

Summary of Electrical Test Results for VRLA Batteries

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Abstract

Sandia National Laboratories conducts the Energy Storage Systems (ESS) Program for the U.S. Department of Energy (DOE). The goal of this program is to collaborate with industry in developing cost-effective electric energy storage systems for many high-value stationary applications. Under the auspices of the ESS Program, electrical tests were performed on two VRLA batteries to compare effects of improvements, evaluate their applicability to stationary applications, and to determine their service lives. One battery represented a baseline design, and the other an improved design resulting from a development project. The two 9-cell, 1050- to 1200-Ah at C/8 batteries were tested over a 7-year period using primarily a 100% DOD, and approximately a C/8 discharge regime. A variety of charge profiles were investigated and characterized. Both batteries reached end-of-life after several hundred cycles. This paper will describe these results, and overall life data and comparison information will be summarized.

Introduction

Energy storage systems for electric utilities, telecommunication systems, and other stationary applications must have high reliability and long life times. It is also desirable that the batteries used in these systems require little maintenance. In general, valve regulated lead-acid (VRLA) batteries require little maintenance, but VRLA-based systems have experienced field failures and questions regarding their reliability have been raised.

In 1991, the DOE Energy Storage Systems Program at Sandia National Laboratories (SNL) began a competitively placed, multi-year, cost-shared contract with GNB Industrial Battery Corporation to enhance

VRLA battery designs, improve performance, and reduce costs for utility applications. This paper will describe the electrical test results from the ABSOLYTE II and ABSOLYTE IIP batteries delivered to SNL during this contract. The testing methodologies and preliminary results were described in another paper.¹ The tests included different charge regimes and specialized discharges for various applications. A future paper will describe an analysis of the results and end-of-life observations.

The ABSOLYTE II modules are designated Type 85A-25, and the ABSOLYTE IIP modules are Type 100A-25. In each case, three modules, each with three cells, were stacked to make a nine-cell battery. The two batteries are externally identical in size and configuration (the ABSOLYTE IIP cell cases are light gray and the ABSOLYTE II cell cases are dark gray). The cells, as installed for use, measure approximately six inches tall, nine inches wide, and 24 inches deep, and are mounted side-by-side in the modules. The terminals are mounted on the 6 \times 9 side. There are four terminals per cell, two positives connected in parallel and two negatives in parallel. Each cell has a vent centrally located on the terminal side. The assembly weighs approximately 1850 pounds. A photograph of the ABSOLYTE IIP battery is shown in Figure 1.

¹ P.C. Butler, J.T. Crow, P.A. Taylor, *Battery Evaluation Methods and Results for Stationary Applications*, Intelec 97 (19th International Telecommunications and Energy Conference), Melbourne, Australia, October 19-23, 1997.

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The nominal fully-charged open circuit voltage of the batteries is 20 V. The rated capacity of the ABSOLYTE II is 1040-Ah discharged at 25°C at a C/8 rate to an average of 1.75 V per cell (Vpc), or 15.75 V for nine cells in series. The ABSOLYTE IIP has a rated C/8 capacity of 1200 Ah at 25°C with a C/8 discharge rate to 1.75 Vpc.

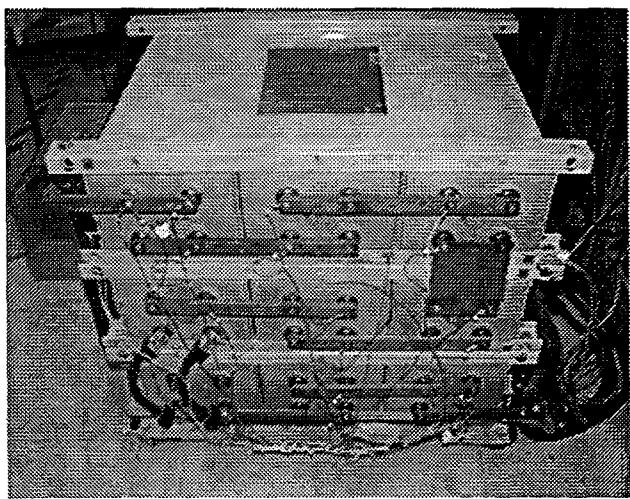


Figure 1. ABSOLYTE IIP Battery.

Initial Evaluation and Testing of ABSOLYTE IIP Battery

In 1994, a test plan was written to evaluate the performance of the ABSOLYTE IIP battery. The testing objectives that were pursued in 1995 included:

1. Confirming the electrical performance ratings under various constant-current loads,
2. Evaluating the battery's capability to meet frequency regulation and spinning reserve requirements for utility energy storage (UES) applications, and
3. Determining the service life of the battery.

A series of capacity measurement cycles were begun using the A-recharge regime shown in Table 1. As shown in Figure 2 (cycles 1-128), capacity was initially measured at C/2, C/8, and C/18 discharge rates. Capacity was initially as-rated at these discharge rates, but tended to decline over a few cycles, calling into question the recharge regime. The manufacturer recommended several recharge sequences as part of a study to determine the appropriate recharge regime. Beginning with cycle 27, a series of capacity discharge cycles was performed at C/8 with various recharge sequences as shown (Table 1), with varying results. All recharge

regimes, except recharge regime B, had a 7% amp-hour return limit in common—that is, charge returned was limited to 7% more than the ampere-hours removed in the previous discharge. In general, capacity continued to decline slowly. At cycle 86, the E-recharge sequence was implemented, with somewhat declining capacity at a C/8 discharge rate, and relatively stable capacity at a C/2 discharge rate. The E-recharge was continued until the beginning of the frequency regulation and spinning reserve testing.

Frequency Regulation and Spinning Reserve Testing of ABSOLYTE IIP Battery

The frequency regulation and spinning reserve tests were designed to be similar to a test performed in the SNL evaluation of the C&D Charter Power Systems Inc. flooded lead-acid battery in 1993 and 1994 for the Puerto Rico Electric Power Authority (PREPA).² The frequency regulation part of the tests consisted of a succession of 160-minute subcycles of constant power charge and discharge. These cycles begin with the battery state of charge (SOC) at 90% (at the beginning of the test, the battery charge is decreased from 100% to 90% by a constant current discharge), and continue until the battery reaches 70% SOC, which requires approximately 20 subcycles. An intermediate charge (constant current of 120 A to 2.35 Vpc, constant voltage to 90% SOC) is applied to return the battery to 90% SOC, assuming 100% charge return efficiency. This sequence is repeated three times, with a spinning reserve discharge added at the end of the third frequency regulation sequence. The spinning reserve test consists of a constant power (11.38-kW) discharge for 17 minutes, with a linear ramp to zero discharge power over the next seven minutes. This sequence is followed by a refreshing charge (300-A constant current to 2.4 Vpc, constant 2.4 Vpc until current tapers to 24 A, 24-A constant current for two hours, then open circuit for 8 hours).

Typical test data (cycle 141) are shown in Figure 3. The spinning reserve discharge at the end decreased the battery SOC from 70% to 46%. A count of the number of frequency regulation subcycles in each set shows 23 subcycles in set 1, and 19 subcycles in sets 2 and 3, implying less coulombic efficiency or less capacity in the second two sets. This phenomenon appears to be correlated with battery temperature during the three sets.

² Boyes J.D. *Lessons Learned from the Puerto Rico Battery Energy Storage System*, English and Spanish versions available (SAND99-2232), Sandia National Laboratories, Albuquerque, NM, September 1999.

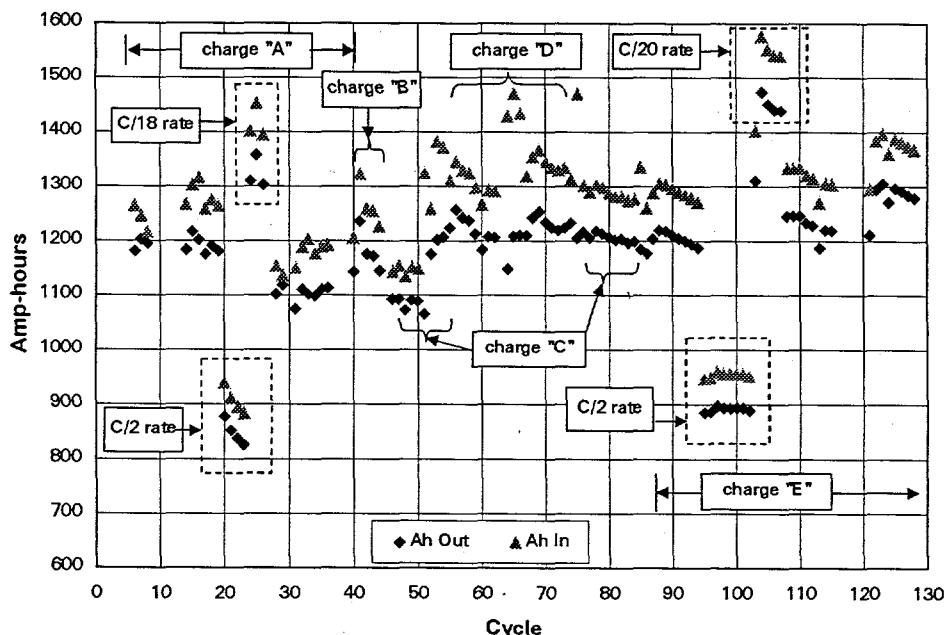


Figure 2. Capacity (Ah out) and recharge (Ah in) for the ABSOLYTE IIP for the first 128 cycles at a C/8 rate except as noted.

ABSOLYTE IIP PV/Renewable Application Testing

At the request of SNL's Photovoltaic (PV) Systems Application Department several tests were performed in order to characterize the ABSOLYTE IIP for an Arizona Public Service Company (APS) remote PV power system application. The characterizations provided SNL with the details it needed to make the appropriate recommendations.

A brief summary of the test regimes and results follows.

1. A constant power discharge at a 281-W rate from 100% SOC to an end-of-discharge (EOD) voltage of 1.75 Vpc (100% DOD) to determine the percentage SOC at the 2.03 Vpc level. This was cycle 145, which yielded 1645-Ah total capacity, with 785 Ah to the 2.03 Vpc level. The battery was then returned to 100% SOC.
2. A recharge time test for three cycles (146-148), with a constant-power, 281-W discharge to 2.03 Vpc, and recharge at 1125-W constant power rate to 2.35 Vpc, and then clamp at 2.35 Vpc to 7% overcharge (1.07 times Ah removed). Results of this test showed that it took 11.1 hr on average for the ABSOLYTE IIP battery to reach the 2.35 Vpc point, at which point 83% of the Ah removed had been returned. Two hours later,

94% had been returned, and after an additional 7.1 hr at the 2.35 Vpc level, 7% overcharge was reached, for a total recharge time of 20.2 hr.

3. A cycling test (cycles 149-168) to determine cycling stability, beginning at full SOC with repetitive discharge at 281 W to 2.03 Vpc, then recharge at 1125-W constant power rate to 2.35 Vpc and clamp at 2.35 Vpc for 2 hr. Cycle 149 discharge began at full SOC from the previous cycle, but the charge regime of this test returns less charge, so the capacity at cycle 150 shows a sharp drop. The gradual decrease in capacity from cycle 150-168 was attributed by GNB to a continual buildup of sulfation on the plates, caused by insufficient recharge. Accumulation of lead sulfate and the corresponding loss of sulfate ions from the electrolyte caused an increase of internal resistance and consequent recharge inefficiency.
4. A discharge capacity test at a 281-W rate to 100% DOD after charging at a 1125-W rate to 2.35 Vpc and clamping at 2.35 Vpc for 2 hours. This test produced a capacity of 1538 Ah, 95 % of the 1625 Ah capacity obtained at a 281-W discharge rate from 100% SOC. A second discharge capacity test was performed using a similar charge with a 12-hr clamp time, but later

examination of the data indicated a discrepancy in the charge profile, invalidating the results.

Table 1. ABSOLYTE II and ABSOLYTE IIP Charge Regimes

Charge regime	Sequence: CI = constant current, CV = constant voltage, OC = open circuit	ABSOLYTE II cycles	ABSOLYTE IIP cycles
A	CI (300 A) to 21.15 V (2.35 Vpc) CV (21.15 V) to 107% charge return OC for 2 hours		1 - 40
B	CI (300 A) to 21.15 V (2.35 Vpc) CV (21.15 V) to 24 A, CI (24 A) for 2 hours OC for 2 hours		41- 45
C	CI (300 A) to 21.15 V (2.35 Vpc) CV (21.15 V) to 107% charge return OC for 8 hours		46-55, and 75-85
D	CI (300 A) to 21.15 V (2.35 Vpc) CV (21.15 V) to 24 A, CI (24 A) to 107% charge return OC for 8 hours	1-59	56-74
E	CI (300 A) to 21.60 V (2.40 Vpc) CV (21.60 V) to 24 A, CI (24 A) to 107% charge return OC for 8 hours	60-76, and 89-446 (float tests 77-88)	86-128
F	CI (300 A) to 21.6 V (2.4 Vpc) CV (21.6 V) to 24 A, cool below 40°C CV (21.6 V) to 24 A, CI (24 A) to 107% charge return OC for 8 hours	118-139 (cycle 140, see text)	171-305 (after frequency regulation and PV test cycles 129-170)
G (8-cell)	CI (300 A) to 19.2 V (2.4 Vpc, 8 cells) CV (19.2 V) to 24 A, cool below 40°C CV (19.2 V) to 24 A, CI (24 A) to 107% charge return OC for 8 hours		306-395
H	CI (300 A) to 21.6 V (2.4 Vpc) wait 1 minute CV (21.6 V) to 24 A, wait 1 minute CI (24 A) to 107% charge return OC for 8 hours	141-445	
H (8-cell)	CI (300 A) to 19.2 V (2.4 Vpc, 8 cells) wait 1 minute CV (21.6 V) to 24 A, wait 1 minute CI (24 A) to 107% charge return OC for 8 hours	445-507 (EOL)	396-699 (EOL)

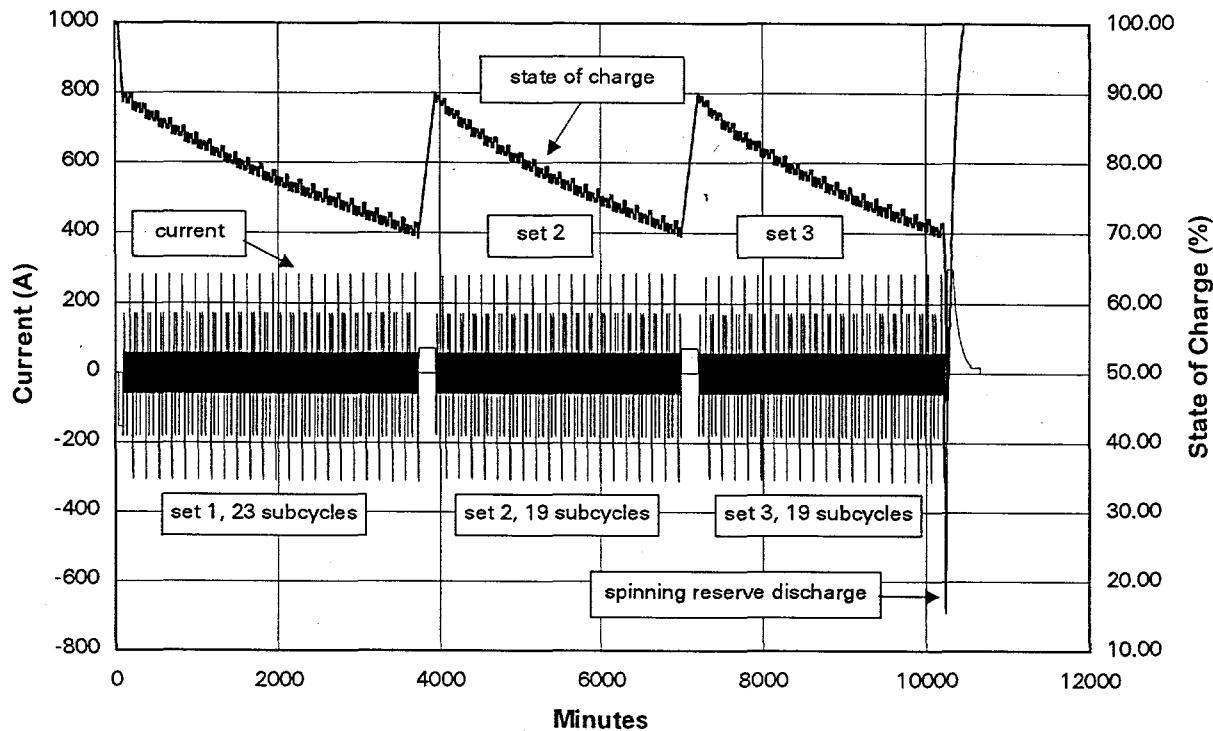


Figure 3. The three sets of subcycles of cycle 141 of the ABSOLYTE IIP frequency regulation and spinning reserve discharge test showing the decline in the state of charge during a set, and the increased number of subcycles obtainable in the first set.

Life Cycle Testing of ABSOLYTE IIP Battery

After the battery completed the PV applications testing in 1996, it was placed on a life cycle test regime, beginning at cycle 171. The battery was repetitively discharged at a C/8 (150-A) rate, and recharged using various charge regimes as indicated in Table 1. While the details of the charge profiles were varied in attempts to refine and improve the charge acceptance of the batteries, all the charge regimes have in common a charge return of 7% more than charge removed on the previous discharge. Capacities measured in these life cycle tests are shown in Figure 4. Cycles are numbered from the beginning of testing of the ABSOLYTE IIP battery, with one cycle being a discharge to a specified level, followed by a recharge. Cycles 1 through 128 previously shown in Figure 2 are included in Figure 4.

The charging regime was modified at cycle 171 to the F-charge regime to improve compatibility between the tester and the battery and to try to improve the charge acceptance of the battery. The result was an improvement in battery capacity from cycle 171 to cycle 180, but a gradual decline thereafter.

At cycle 266, each cell was removed and weighed and the weights compared with the original weights. The cells showed an average weight loss of 1 kg. At cycle 270, 300 ml of deionized water were added to each cell. Tester malfunctions produced incomplete data and uncertain charging through cycle 274. An equalization charge of 1720 Ah was performed at cycle 275, with slight improvement in capacity. At the end of cycle 281, 400 ml to 900 ml of deionized water were added to each cell to bring the individual cell weights back up to their original values. Cells 1, 4, and 6 vented on cycle 282, and testing was halted. All cells were examined for electrolyte level and found to be satisfactory. Also at this time, Cell 3 was

bypassed because of chronic low voltage; thus the battery became eight cells in series.

Capacity life cycles were then continued during 1997 until cycle 394, when a tester malfunction halted testing. The battery was on open circuit from September 19, 1997, to resumption of life cycle testing on February 23, 1998. Testing resumed using the H-charge regime, which removed the battery temperature limits on wait, and substituted specific wait times. Testing continued to cycle 610, with the same rate of capacity decline. At this point, the capacity had decreased to 972 Ah, near the defined end of life of 960 Ah. Cell 5 EOD voltage, which had been low throughout life cycle testing, began to decline more rapidly through cycles 500 to 600. Testing was halted at cycle 610 on September 16, 1998, to diagnose erratic cell 1 voltage readings, and pending decisions on continued testing. Testing was resumed November 30, with nine diagnostic C/8 discharge cycles that used the H-charge regime.

By cycle 693, capacity had declined to 914 Ah. An 18% boost overcharge was performed on cycle 694, with slight improvement in capacity. Testing was halted on May 23, 1999, at cycle 699, pending a decision on post-service-life tests.

Initial Evaluation and Testing of ABSOLYTE II Battery

In the third quarter of 1995, the ABSOLYTE II battery was placed on test with the objective of evaluating improvements from the ABSOLYTE II design to the ABSOLYTE IIP design. Initial capacity tests were made at a C/8 rate of 130 A, corresponding to the 1040 Ah at C/8 discharge rating of the battery. In these capacity cycles, the battery delivered nearly 1300 Ah (all cycles are shown in Figure 5), substantially higher than its rating, and somewhat higher than the ABSOLYTE IIP. After cycle 31, the discharge rate was changed to a constant 150 A, to make a comparison at the same discharge current of the ABSOLYTE II and ABSOLYTE IIP designs. The D-charge regime (Table 1) was used for the ABSOLYTE II for these initial tests. These early results indicated that the early-life available capacity of the ABSOLYTE II design was very comparable to the ABSOLYTE IIP design. Capacity generally decreased gradually over the first 59 cycles.

In the first quarter of 1996, measurements of the capacity of the ABSOLYTE II were also made at C/2

(actual current 422 A) and C/20 (actual current 68 A) rates to compare with the measurements of the ABSOLYTE IIP at C/2 (428 A) and C/18 (74 A). At C/2, the ABSOLYTE II averaged 857 Ah over cycles 60-63, and the ABSOLYTE IIP averaged 892 Ah over cycles 95-102. At the lower currents (C/20 for the ABSOLYTE II and C/18 for the ABSOLYTE IIP), the ABSOLYTE II averaged 1413 Ah, and the ABSOLYTE IIP averaged 1451 Ah. These capacity measurements used the E-charge regime, which began with cycle 60.

ABSOLYTE II Float Charge Testing

In mid-1996, a special study was initiated to determine the effect on discharge capacity of float charging at specific constant voltage levels. The purpose of the study was to provide guidance to New Mexico State University in the setup of renewable energy systems for the U.S. Coast Guard that utilizes the ABSOLYTE technology. The charge sequence was 100-A constant current charge until the specified float voltage was attained, then constant voltage charge until the total charge time reached 72 hours. A trend of increasing capacities with increasing float voltages was observed. This trend suggests that charging at 2.25 Vpc would provide approximately 100% of the battery's capacity, and 2.25 Vpc is the lowest recommended float voltage specified in the operating manual for the ABSOLYTE II. A tester malfunction halted testing before these tests could be done at 2.25 Vpc, and the float charge testing program ended before the tester could be repaired.

ABSOLYTE II Life Cycle Testing

After the float charge tests, life cycle testing was resumed. Six cycles were performed (89-94) when a tester-to-database transfer problem occurred. Testing was suspended on April 5, 1996, and resumed on November 5, 1996. Life cycle testing continued through cycle 113 on December 16, 1996, when testing was suspended for 6 weeks. Life cycle testing resumed on January 31, 1997, following the ABSOLYTE II E-charge regime, with charge cycles occasionally interrupted by battery high temperature alarms.

To avoid the high temperatures, a change was made at cycle 118 to the ABSOLYTE II F-charge regime (Table 1), which includes a cool down period to temperatures less than 40°C after charge 1 and two separate 24-A charge periods. The charge times proved to be unacceptably long, and at cycle 140 a change was made to the ABSOLYTE II charge regime (Table 1), in which the second 24-A charge was eliminated. One cycle (140) was done with this charge, on March 11, 1997, when a tester

malfunction halted testing. At this time, the battery capacity had declined slightly to 1160 Ah.

The battery remained on open circuit for one year. Testing was resumed on March 7, 1998, with a discharge to 1.75 Vpc, and a moderate boost charge with 1348-Ah returned. Life cycle testing resumed using the H-charge regime. Capacity had declined markedly from the 1160-Ah measured prior to the testing halt. Capacity increased slowly over the next 20 cycles, perhaps limited by the 7% overcharge. Capacity held reasonably steady at approximately 1100 Ah, with some fluctuations, over the next 50 cycles, then began a gradual decline.

Temperature Effects on Capacity

The ABSOLYTE II battery was located in a laboratory in a temporary building, along with several other systems under test. The air conditioning was generally not sufficient, and cyclic ambient temperature fluctuations of 3°C to 5°C were common, with occasional larger fluctuations. The air conditioning system became increasingly erratic, and by cycle 373 was causing erratic tester operation. Testing was halted at this point for air conditioning repair.

During a review of the data following the test halt, a cyclic fluctuation in the capacity of the ABSOLYTE II was noted. Comparison of the battery capacity with the ambient temperature of the laboratory in which the measurements were being made showed a strong correlation between an increase in ambient temperature and an increase in battery capacity, of approximately 0.4%/°C.

Continued Life Cycle Testing to End of Life

Cell 4 was especially affected by the air conditioning failure at cycle 373. Cell voltage was improved somewhat by the boost charge at cycle 441, but not up to the level of the other cells. Cell 4 was bypassed after cycle 446. Voltage levels in the H-charge

regime for the ABSOLYTE II were adjusted to compensate for the bypassed cell, so after cycle 446 the ABSOLYTE II H-charge regime corresponded to the ABSOLYTE IIP H-charge regime.

Life cycle tests continued with declining battery capacity. By cycle 506 (June 15, 1999) capacity was consistently below the 832 Ah that corresponded to 80% of rated capacity, and testing was halted.

Comparisons between life tests of the ABSOLYTE II and ABSOLYTE IIP

The energy efficiencies of both batteries (Figure 6) was approximately 81% at the beginning of testing. The efficiency of the ABSOLYTE II declined approximately linearly through the tests, while the efficiency of the ABSOLYTE IIP remained relatively constant.

Summary

Initial capacities of the two batteries were very similar, even though the ABSOLYTE IIP was rated at 1200 Ah, and the ABSOLYTE II at 1040 Ah. Both batteries had one cell fail during the testing. The ABSOLYTE IIP achieved approximately 40% more cycles than the ABSOLYTE II before reaching end-of-life. The ABSOLYTE II had extended open circuit periods, although the battery was kept charged during the open circuit times. The energy efficiency of both batteries was approximately 81% at the beginning of testing, but the efficiency of the ABSOLYTE II declined approximately linearly through the tests, while the efficiency of the ABSOLYTE IIP remained relatively constant. The total energy extracted from the ABSOLYTE IIP through 699 cycles was 12.4 MWh, and for the ABSOLYTE II, the energy discharged in 506 cycles was 8.9 MWh.

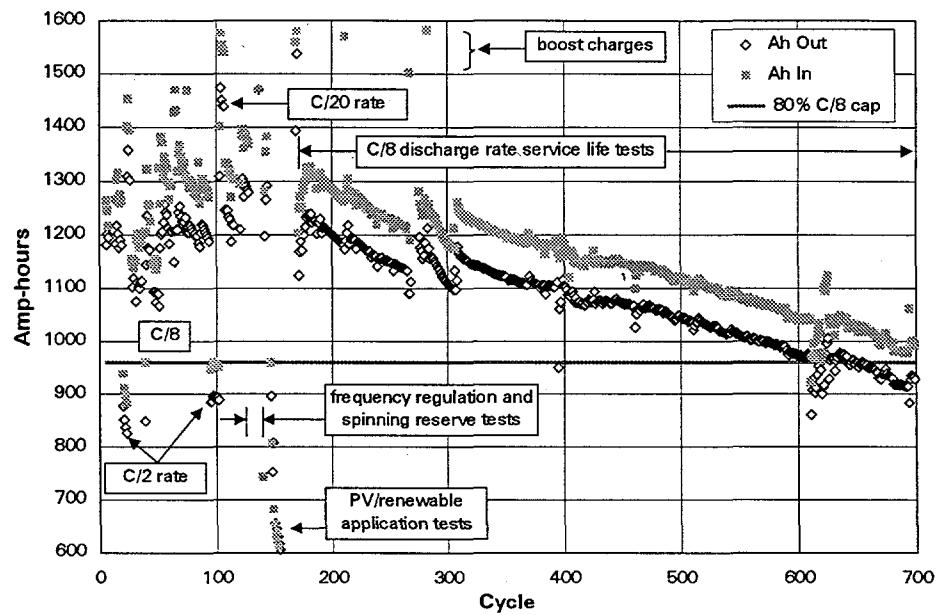


Figure 4. Amp-hours removed (capacity) and returned for all cycles of the ABSOLYTE IIP battery. The horizontal line at 960 Ah indicates the end-of-life at 80% of rated capacity.

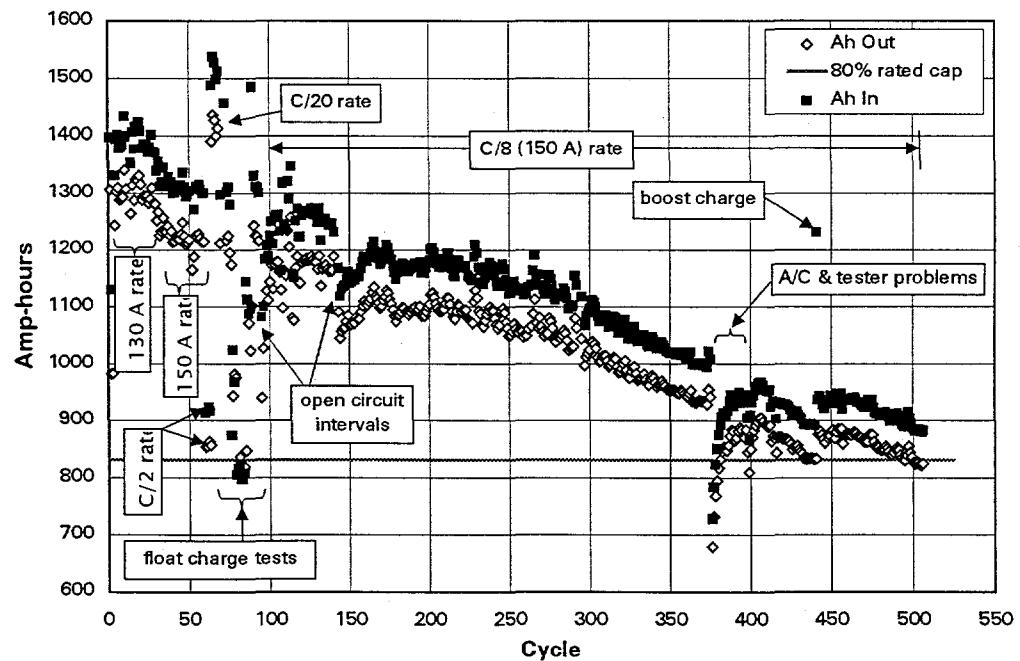


Figure 5. Capacity (Ah out) and charge returned (Ah in) for the ABSOLYTE II battery for all cycles.

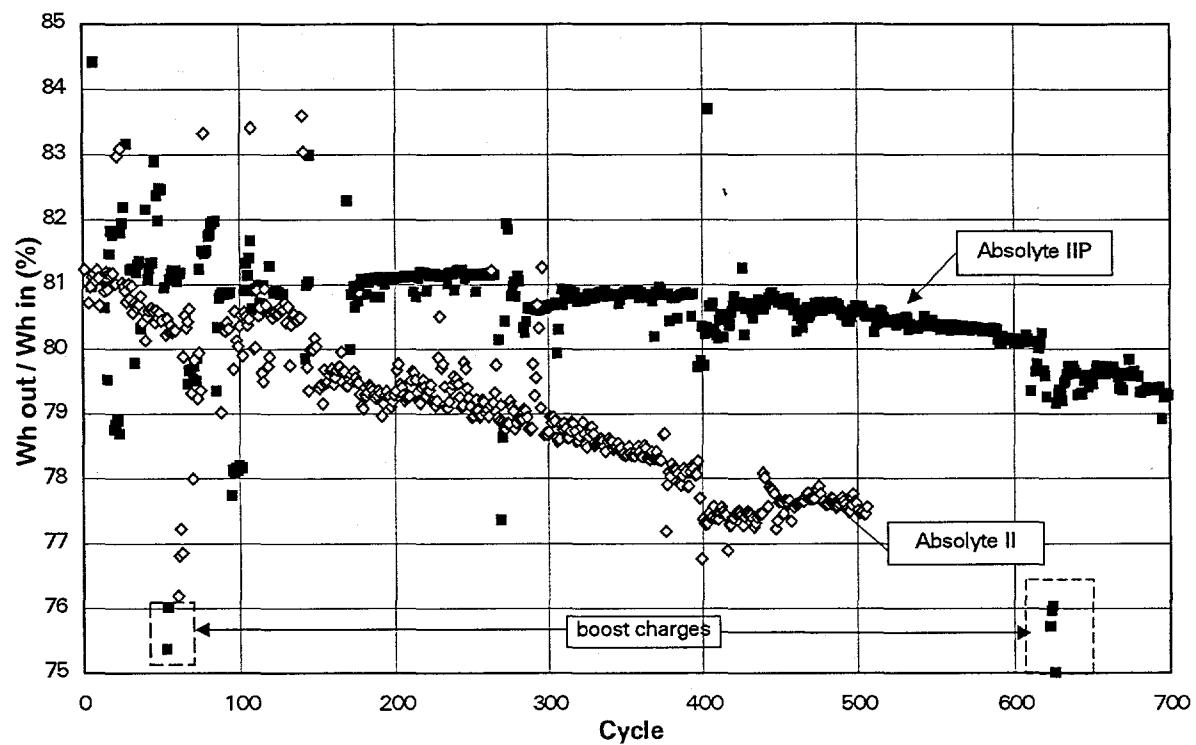


Figure 6. Comparison of the ratio of energy discharged to energy charged for the ABSOLYTE II and ABSOLYTE IIP batteries through their lifetimes.