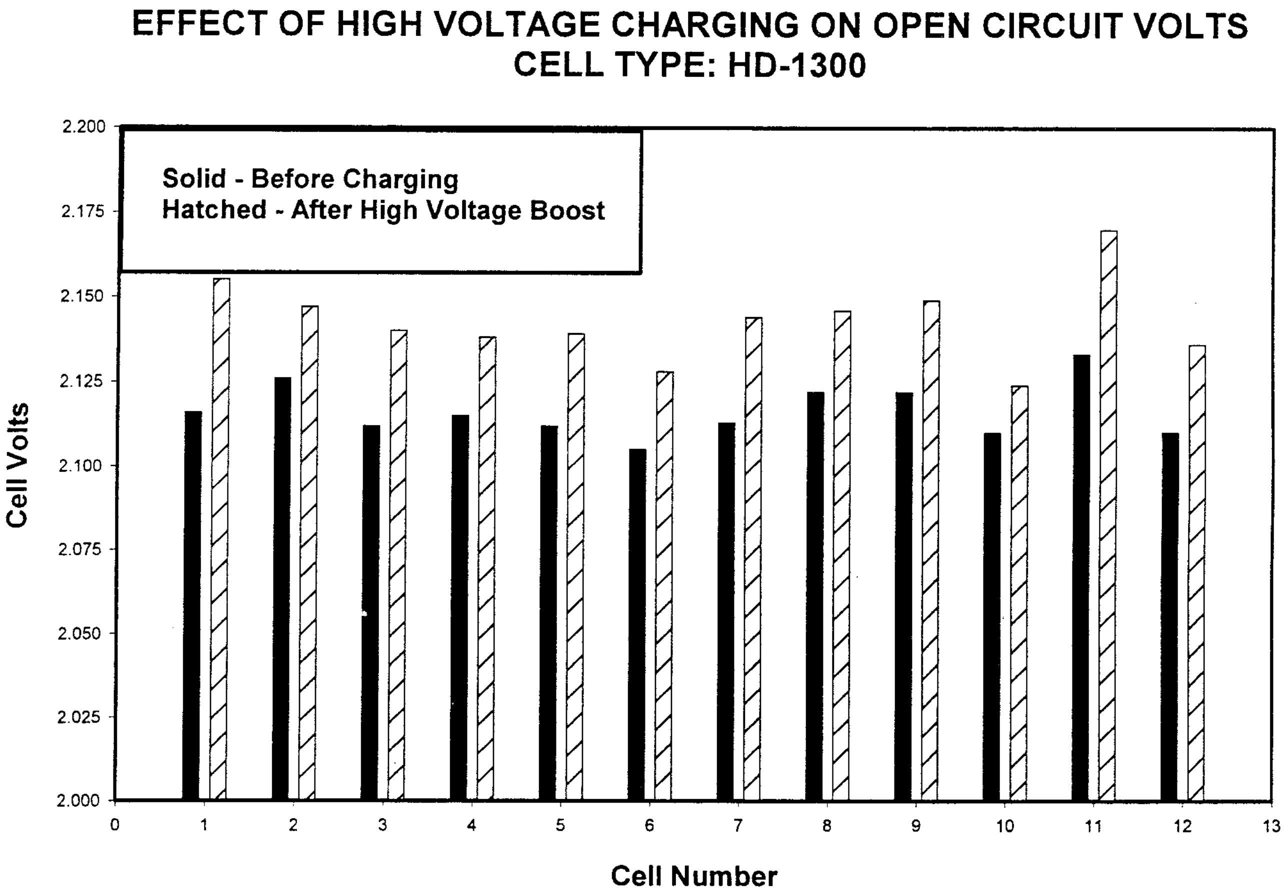
For specific sites the following are readings that have been observed:

Table 2

Typical Open Circuit Voltages					
	Sprint	Sprint	Air Touch	BAMS	BAMS
	HD-700	HD-700	HD-700	HD-700	HD-700
Date of Manufacture	9-94	9-94	10-95	8-93	8-92
			Read 01-00	Read 6-97	Read 6-97
Avg. OCV	2.091 after 2 months O/C	2.063 after 3 months O/C	2.116	2.114	2.123

In the short term, we found that the addition of an internal catalyst to cells where the negative plates were self-discharged, did not significantly improve the cells performance. Although the negatives are being polarized as can be seen from the third electrode experiments, it appears we need a higher level of charge to recover the full capacity of the cells. However, we have found excellent results if the negative plates can be recharged before adding the catalyst to the cells. This recharge must be accomplished at a voltage above 2.40 volts per cell. This is the approximate voltage at which the negatives plates can reach top of charge and evolve hydrogen. We initially tried to charge a 48 volt string at 59 volts or an average of 2.45 volts per cell for 24 hours. The problem here is that not all cells are at the same level of discharge and will recharge at different rates. Therefore, while some of the cells will recharge, others in the string will remain below 2.4 volts and not be recharged at all. A better solution is to recharge at 60 volts or 2.50 volts per cell for a 48-volt string or 30 volts for a 24-volt string. Charts 2 and 3 show open circuit voltages and impedance data before and after attempts to recharge at 2.45 volts per cell. These are cells from Regen sites.

Chart 2



You will notice that the impedance data have improved and that some of the charge voltages were high enough to enable some of the cells to charge back. This is verified by the subsequent improved open circuit readings. However, at the 2.45 volts per cell average many cell voltages did not reach the 2.40 volt minimum level necessary to enable the negative plates to charge. In addition, as the majority of the cells reach a fully charged state at a constant voltage, the current drawn by the string will fall off and limit the ability of the under charged cells to reach top of charge.

Chart 3

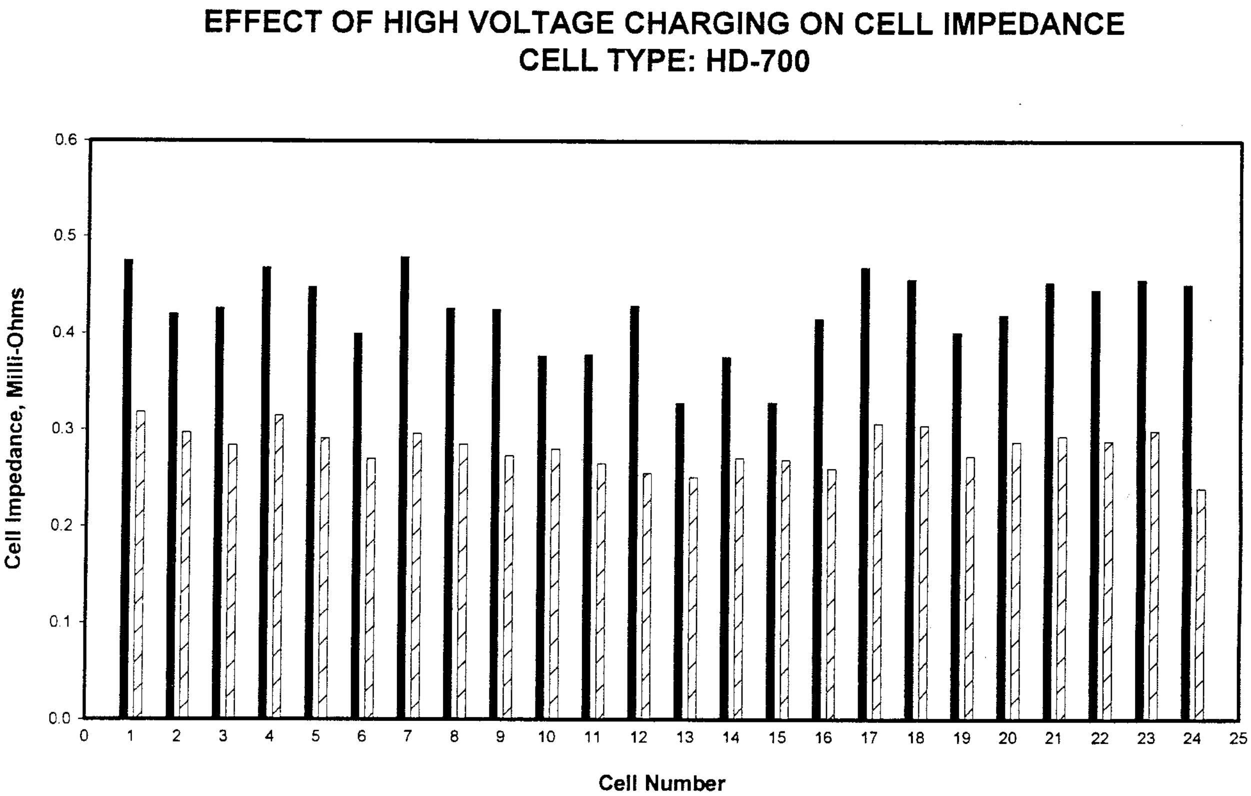
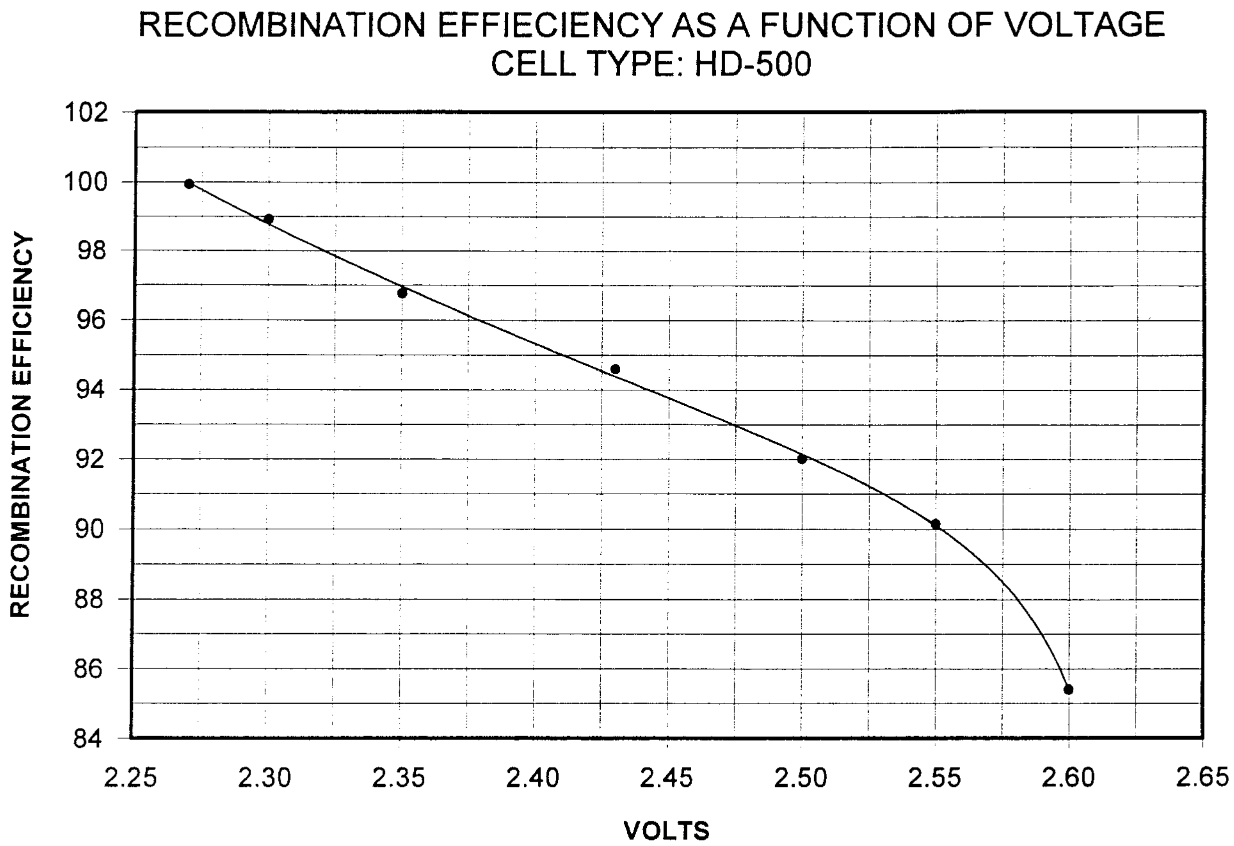


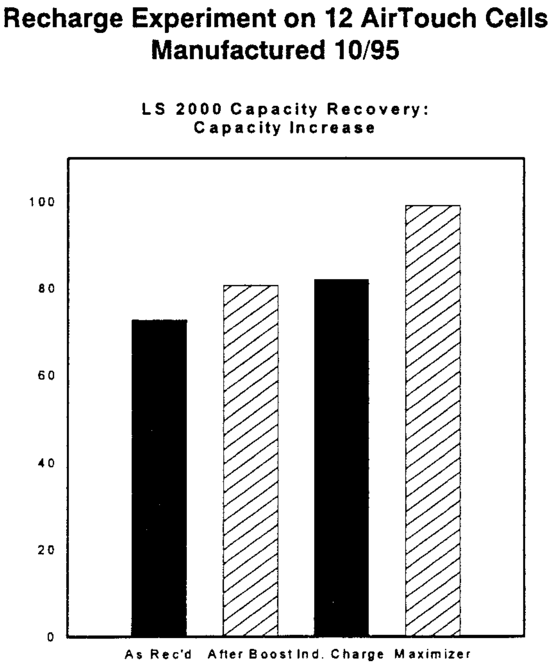
Chart 4 shows the recharge efficiency versus charge voltage for VRLA product. From past presentations it was shown that there is very little hydrogen evolution during charging until we get to 2.40 volts per cell[2]. From the chart we see that is equivalent to approximately 95% recharge efficiency. Therefore, the recharge efficiency must be below 95% to enable the recharge of the negative plates. The chart shows that even at these higher voltages most of the oxygen given off is still being recombined at the negative and at least partially explains why it is necessary to get to at least 2.45 – 2.50 volts per cell on a string basis to be effective in recharging the negative plates.

Chart 4



Unfortunately, it is a lot easier to do experiments in the lab rather than in the field. However, a good example of what level of improvement can be achieved, is shown below. The following chart documents recharge experiments with a string of cells we brought back from AirTouch in Michigan.

Chart 5

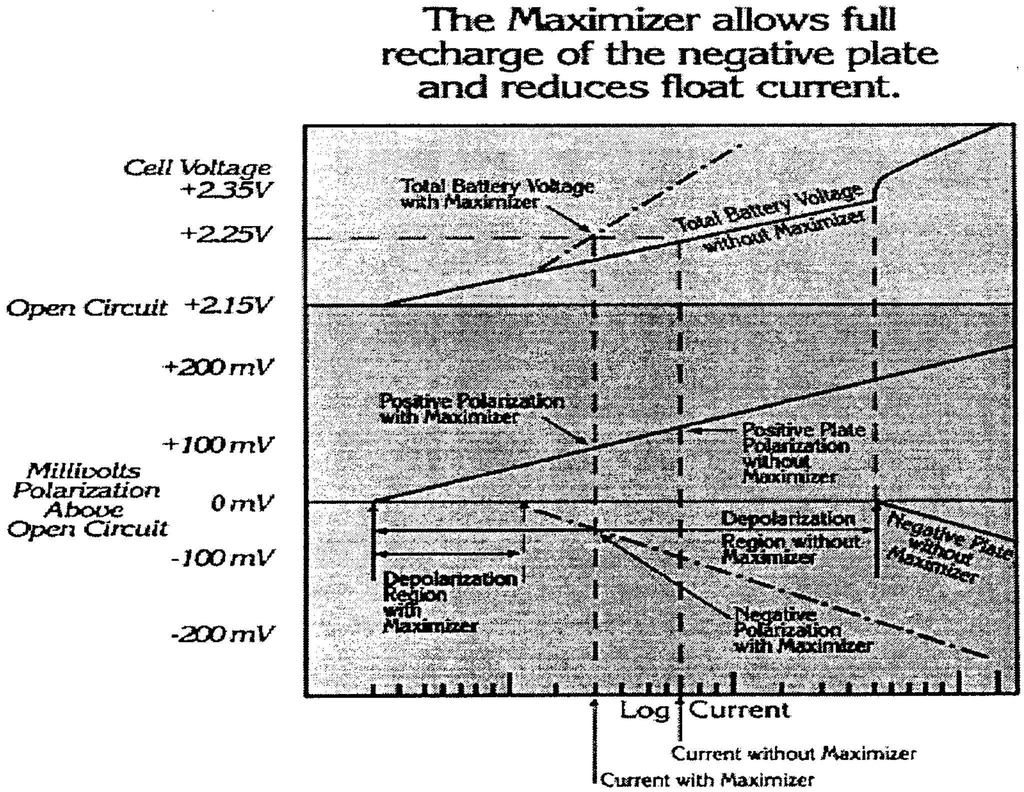


We did a verification discharge on 12 cells manufactured October 1995. The initial discharge showed the string at 72.7% average capacity. A 48 hour recharge at 2.45 volts per cell did not get all cells fully recharged as can be seen from the open circuit readings, but the average capacity improved by a few percent. The major improvement occurred with the addition of the catalyst with the average capacity improving to 99.2%. Subsequent discharges did not do quite as well but was still above 90%.

We believe the catalyst helped improve the cell compression (vacuum created by the recombination of Oxygen and Hydrogen in the headspace) and thus the resulting extra capacity. This shows that although we have a compression plate to maintain compression and the fact that we could obtain 99% capacity, proved the prior loss of capacity was not the result of water loss but the result of sulfated negative plates and compression. We are losing more water due to the self-discharge of the negatives and overcharge of the positive plates then would normally be lost to a recombinant cell in good electrochemical balance. This is exactly why it so important to get the benefit of the catalyst as early in a cells life as possible and the following will support this assertion.

One other point that I feel is very important to discuss at this point in the presentation is the one other measurement, "current". This is also indirectly a very good indication of the negative plate sulfation. However, because of the past difficulty obtaining accurate current readings this measurement is very rarely taken. The reasons for the increasing current draw can be seen in the VRLA tafel, chart 6 below. When the negative plates loose polarization the positive plates increase polarization. As can be seen from a typical tafel curve, the current will increase log linearly. Therefore, when recharge and addition of catalyst cannot be done our recommendation is to lower the float voltage levels to between 2.20 volts and 2.22 volts per cell or 52.8 volts to 53.3 volts for a 48 volt string. This will reduce the over voltage on the positive plates and slow the corrosion rate while limiting the string current draw, internal heating and possible thermal runaway of the cells.

Chart 6



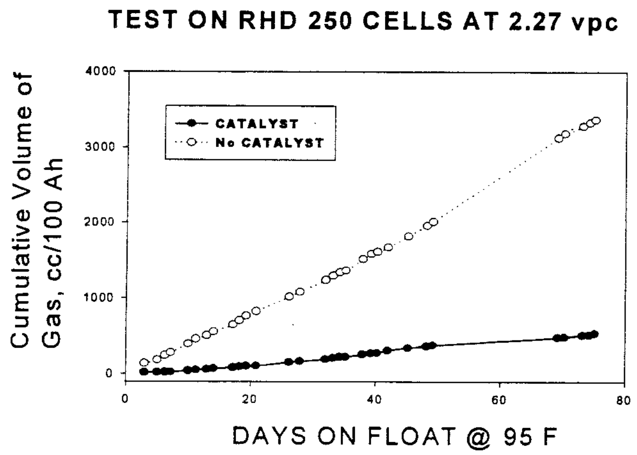
One of the best ways to show long term effects of the catalyst is by looking at the open circuit voltages of cells that have only been on float. C&D 's Conshohocken facility has a large (120 volt) string of HD-700 cells used for our lab UPS system. This was a string manufactured with the catalyst in June 1998 and put into operation at that time. We recently took open circuit readings this past February 2000. You can see in table 4 below that while there has been some variation in readings the average OCV reading is the same.

Table 4

C&D UPS String					
Cell #	w/Catalyst OCV 6/98	OCV 2/00	Cell #	OCV 6/98	OCV 2/00
1	2.144	2.142	31	2.141	2.137
2	2.145	2.143	32	2.142	2.141
3	2.143	2.143	33	2.139	2.137
4	2.143	2.137	34	2.139	2.136
5	2.138	2.139	35	2.138	2.136
6	2.138	2.140	36	2.139	2.136
7	2.140	2.138	37	2.143	2.140
8	2.141	2.133	38	2.147	2.141
9	2.140	2.133	39	2.136	2.119
10	2.142	2.137	40	2.146	2.141
11	2.140	2.139	41	2.144	2.133
12	2.142	2.135	42	2.138	2.135
13	2.143	2.142	43	2.143	2.139
14	2.142	2.142	44	2.140	2.135
15	2.141	2.146	45	2.141	2.135
16	2.140	2.146	46	2.140	2.133
17	2.140	2.132	47	2.142	2.136
18	2.142	2.138	48	2.130	2.133
19	2.142	2.148	49	3.135	2.135
20	2.144	2.141	50	2.142	2.142
21	2.142	2.147	51	2.133	2.135
22	2.159	2.157	52	2.134	2.137
23	2.139	2.143	53	2.132	2.139
24	2.136	2.139	54	2.132	2.137
25	2.140	2.151	55	2.131	2.133
26	2.135	2.144	56	2.130	2.135
27	2.135	2.142	57	2.131	2.137
28	2.132	2.143	58	2.133	2.137
29	2.132	2.143	59	2.132	2.138
30	2.133	2.149	60	2.135	2.142
Average OCV				2.139	2.139

An additional way to show the long-term benefit of the catalyst in as short a period of time is of course the water loss studies. Last year we presented the following chart with showed the cumulative water loss in Liberty 2000 cells at 95°F with and without the catalyst.

Chart 7



This year we have completed more work with the catalyst assemblies placed into "ten year" design Liberty 1000 type product, specifically LS 6-125. Gas evolution was measured at varying voltages. Those results are shown in table 5 below.

Table 5

Gassing Rates on LS 6-125 Batteries with and without Catalyst Assemblies

Battery #	Test Voltage	Test Time (hrs.)	cc/cell/hr
1 (Control)	2.27 vpc	7.1	0.93
	2.35 vpc	4.5	16.8
2 (Control)	2.27 vpc	48.5	1.4
	2.35 vpc	5.8	7.8
3 (w/Catalyst)	2.26 vpc	27	0
	2.35 vpc	27	0.62
	2.45 vpc	22	2.2
4 (w/Catalyst)	2.26 vpc	27	0
	2.35 vpc	27	0
	2.45 vpc	22	0

Clearly, the same trend reported earlier[3] of reduced gassing in batteries with the catalyst was observed in these tests. Little or virtually no gassing was observed in cells with the catalyst, even at high voltages and over extended periods.

We are now in the middle of one of the most effective test to verify the benefits of the catalyst. This is an accelerated life test at 133°F. Table 6 below shows results up to 95 days at 133°F, which is equivalent of at least 2 ½ years of normal float. The water loss is negligible and the capacity performance has not changed. We are looking at this life test mainly to see the benefit in water loss reduction. From the days of flooded lead-acid batteries, life tests have been used to predict end of life from grid corrosion. However, in VRLA product, the accelerated life tests have not been a valid predictor of life because it did not accurately represent what was happening to VRLA batteries in a controlled environment. The high temperatures actually prevent the negative plate degradation while accelerating water loss due to internal pressure build up. Moderate temperature life testing with the catalyst allows for a real evaluation of the grid growth phenomenon while exhibiting the great benefit of the catalyst to prevent water loss in the VRLA product.

Table 6

BLT 3889 LS6-200 w/ CATALYST		
Battery ID:	1	2
Temp:	133°	133°
Jar:	PVC	PVC
Restraint:	Yes	Yes
Baseline	116.6%	113.3%
Initial Wt.	44310	42232
Initial Kmhos	2.99/2679	2.40/2478
Days	33	33
Capacity	121.2%	116.9%
Wt. Loss	0	0
Kmhos	3.88/3273	3.77/3156
Days	65	65
Capacity	119.9%	117.4%
Wt. Loss	2 g	9 g
Kmhos	3.99/2865	3.84/3117
Days	95	95
Capacity	117.6%	114.9%
Wt. Loss	22g	4g
Kmhos	3333	3182

Conclusions

- Clearly the evidence that the catalyst is beneficial is overwhelming.
- The long-term performance verification will take a few more years in actual service.
- Degradation of the negative plates of VRLA product due to the highly efficient recombination mechanism has been verified by open circuit voltage readings.
- There is strong evidence that the negative plate sulfation can be reversed, at least within the first four years of life for a VRLA battery.
- Where it is not possible to recharge older VRLA product, serious consideration should be given to reducing the string voltage to between 2.20 and 2.22 volts per cell.
- C&D is convinced that there are benefits from the catalyst and will be introducing the catalyst in a new series of "ten year" design products next month.

I would also like to thank the many contributors to the information presented in this paper including Sprint, AirTouch Cellular, Bell Atlantic Mobile Systems, Expo Power Systems, Ash Battery Systems as well as many of the engineers at the C&D Battery Laboratories who have provided input to this paper.

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[1] Bruce Dick et al: Battcon 98 and Battcon 99, 2nd & 3rd national battery conf., Boca Raton, FL

[2] S. Misra & A. Williamson, Intelec 96, Boston, MA

[3] Misra et al., Intelec 99, Copenhagen Denmark