Real Time Aging Effects On Vrla Batteries In A Bess Application

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Abstract:

Exide Technologies has two batteries deployed in Battery Energy Storage Systems (BESS). Commissioned in November of 1996, the older of the two is in Vernon (Los Angeles), California and backs up critical environmental controls in a lead smelter. It also functions in a more interesting role: Using the BESS, the plant is able to peak shave the electric draw to the utility when the energy is at its most expensive per kilowatt. The battery in turn is recharged during times of off-peak energy costs.

The other BESS began operating in February 1997 and is located in southwest Alaska. It functions to supplement the slow-reacting hydroelectric power generated by the utility. When an inductive load such as an electric motor starting produces a demand spike, the BESS seamlessly picks up the excess draw and keeps the grid stable. It also absorbs excess energy that could cause over voltage on the grid.

Conventional wisdom has always held that lead-acid batteries should spend as little time in a discharged state as possible or permanent sulfation, increased grid corrosion and diminished life would result. And yet here are two batteries that by design spend a substantial amount of time in a discharged state. Both batteries have to maintain a state of charge that is high enough to deliver energy that is required but low enough to have excellent current acceptance properties. Could the batteries operated in this unconventional charge environment last long enough to be economically viable? Now as 2003 draws to a close, this paper seeks to examine the viability and health of these batteries as their service life reaches 7 and 8 years.

This paper will report on the analysis performed on cells culled from both of these BESS batteries. These data were not obtained by accelerated means in a laboratory but from real time aged cells. We believe the outcome of this testing will have a great deal to say about the long-term viability of Battery Energy Storage Systems.

Vernon Background

The input of the Vernon smelter is spent automotive batteries. Its output is purified lead for the manufacture of new batteries; plastic for non-food uses and neutralized sulfuric acid from which fertilizers and other commodities are manufactured. From start to finish, little is wasted. In between is a gritty manufacturing operation that involves handling toxic and corrosive materials.

The original intent of the Vernon BESS was as back up for the bag houses and other environmental controls that prevent toxic emissions and can get the plant fined. To further defray the costs of the unit, the BESS has been used for peak shaving.

The electric utility for the City of Vernon has a "Time of Use" rate structure, meaning that costs for kilowatt demand and kilowatt-hour vary by time of day and time of year. Predictably these rates are highest in the summer and mid-day. Peak shaving enabled the plant to reduce its demand during the time when the rates are highest. That energy is returned to the battery during off-peak times, when electrical energy is cheaper to buy. In this way the plant was able to reduce its electric bills by between $4000 and $7000 per month. In the lean and low margin business of lead smelting, that's not insignificant.

Metlakatla Background:

A world away from the densely populated and urban environment of Los Angeles is Metlakatla, a place of awesome beauty and fewer sports teams and latte joints. This island community has as its utility Metlakatla Power and Light (MP&L). Receiving upwards of 330 centimeters (130 inches) of rain per year, the island has water reservoirs in the mountains surrounding the settlement. Gravity brings the water down the mountains through pipes that spin the turbines and generate electricity. It is an elegant and nearly free way to provide power to the island but not without its own problems.

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Hydro by its nature cannot quickly respond to large load shifts or spikes. As it turns out, there was a sawmill on the island that subjected the power grid to large transients. When it did, the entire grid would suffer voltage sags and frequency variation. This poor power quality occasionally caused damage to electric appliances and always caused annoyance to residents. 18 years ago in order to improve grid stability, the utility purchased a $2 million, 3.3 MW diesel generator system to augment the hydro. But the only way to get reasonable efficiency from the diesel was to load it heavily with the grid demand and shift away from the cheap hydro. Further, even with the diesel, not only did the system voltage and the electrical frequency problems persist, but also the cost of operating it proved burdensome to the small utility.

Enter the BESS: Always on line, the BESS is intended to be operated at approximately an 80% state of charge (SOC). This SOC ensures that it is always available to provide instantaneous power when demand spikes higher than hydro output, but also always capable of accepting excess energy that could cause over-spin or over-voltage from a sudden dip in demand. The implementation of the BESS virtually eliminated the need for the diesel resulting in fuel savings alone of $360,000 to $400,000 per year. The utility saved an additional $400,000 over six years in diesel overhaul costs. Together, the system paid for itself in three years. It vastly improved power quality and spared the island noise and air pollution as well as the hazard of transporting almost 500,000 gallons of fuel per year into the environmentally sensitive region.

<u>Testing:</u>

Typically, battery manufacturers contemplating product changes will prototype a battery and subject it to accelerated life testing methods. This usually involves floating the battery in a chamber at elevated temperatures. While this can work to simulate the passage of time to, for example, determine grid corrosion rates, high temperature increase self-discharge rates. Since charge balance is precisely the item being evaluated here, it seems doubtful that accelerated techniques would accurately model system behavior. The value of this study therefore, is having real time aged product for evaluation.

Cells from both systems were removed and shipped to our lab for testing with the same basic procedure was applied to both. The cells were discharged as received to get a sense of their SOC in service. The cells were then boosted, floated to characterize their float current and discharged at their C/8 rate. After several more cycles at the C/8 rate, the cells were tested for compliance at other rates, including C/1, C/3, C/5 and C/12.

After the electrical testing, samples from the Metlakatla battery were torn down to examine and assess cell internals. Grids were cross-sectioned and polished. Analysis using BET surface area and X-ray diffraction techniques revealed compositional and structural characteristics of the battery plate active material. This work has not yet been scheduled for the Vernon battery.

<u>Electrical Test Results:</u>

Cells from the Vernon battery were sampled and tested in March of 2000 after almost four years into its service life. Overall rate compliance at that time was 95%. Almost four years later, cells were sampled and tested again. This time, as-received capacities were measured to be 44% but after a boost, were brought up to 78% where they stayed. While IEEE would view this battery as at its end of life (being below 80% of rated), it is still functional in that it can provide energy for an orderly shutdown of the plant and peak shaving. Table 1 summarizes the performance of twelve cells over four discharge cycles. The small spread in cell capacities suggests that they are degrading uniformly and in a predictable rather than catastrophic manner.

Cell	C 1	C 2	C 3	C 4	C 5	C 6	C 7	C 8	C 9	C 10	C 11	C 12	Avg
Disch 1	46%	48%	43%	43%	48%	48%	43%	43%	40%	45%	43%	44%	44%
Disch 2	76%	80%	76%	76%	76%	79%	71%	75%	69%	74%	73%	75%	75%
Disch 3	78%	83%	79%	79%	80%	81%	73%	78%	71%	77%	75%	78%	78%
Disch 4	78%	83%	80%	80%	80%	81%	73%	79%	71%	78%	75%	78%	78%

Table 1: Vernon C/8 Cell Capacities after 94 Months Service

Metlakatla was also tested previously, about 32 months into its service life. At that time, C/8 rate compliance was 99% and overall compliance to rates between C/1 to C/24 was 106%. The latest data produced some 73 months into the battery's service life shows compliance to be 98% and 97%, respectively. Tables 2 and 3 summarize the latest available Metlakatla rate conformance data. The tables show excellent capacities with little variability between cells.

Cell	Disch 1	Disch 2	Disch 3	Disch 4	Disch 5	Disch 6
Cell 1	64%	101%	103%	102%	103%	102%
Cell 2	55%	92%	96%	94%	95%	95%
Cell 3	58%	99%	101%	101%	101%	101%
Cell 4	66%	98%	101%	100%	102%	101%
Cell 5	58%	89%	94%	91%	93%	92%
Cell 6	61%	94%	99%	97%	99%	99%
Cell 7	53%	96%	98%	98%	99%	98%
Cell 8	53%	96%	99%	98%	100%	99%
Cell 9	58%	96%	99%	98%	100%	99%
Cell 10	61%	94%	97%	95%	97%	96%
Cell 11	59%	99%	103%	102%	103%	102%
Cell 12	52%	94%	97%	95%	97%	96%
Average	58%	96%	99%	98%	99%	98%

Table 2: Metlakatla 73 Month C/8 Capacities – Discharge 1 represents As-Received Capacity

Cell	C/5	C/12	C/3	C/8	C/1
Cell 1	98%	95%	95%	98%	90%
Cell 2	96%	96%	97%	99%	90%
Cell 3	97%	95%	99%	98%	96%
Cell 4	94%	93%	95%	95%	93%
Cell 5	100%	98%	105%	101%	107%
Cell 6	95%	93%	98%	97%	100%
Average	**97%**	**95%**	**98%**	**98%**	**96%**

Table 3: Metlakatla 73 C/x Capacities

Metlakatla Tear Down and Analysis:

Positive Plates:

The positives were in good shape and consistent with their age. The positive active material (PAM) was black and crunchy in texture. It exhibited good adhesion to the grid, suggesting a well developed grid-PAM corrosion layer and electrical continuity. The grid frames were in excellent shape as were most minor vertical and horizontal members. There was some fragility in the upper center portion of the grid where current densities would have been highest but there was plenty of cross-sectional metal to carry current still left. Figure 1 shows the polished cross section of a non-frame vertical grid member. The corrosion layer averaged 0.10 to 0.19 mm compared to 0.13 to 0.18 mm at the 32 month point. This puts the corrosion rate at about 0.03 mm per year which is well below a typical Absolyte value of 0.06 mm per year.

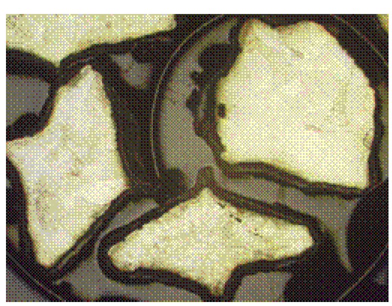

Figure 1: Polished Metlakatla Vertical Grid Wire at 73 Months Service

X-ray diffraction analysis (XRD) of the PAM indicated a compositionally high percentage of β-PbO_2 favored over α-PbO_2. This is balance is typical for a battery in a cycling application where the active material has been extensively "worked".

BET Surface Area indicated fairly typical values which increased as the distance from the lug increased. This indicates that the paste is expanding near the top of the plate where it is more utilized as the bottom PAM is only used in deeper discharges. As long as the PAM stays solid, which it was observed to be, shedding and degradation should not be a problem.

Negative Plates:

The negative active material (NAM) readily oozed electrolyte when pressured which meant that it was fully saturated. The NAM was shiny when scratched, indicating that it was charged. The shiny NAM, good specific gravity readings of 1.313 (1.310 mid-spec) and normal open circuit voltage readings (2.15 V) suggests that the substantial $PbSO_4$ noted by the XRD testing was introduced at tear down and not its natural state in service. Negatives sulfate rapidly in air. It can be avoided but only with difficulty. Table 4 summarizes the XRD and BET data.

	XRD (+/- 5 wt %)				BET Surface Area	
Sample	**Pb**	**$PbSO_4$**	**α-PbO_2**	**β-PbO_2**	**m^2/g**	**+/-**
Positive Top #1	-	-	6	94	1.20	0.0086
Positive Mid #2	-	-	9	91	1.32	0.0072
Positive Btm #3	-	2	6	92	1.40	0.0064
Positive Top #4	-	-	5	95	1.24	0.0070
Positive Top #5	-	-	7	93	1.35	0.0063
Positive Top #6	-	-	7	93	1.45	0.0088
Negative Top #7	90	10	-	-		
Negative Mid #8	100	-	-	-		
Negative Btm #9	84	16	-	-		

Table 4: Metlakatla XRD and BET Data from 73 Month Old Cell Plates

Decreasing BET values signals increasing PAM expansion and is occurring at the most utilized top of plate. α-PbO_2 is converted to β-PbO_2 in cycled batteries. $PbSO_4$ was probably introduced at the tear down.

General Observations:

As noted above, the specific gravity of the electrolyte was in specification and not stratified. The separator was adequately wetted. The straps or bus bars exhibited no corrosion or wear. In short, the condition of the cell element was unexceptional.

Summary and Conclusions:

- While the Vernon battery is nearing its end of life at its design 8-year point, Capacity data suggests that while it can still function effectively.
- The Metlakatla battery capacity is still extremely strong. This second data point shows the battery capacity to be stable and suggests that it will achieve its 8-year design life. Continued operation at an SOC of less than 100% has not appeared to have caused an early end of life.
- Cell internals of the Metlakatla cells were unexceptional with no obvious degradation other than normal aging patterns. In fact, the grid corrosion rate is lower than expected. XRD and BET surface area analysis indicate normal compositional and structural characteristics for a cycling application battery.
- These two VRLA batteries have proved to be viable in these unconventional charging regimes.

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