NICKEL-CADMIUM CELL DESIGN

VARIABLE PROGRAM

DATA ANALYSIS

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ABSTRACT

A program was undertaken in conjunction with the General Electric Company to evaluate eight of the more important nickel-cadmium cell designs that are currently being used or that have been used during the past 15 years. Design variables tested in this program included teflonated negative plates, silver treated negative plates, light plate loading level, no positive plate cadmium treatment, plate design of 1968 utilizing both old and new processing techniques, and electrochemically impregnated positive plates. The data acquired from these test packs in a low earth orbit cycling regime is presented and analyzed here. This data showed conclusively that the cells manufactured with no positive plate cadmium treatment outperformed all other cell designs in all aspects of the program and that the cells with teflonated negative electrodes performed very poorly.

INTRODUCTION

A review of the design history of nickel-cadmium aerospace cells indicates that present cells bear only a slight resemblance to those used in the first satellite applications. The changes that have occurred in the cells can be attributed to a number of factors. The desire to improve energy density, the need for longer life, the need to improve production yield, the desire to enhance cell performance and the competitive drive to meet customer's requirements. Many of the changes have been tested and evaluated by the various users but there has been no systematic approach to compare to relative merits of each design. Consequently, a program was undertaken in conjunction with the General Electric (G.E.) to evaluate eight of the more important designs that are currently being used or have been used in the space program during the past 15 years. The objective of this paper is to present the test results and conclusions drawn from the Design Variable Program.

APPROACH

A cell with a proven heritage and a physical design similiar to that of other widely used aerospace cell sizes was a necessity in order to assure the validity of the data collected in this program. For these reasons the

G.E. 12Ah cell was selected as the Design Variable test cell. It had been used in the past with much success, therefore, its behavior was well documented and because its design is much like that of the 6 and 20Ah cells, the data collected could be adapted with confidence to those cells.

Eight of the most frequently used designs during the past 15 years were selected as the design variables to be used in this program. A specification was written for these designs and was incorporated into a G.E. manufacturing control document. After acceptance testing by G.E. and review and acceptance by the Goddard Space Flight Center (GSFC), the cells were shipped to the NASA Battery Test Facility at the Naval Weapons Support Center (NWSC) in Crane, Indiana were the Design Variable Test Program was carried out.

The test program consisted of two segments (Figure 1). First, an initial evaluation program was conducted. These tests were preformed in order to characterize each cell, to compare initial behavior, and to look for any manufacturing defects overlooked during acceptance testing. These tests were repeated on one cell from each design after 1 year and on all cells remaining from each group at the end-of-cycling. The two repetitions were carried out in order to compare degradation and performance based on the same criteria at different points during the life of the cells.

The second segment and principal part of the Design Variable Program was extended cycling in the low earth orbit (LEO) regime (Figure 2). This cycling regime utilized a higher than normal depth-of-discharge (DOD) of 40 percent in order to accelerate the cell degradation and therefore the test results. Data from this testing will indicate whether each variable is detrimental or beneficial to Ni-Cd cell performance in normal LEO orbit.

DESCRIPTION OF DESIGN VARIABLES

Using 12Ah cells, a control group and eight design groups of six cells per group were manufactured with the design paramenters as shown in Figure 3. A discussion of each group is as follows:

1. Control: This group represents G.E.'s basic aerospace design and processes as of 1978. The positives of these cells were subjected to cadmium treatment (PQ) as is indicative of G.E.'s process since 1970. The loading was somewhat lighter than normally used by G.E. during this time-frame. These lighter levels were chosen because the GSFC had recently procured two flight lots (IUE) with this design. The cells were manufactured with nonwoven nylon separator (Pellon 2505) and all cells recieved decarbonation treatment.

2. Teflon: These cells are identical to the control with the exception that the negatives were treated with teflon. As a result these cells also contain slightly more KOH than the Control.

3. Silver: This group is identical to the Control except the negatives had silver treatment and, as with Teflon, slightly more KOH.

4. Light Loading: The plates of this group have lighter loading (less active material) than those of the previous three groups. These plates are from the same impregnation post as the Control but are from different spirals. The purpose of this group was to evaluate a further reduction of plate loading with respect to initial and life benefits. Though no teflon or silver treatments were used, these cells contain 5cc more electrolyte than the Control cells.

5. No PQ: This group is identical to the Control except that the positives were not subjected to the PQ treatment. The positive plates are from the same impregnation post as the control but from different spirals. The negative plates are from the same spiral as the Control.

6. Polypropylene: This group contains all of the design parameters of the Control except that GAF polypropylene separator material was used in place of nylon.

7. A.K.-Old Process: This design is indicative of cells made during the middle sixties, i.e., the cells are made with the plate design and processes of that era. Specifically, no PQ treatment was used, the negatives were not depleted during the flooded cell test, and there was no decarbonation. Also, the plate design was different than the control and there was no precharge adjustment made to the cells.

8. A.K.-Present Process: This group contains the same plate lot as the A.K.-Old Process. However, these cells were processed using the same aerospace procedures and practices as the Control.

9. Electrochemical: This design contains electrochemically impregnated positives. All other variables are identical to the Control. This was an early attempt by G.E. to use electrochemical impregnation in cell manufacture.

It is noted that the amount of KOH varies from group-to-group. The criteria for determining the amount of KOH was to obtain the maximum KOH allowable in each group consistent with reasonable overcharge pressures. The overcharge pressure design goal was 30 to 76 PSIA.

The cell procurement specification requires the precharge to be set to 40 $\pm$ 5 percent of the excess negative. Since 4.6 ampere-hours of precharge on Group 1 through 6 represents between 38 and 41 percent of the excess negative, it was decided to precharge all cells in these 6 groups the same. As stated previously the A.K.-Old Process group not was precharged. The A.K.-New Process was precharged to 1.8 ampre-hours which represents 37 percent of the excess negative. The Electrochemical group was precharged to 5.8 ampere-hours which is essentially the same percentage that was used in groups 1 through 6.

INITIAL EVALUATION TEST RESULTS

Initial evaluation tests were carried out at NWSC-Crane before the start of LEO cycling, after 1 year on one cell from each group, and all remaining cells in each group at the end of cycling. All evaluation tests were performed at room ambient pressure and temperature with discharge at the 2-hour rate unless otherwise noted. The tests consisted of the following:

a. Phenolphthalein leak test.

b. Three capacity tests, the third at 20°C and internal resistance measurements made during the second.

c. Charge retention test, 20°C.

d. Internal short test.

e. Charge efficiency test, 20°C.

f. Overcharge tests at 0°C, 25°C, and 35°C.

g. Phenolphthalein leak test.

The room ambient capacity test, the 25°C overcharge test, and the 0°C overcharge test proved to be the most benefical for behavior comparison between the groups.

ROOM AMBIENT CAPACITY TEST RESULTS

The room ambient capacity test consisted of a charge at the 20-hour rate for 48 hours followed by a discharge at the 2-hour rate to 0.7 volts per cell. The initial, 1 year, and end-of-cycling capacities are shown in Figure 4.

This data indicates that the capacity loss for most groups to the end-of-cycling (3 to 4 years) was between 24 percent and 35 percent excluding only the Polypropylene, Electrochemical and No PQ groups.

Thirty-nine precent of the initial tested capacity of the Polyropylene group was gone within the first year under the LEO cycling regime. This first year capacity loss was the greatest among any of the groups as was the total capacity loss of 49 percent at the end of 3 years of cycling. Conversely, the Electrochemical group appears to have lost the least capacity with a loss of only 2 percent at the end-of-cycling. This is misleading, however, because this group remained on test for only 2.5 years (14000 cycles), and there was no 1-year test point available for comparison.

The No PQ group remained on test for 4 years (23300 cycles) and had lost the least amount of capacity of any group at the 1 year point, only 6 percent, but could not be recharged after the end-of-cycling and, therefore, no capacity data point was obtained. The other groups that remained on test for 4 years, Control and A.K.-Old Process, showed average capacity performance not only to the 1 year point showing 21 percent and 16 percent capacity losses respecitvely, but also to the end-of-cycling as was mentioned above.

25°C OVERCHARGE TEST RESULTS

The 25°C overcharge test consisted of a constant current charge at the 10-hour rate for 24 hours. The initial, 1 year, and end-of-cycling, end-of-charge (EOC) voltages reached during this test for all design groups are presented in Figure 4. Groups 1, 2, 3, 5, 6, and 9 showed little or no change in the EOC test voltage levels during life. The voltages reached by these groups were in the normal range for aerospace Ni-Cd cells and ranged from 1.454 volts to 1.465 volts. Of the groups mentioned above, the Control group showed the highest voltage each time tested followed by Polypropylene and the A.K.-Old Precess group.

Group 4, Light Loading, initially has an average EOC test voltage of 1.458 volts but when the test was repeated at the 1-year point the test voltage had risen to 1.477 volts. However, the EOC test voltage at the end-of-cycling was in the normal range. Group 8, A.K.-Present Process, also showed an EOC test voltage rise at the 1-year point with a voltage of 1.520 volts causing the charge to be stopped prematurely. Unlike Light Loading, however, an abnormally high EOC test voltage remained at the end-of-cycling indicating that these cells were "negative limited" and had been so since before the 1 year retest. The A.K.-Old Process group, even though it was made with the same plate as Group 8, surprisingly showed no signs of being "negative limited" until the remaining cells were tested at the end-of-cycling (4 years). This difference, therefore, has to be due to the differences in the plate processing techniques used on each group. Both groups initially had a lower negative to positive ratio than the other groups because of the 1968 design and so from the beginning possessed a strong tendency to becoming "negative limited." In addiiton to this, the plate forming or ECT processes of the present process, because of a longer reversal time and additional precharge adjustment, caused the amount of excess negative in the group to be reduced to a much greater extent than in the old process group. The effect of less excess negative is a rise in voltage during overcharge, a condition in which cells are said to be "negative limited." This is exactly the effect shown during this test.

0°C OVERCHARGE TEST RESULTS

The 0°C overcharge test consisted of a constant current charge at the 20-hour rate for 60 hours. The initial EOC voltages, and the 1 year, and end-of-cycling EOC and peak voltages are presented in Figure 5.

The overcharge test produced contrasts of a much greater magnitude between the groups on test than did the 25°C test. It showed that by the 1 year retest the Light Loading, No PQ, Polypropylene, A.K.-Old Process, and A.K.-Present Process groups all had higher than normal peak and EOC test voltages which indicated they had become "negative limited." In fact, the charge was stopped prematurely on each of these groups because of high voltage or pressure. By contrast, the Teflon group showed the lowest peak test voltage of any group, at 1 year, at 1.529 volts followed by Silver at 1.546 volts, and the Control at 1.551 volts.

At the end-of-cycling only the A.K.-Present Process and A.K.-Old Process groups had high EOC test voltage and therefore, were the only groups which appeared to be "negative limited" at the end-of-cycling. This agreed with the results obtained during the 25°C overcharge test. The Teflon group showed many intermittent shorts during this test at the end-of-cycling and thus, the data obtained is not valid and, in fact, represents on one of the four cells; the others could not be charged. The No PQ group formed internal shorts prior to the start of the end-of-cycling evaluation tests as was discussed previously.

LOW EARTH ORBIT CYCLING TEST RESULTS

The data analysis to be presented will concentrate on the 6 design groups that performed the best during the test program and that provided the most pertinent information with regard to the application of aerospace Ni-Cd cells. The 6 groups are the Control, Teflon, Silver, No PQ, A.K.-Old Process, and Electrochemical.

A comparison of the capacity performance of each of the groups during cycling is very beneficial to the evaluation of each design variable. Therefore, capacity checks were performed on different cells in each group at 6 month intervals through 2 years and then yearly to the end-of-cycling. These capacity checks consisted of a discharge at the nominal cycling discharge rate (9.6 amps) to a voltage of approximately 0.75v.

The 1, 2, and 3 year capacity plots for the 6 groups are shown in Figures 6, 7, and 8 respectively. A 4-year capacity plot for the Control, No PQ, and A.K.-Old Process group is shown in Figure 9. These plots indicate that the above 3 groups consistently maintained a greater capacity than any of the other groups tested and of those 3, the No PQ performed better than the other 2.

A more accurate representation of this behavior is presented in Figure 10, where the precent of the initial actual capacity versus cycle number is plotted for each group. This plot decisively shows that the No PQ group, from the beginning, lost the least amount of capacity on a precentage basis than any other group. This group lost only 15 percent of its initial capacity during 3 years of cycling and 55 percent by the end-of-cycling.

This is compared to the Control group loss of 35 percent in 3 years and 60 percent by the end-of-cycling, and the A.K.-Old Process group loss of 40 percent in 3 years and 52 percent when taken off test. The Teflon and Silver groups lost 65 percent and 59 percent of their initial capacities in 3 years and the Electrochemical group lost 22 percent of its capacity in 2.5 years. The capacity loss percentages do not necessarily agree with the capacity loss percentages presented for the evaluation tests. The discrepancies resulted from differences in the discharge current used in each of the tests. All discharges during the evaluation tests were at the 2-hour rate while those performed during the cylcling capacity checks were at the 1.3-hour nominal cycling rate. Also, a partial reconditioning took place before the evaluation test each time.

Another parameter that provides a good indication of the performance of a cell during LEO cycling is the end-of-eclipse (EOE) voltage. A comparison of the EOE voltages throughout life for the 6 groups selected is found in Figure 11. The figure again shows that the No PQ group outperformed the other groups by maintaining an EOE voltage of 1.14 volts from 7500 through 19000 cycles after slowly declining from a beginning-of-life EOE voltage of 1.21 volts and before beginning a sharp decline at the end-of-cycling. The A.K.-Old Process group performed better than the No PQ group at the beginning-of-life but leveled off at a lower EOE voltage of 1.12 volts. The Control group also provided adequate performance after a sharp decline at the beginning-of-life but maintained an EOE average voltage of only 1.03 volts throughout most of its cycle life.

The Silver, Teflon, and Electrochemical groups did not perform as well as the others. The Silver group parallelled the Control group until approximately cycle 11000 then it began a steady EOE voltage decline ending with an EOE voltage of 0.94 volts at the end-of-cycling (17300 cycles). The Electrochemical group began life by making a very sharp EOE voltage drop to 1.06 volts at 1500 cycles. It then maintained approximately this voltage until the end-of-life. The Teflon group performed worse than any other group showing a steady voltage decline throughout life. The EOE voltage of this group was 0.89 volts at the end-of-cycling (17300 cycles) the lowest end-of-cycling voltage of any of the 6 groups.

A plot of the percent recharge for each group throughout life is presented in Figure 12. A nominal percent recharge of 115 percent was to be maintained throughout life by adjusting the charge voltage limit of each pack. A percent recharge of 115 percent was not maintained. However, this plot shows that all groups maintained a recharge percentage high enough to assure that full charge was being achieved and the delta between the groups was less than 5 percent with few exceptions. Therefore, all groups were maintained in approximately the same state throughout life which indicates that all data collected during the LEO cycling test was valid.

CONCLUSIONS

The No PQ group outperformed all other Design Variable Program groups in both the area of capacity and end-of-eclipse voltage. This performance was rivaled only by the Control group that had PQ but no other treatment and the 1968 A.K.-Old Process group which did not have PQ. The failure of the No PQ group to accept charge at the end-of-cycling did leave a question mark by its performance. Inability to accept charge is an indication that hard shorts had developed between the plates in all cells, a condition that is caused by excessive cadmium migration.

The Electrochemical group showed a capacity loss lower than most other groups, especially during the evaluation tests, and enhanced active material utilization. It did not perform at the same level as the No PQ group, however, and had a very low beginning-of-life capacity as a result of the low positive plate loading levels it possessed. Undoubtedly, the cause of these low positive loading levels was that this was an early attempt by G.E. to use electrochemical impregnation in cell manufacture. Because of the indications of decreased capacity loss and enhanced active material utilization, and in light of the advances made in this area in the past 6 years, this process should be reevaluated with respect to the aerospace energy storage program.

The Teflon and Silver treatments enhance the rate of oxygen recombination and thus allow a greater amount of electrolyte to be added to the cells. One or the other of these treatments is strongly recommended by the manufacture and previous acceptnace and life test data indicated that these treatments improved cell performance. On the contrary, these groups showed the poorest performance of any of the 6 groups analyzed. The Teflon group, which is the currently accepted GSFC design, consistently gave the poorest performance of any group in all aspects of the design variable test program. This group had the highest capacity loss and the lowest end-of-eclipse voltages of any group tested. It also had intermittent shorts at the end-of-cycling (17300 cycles) which indicates excessive cadmium migration. A condition the Teflon supposedly prevents. The merits of this design should clearly be reevaluated in light of its poor performance and the strong performance of other designs.

References

1. Baer, D. and Ford, F., Proceedings of the Symposium on Battery Design and Optimization, the Electrochemical Society, Inc., 1979, page 114.

2. Baer, D., 1978 GSFC Battery Workshop, NASA CP 2088, pages 49-56.

- INITIAL EVALUATION TEST*
  - LEAK TESTS
  - CAPACITY TESTS
  - INTERNAL RESISTANCE AND SHORT TEST
  - CHARGE RETENTION TESTS
  - CHARGE EFFICIENCY TEST
  - OVERCHARGE TESTS
  - PRESSURE VERSUS CAPACITY TESTS
- LOW EARTH ORBIT CYCLING

* TESTS REPEATED AFTER 1 YEAR CYCLING AND AT END OF PROGRAM

Figure 1. Design Variable Test Program

o TEMPERATURE	20°C
o DEPTH-OF-DISCHARGE	40 PERCENT
o ORBIT PERIOD	90 MINUTES
o CHARGE CURRENT	9.6 AMPS TO A VOLTAGE LIMIT (1.453 V/CELL TYPICAL)
o DISCHARGE CURRENT	9.6 AMPS

Figure 2. Leo Cycling Test Regime

	VARIABLE	PACK NO.	POS LOADING G/DM^3 OF SINTER	NEG LOADING G/DM^3 OF SINTER	FINAL KOH QUANTITY, CC	PRECHARGE[1] ADJUST AH
1.	CONTROL	3D	2095	2180	40	4.6
2.	TEFLON	3E	2095	2180	48	4.6
3.	SILVER	3F	2095	2180	43	4.6
4.	LIGHT	3G	1840	1833	45	4.6
5.	NO PQ	3H	2113	2180	40.3	4.6
6.	POLYPROYLENE	3I	2095	2180	39	4.6
7.	AK-OLD PROC	3J	2130	2542	38	0.0
8.	AK-PRES PROC	3K	2130	2542	39	1.8
9.	ELECTROCHEM	3L	1276[2]	2280	48	5.8

[1] BASED ON 228 CC O_z/Ah

[2] BY HYDRATE PICK-UP, NOT HYDRATE REDUCTION

Figure 3. Design Variable Program—Cell Manufacturing Information

			EOC VOLTAGE C/10 CHARGE FOR 24 HOURS AT 25°C			25°C CAPACITY TO 0.7V (AMP HOURS)		
	VARIABLE	PACK NO.	INITIAL	1 YEAR	EOL	INITIAL	1 YEAR	EOL
1.	CONTROL	3D	1.462	1.465	1.461	15.3	12.1	10.6 (4 YEARS)
2.	TEFLON	3E	1.455	1.457	1.447	14.7	12.5	10.1 (3 YEARS)
3.	SILVER	3F	1.456	1.458	1.450	15.2	12.1	11.5 (3 YEARS)
4.	LIGHT	3G	1.458	1.477	1.455	13.9	11.6	10.1 (3 YEARS)
5.	NO PQ	3H	1.454	1.452	--	16.0	15.1	-- (4 YEARS)
6.	POLYPROPYLENE	3I	1.459	1.457	1.450	15.6	9.5	8.0 (4 YEARS)
7.	AK-OLD PROC	3J	1.459	1.419	1.520[1]	17.7	14.9	11.5 (4 YEARS)
8.	AK-PRES PROC	3K	1.458	1.520[2]	1.522[3]	17.4	18.0	12.5 (3 YEARS)
9.	ELECTROCHEM	3L	1.456	--	1.480	10.8	--	10.6 (2.5 YEARS)

[1] TEST TERMINATED AT 17 Ah IN DUE TO HIGH VOLTAGE

[2] TEST TERMINATED AT 23.4 Ah IN DUE TO HIGH VOLTAGE

[3] TEST TERMINATED AT 15 Ah IN DUE TO HIGH VOLTAGE

Figure 4. Design Variable Probram, Initial Evaluation Test Results
Initial, After 1 Year, End of Program

	VARIABLE	INITIAL EOC	AFTER 1 YEAR EOC	AFTER 1 YEAR PEAK	END-OF-CYCLING EOC	END-OF-CYCLING PEAK
1.	CONTROL	1.496	1.508	1.552	1.510	1.537
2.	TEFLON	1.486	1.496	1.529	1.433[3]	1.433[3]
3.	SILVER	1.494	1.494	1.546	1.496	1.527
4.	LIGHT	1.492	1.567	1.577[1]	1.512	1.542
5.	NO PQ	1.508	1.599	1.600[1]	---[4]	---[4]
6.	POLYPROP	1.497	1.578	1.583[1]	1.509	1.540
7.	AK-OLD PROC	1.575	1.585	1.583[2]	1.602	1.610[1]
8.	AK-PRES PROC	1.578	1.572	1.585[2]	1.608	1.611[1]
9.	ELECTROCHEM	1.495	---	---	1.506	1.539

[1] TERMINATED DUE TO HIGH VOLTAGE (VOLTAGE EXCEEDED 1.56V FOR 2 HOURS)

[2] TERMINATED DUE TO HIGH PRESSURE, > 100 PSIA.

[3] ALL CELLS IN TEFLON GROUP SHOWED INTERMITTENT SHORTS.

[4] ALL CELLS IN NO PQ GROUP SHORTED.

Figure 5. Design Variable Program, Initial Evaluation Test Results (Continued)

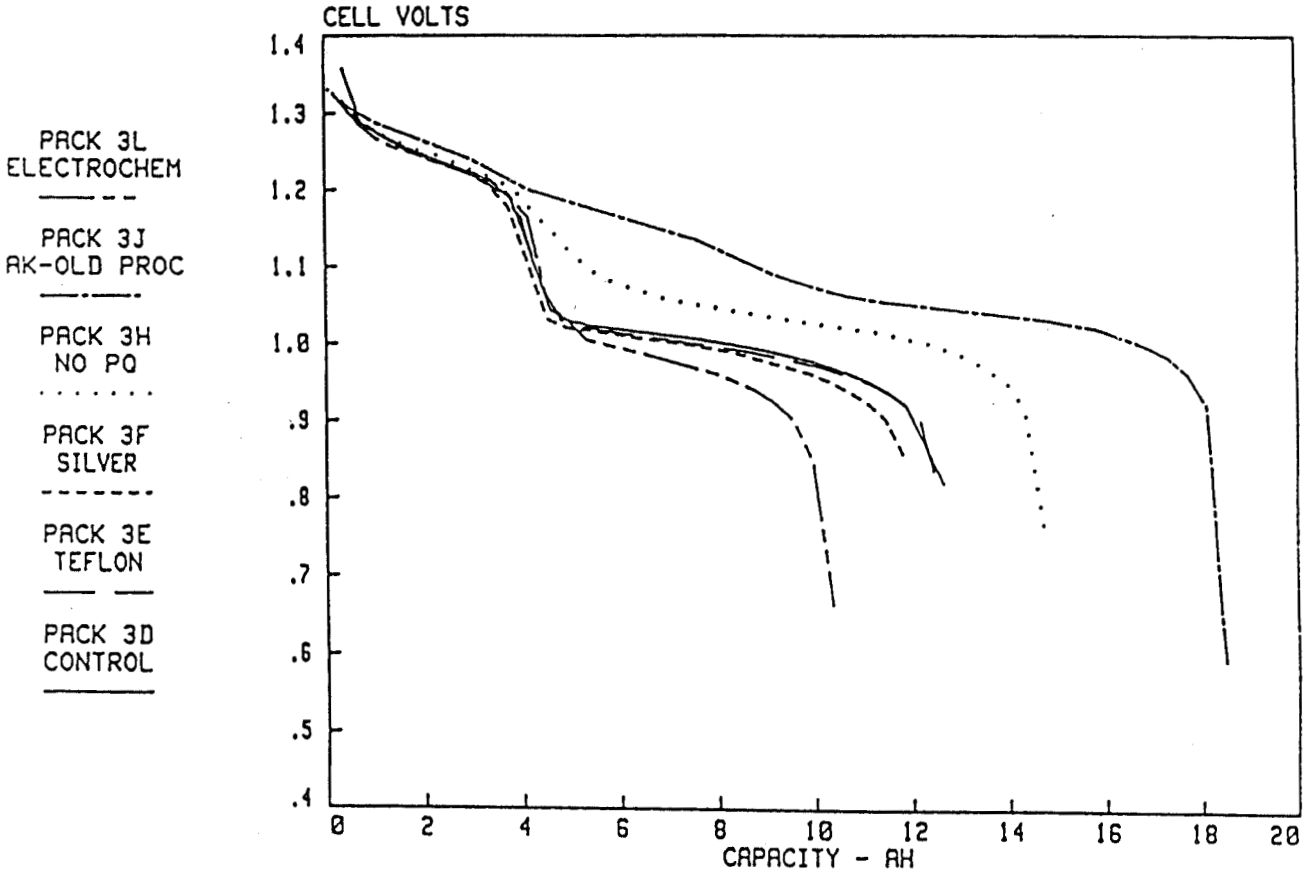

Figure 6. Design Variable Program
1 Year Capacity Comparison—9.6 Amp Discharge

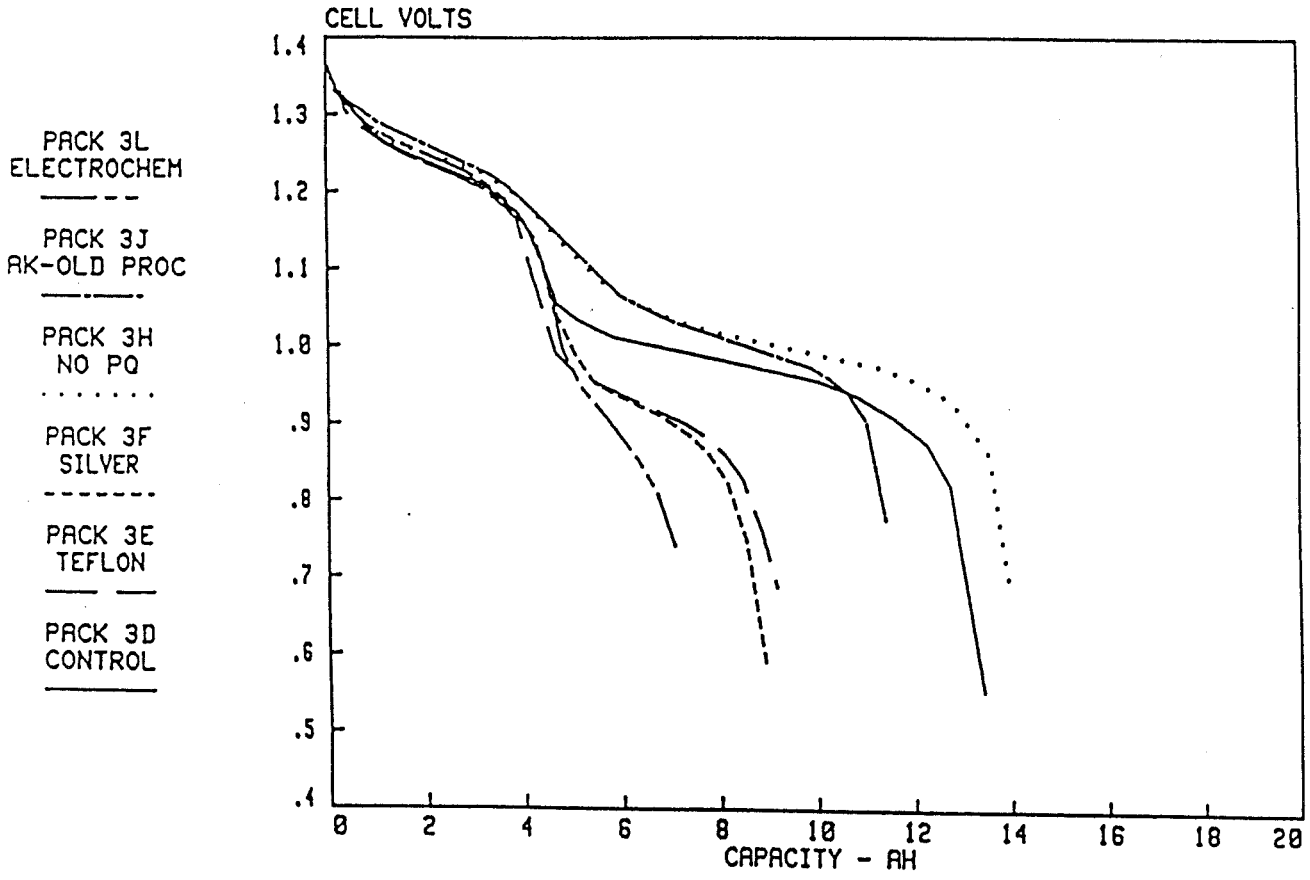

Figure 7. Design Variable Program
2 Yr Capacity Comparison–9.6 Amp Discharge

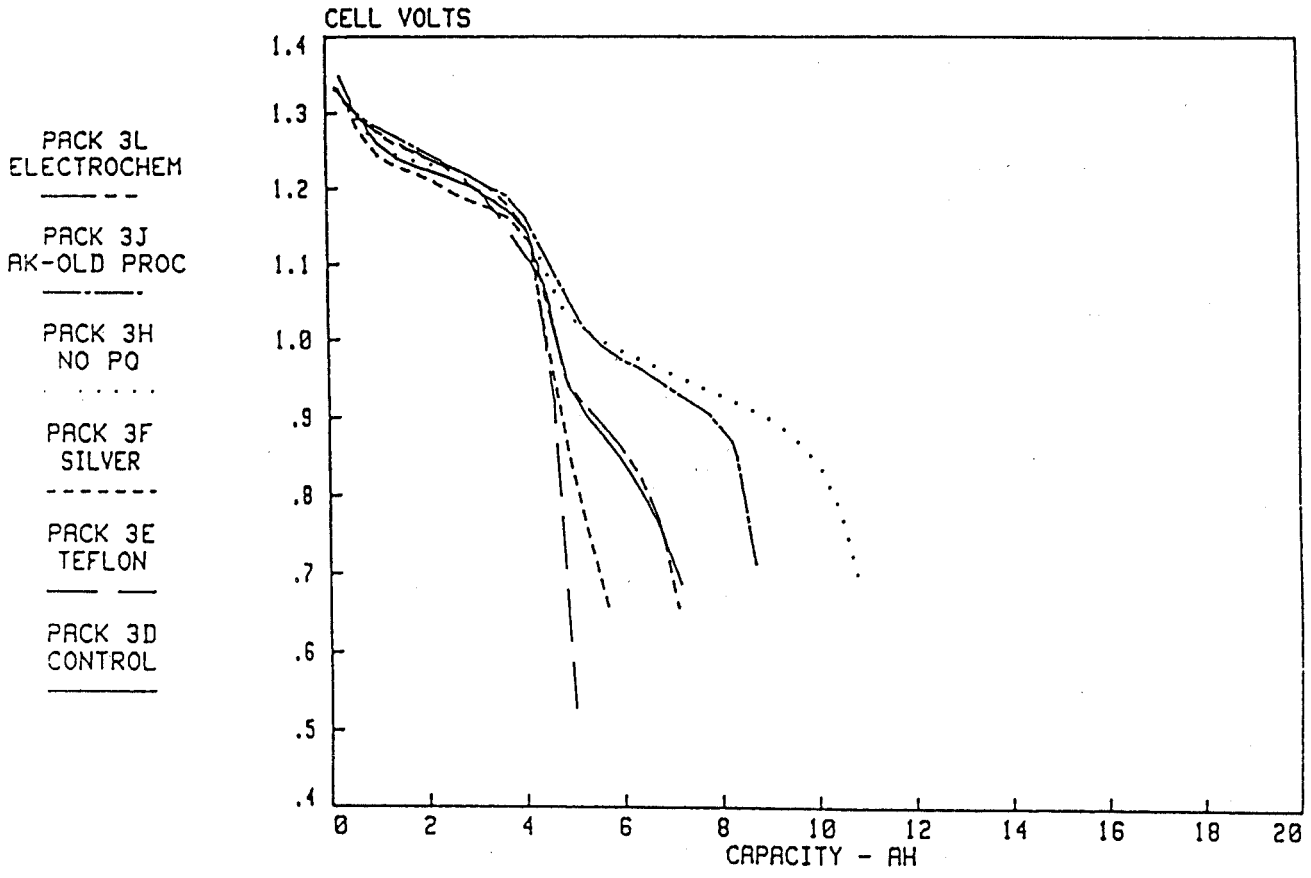

Figure 8. Design Variable Program
3 Yr Capacity Comparison–9.6 Amp Discharge

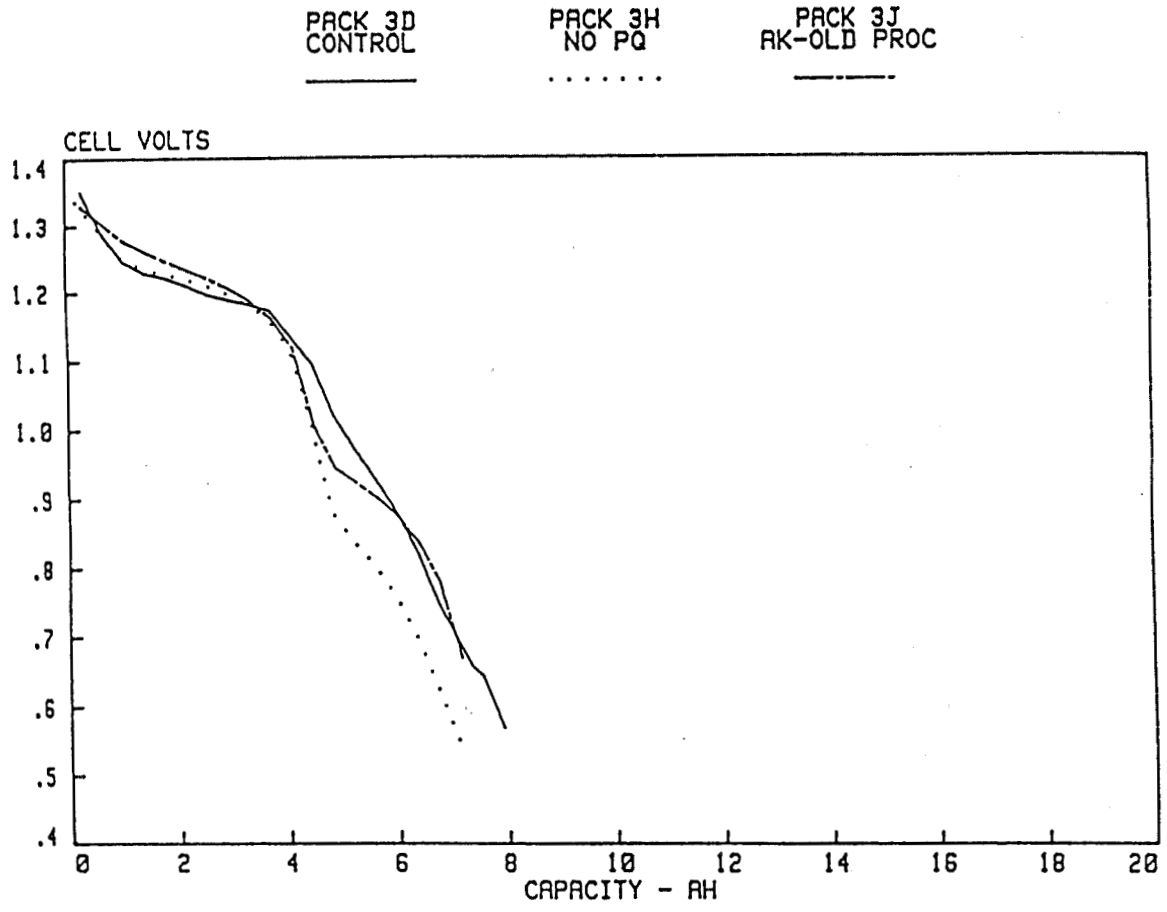

Figure 9. Design Variable Program
4 Yr Capacity Comparison–9.6 Amp Discharge

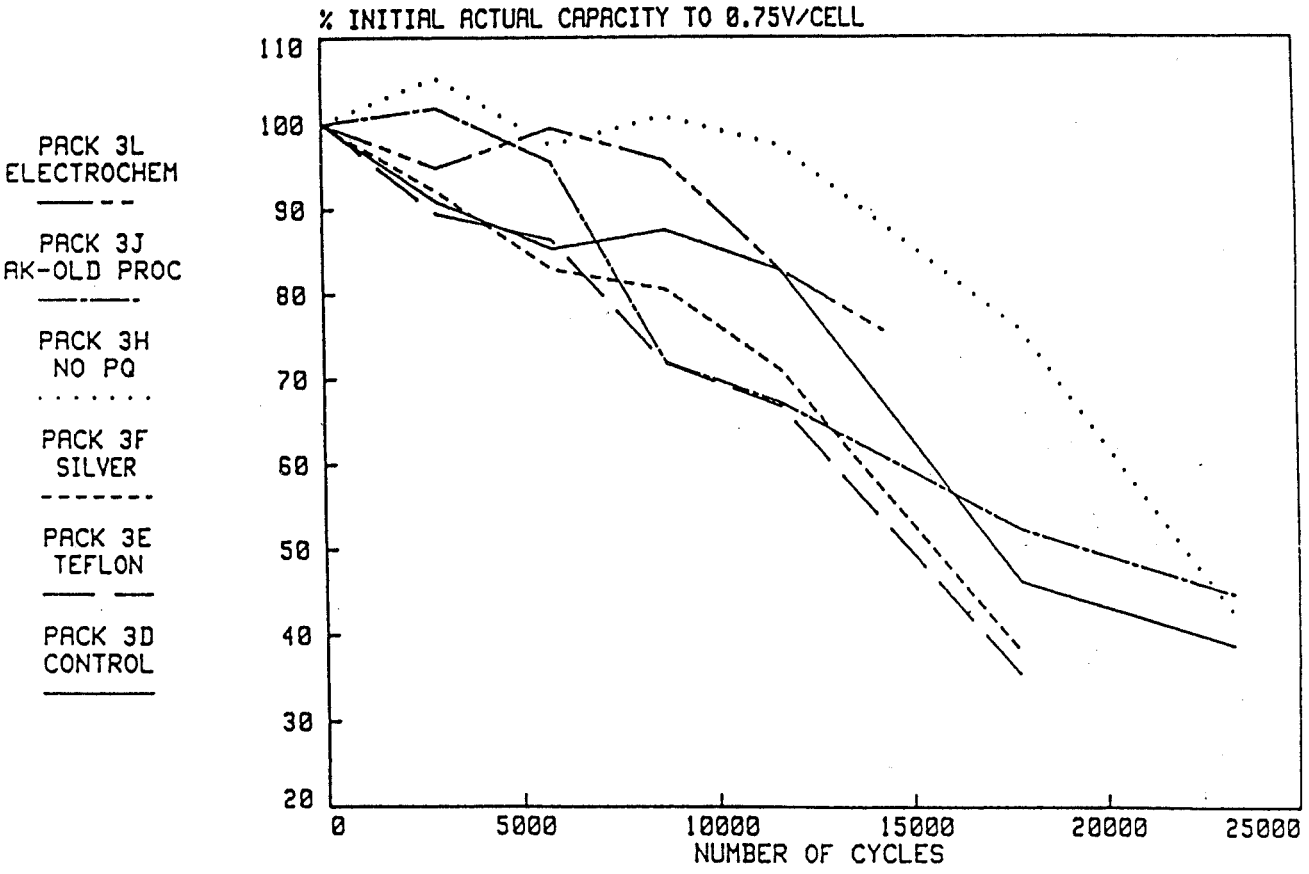

Figure 10. Design Variable Program
Percent of Initial Actual Capacity Comparison

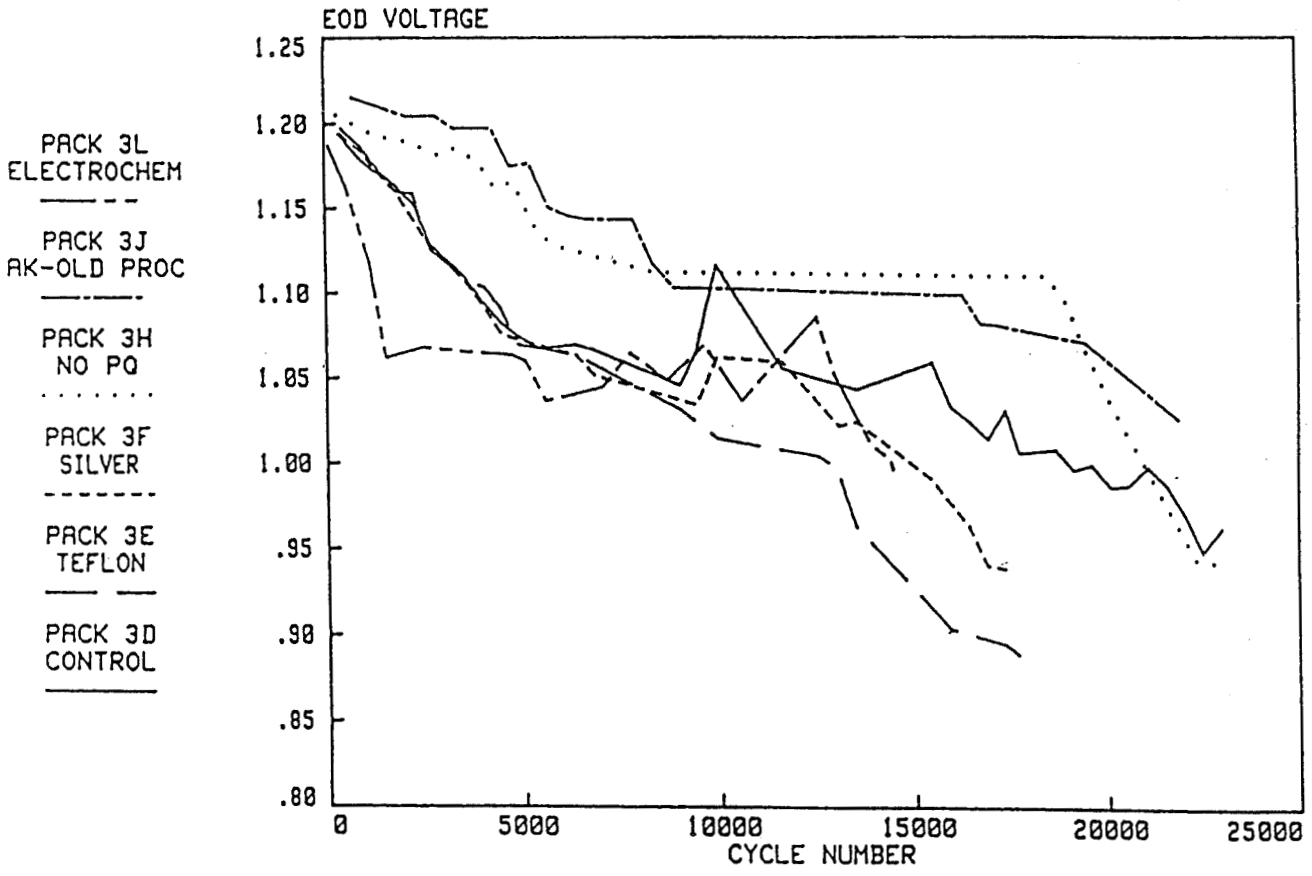

Figure 11. Design Variable Program
End of Eclipse Voltage Comparison

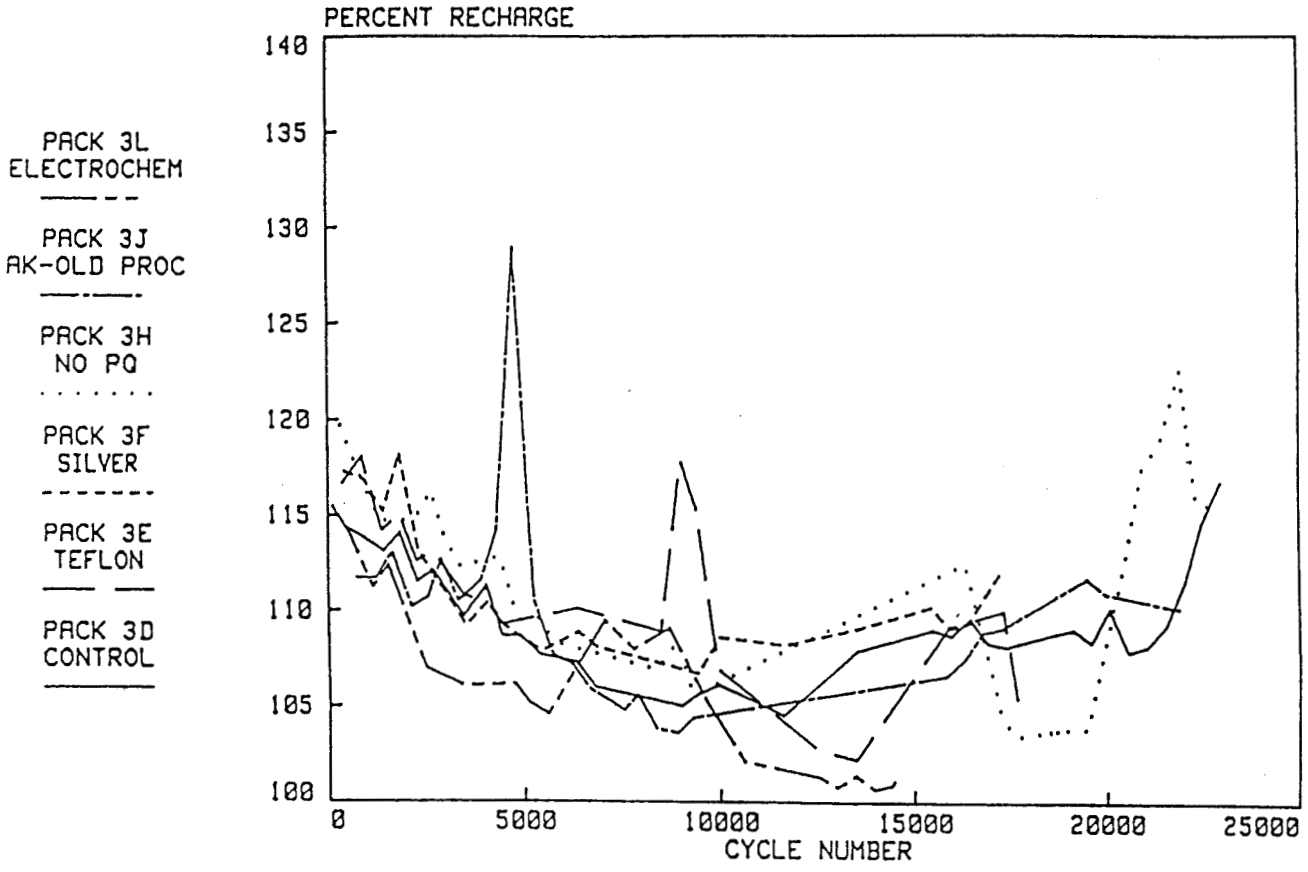

Figure 12. Design Variable Program
Percent Recharge Comparison