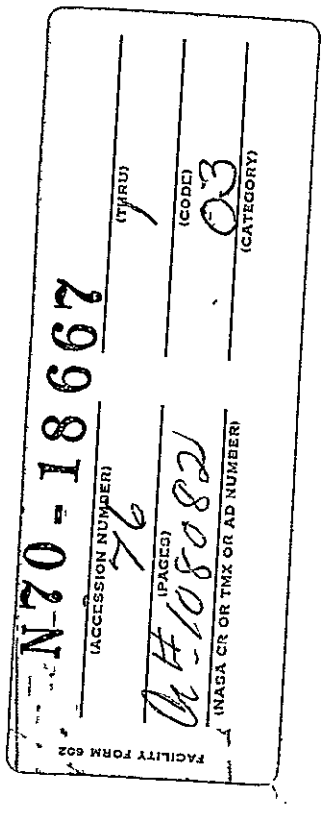
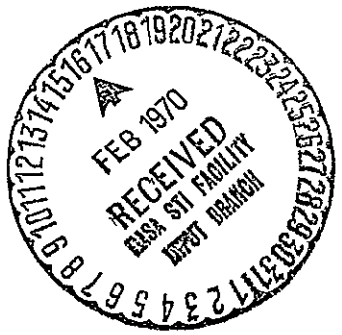
HEAT STERILIZABLE IMPACT RESISTANT CELL DEVELOPMENT

JET PROPULSION LABORATORY
CONTRACT NO. 951296

REPORT FOR SECOND QUARTER, 1969
APRIL 1 TO JUNE 30, 1969





ESB INCORPORATED
THE CARL F. NORBERG RESEARCH CENTER
Yardley, Pennsylvania

EXIDE MISSILE AND ELECTRONICS DIVISION
Raleigh, North Carolina

January 1970

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Prepared By: A. M. Chreitzberg
Ass't. Director of Engrg.

Approved By: G. S. Hartman
Director of Engrg.

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ABSTRACT, CONCLUSIONS AND RECOMMENDATIONS

Electrochemical studies during the Second Quarter of 1969 have been directed toward a study of those factors contributing to long cycle life of silver-zinc cells and those factors affecting grid embrittlement. Cycle life is promoted by increased electrolyte concentration, the presence of an absorber around the silver electrode and the presence of Compound 323-43. Sterilized cells give fewer cycles than unsterilized cells and fewer cycles are obtained after floating than if the cells have not been floated. Other factors such as MPR negatives, pressed powder negatives, tapered cell cavities, etc. are under test on the automatic cycling equipment.

Grid studies indicate that the strength of the amalgamated grid may be time dependent with grids becoming stronger with age. X-ray diffraction data raises the question as to whether zinc penetration into the silver is involved in embrittlement. Since mercury is required to minimize gassing of the negative, preamalgamation of the heavy grids used in high impact cells is required, but how much mercury is necessary to insure a high enough surface concentration after the heat and time of sterilization remains to be established. Lead-plated silver grids are being investigated to see if the plating will lengthen the mercury diffusion path into the silver and thus offer some measure of protection against embrittlement. Cells containing these grids are being life cycled also as part of the cycle life study.

Five ampere-hour experimental cells, designed with massive etched Ag grids for mechanical support of negative active material and a solid zirconium sheet-expanded Ag core for support of positive active material, failed by buckling at the plate strut positive material interface after repeated shocks terminals forward at 4,000 "g". An increase in zirconium thickness and inter-strut spacers are proposed for prototype cells to eliminate this failure mode.

Seventy ampere-hour low impact prototype rechargeable primary cells have been redesigned and released to manufacture. Design improvements increased plate tab to plate frame strength, negative erosion resistance, separator wet thickness, and the reliability of the case to cover epoxy seal.

ABSTRACT, CONCLUSIONS AND RECOMMENDATIONS (continued)

Twenty-five ampere-hour low impact cells in five designs have been placed on 10-hour charge/2 hour discharge cycling routines to demonstrate a capability of 90 50% depth of discharge cycles after wet heat sterilization and 9 months interplanetary cruise on float. Design variables are separator system, negative plate density, positive or negative wrap, plate-lock for vibration resistance, and pretest capability. After 90 cycles in 4 months total wet life the most desired design factors chosen to increase capacity are: positive plate absorber > positive wrap > layers of membrane (7 plus absorber preferred over 9 and no absorber) > a low density negative > platelock. Two groups of 20 cells each were delivered to JPL for tests.

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ELECTROCHEMISTRY

I. INTRODUCTION

During the period of April to June, 1969, work was centered on a study of cycle life and grid embrittlement by mercury. The characteristics of parameters which may influence the cycle life of heat sterilizable, high impact cells were examined and while they are discussed in detail below, these variables, along with brief comments, are summarized in Table I.

The high impact requirement for some cells still causes concern over the effect of mercury on the strength of the silver grid in the negative plates. Since some grids become brittle whereas others do not, a study of the problem may improve the reliability of impacted cells.

II. LONG CYCLE LIFE STUDY

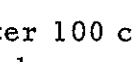
In building a cell for long cycle life, all parameters should be optimized for maximum cycles. That the separator, negative electrode, and cell pack tightness might have an effect on cycle life is obvious, but for secondary interplanetary cells cycle life starts only after a long period of stand or float. While it is not practical to stand or float cells prior to determining cycle life, it is important to know the effect of stand and float on this variable.

A. Stand-Float Performance of Some Sterilized Cells

In the last Quarterly Report, (report for First Quarter, 1969), a group of cells were described which had been sterilized at 135°C for 120 hours, cycled four times, charged, and then placed either on stand or float. Those cells placed on float were maintained at a constant potential of 1.96 volts. All but one of the cells were on the float-stand regime for about 2 years. The one exception was constructed about six months later.

Based on the ability of these cells to be discharged and to accept a recharge, it was concluded that only floated cells were satisfactory. The floated cells were placed on a 50 percent d.o.d. cycle regime but most of the cells failed to cycle. Only two of them lasted more than 19 cycles. Some of the cells lost their capacity during a 46-day stand during which time the data acquisition system was being repaired.

TABLE I
Characteristics of Cell Parameters *

Variables	Comments
(1) Float-Stand Characteristics	Float is preferred.
(2) Separator	8 Layers of SWRI-GX.
(3) Compound 323-43	7%, No detrimental Effect on Cell Performance.
(4) Compound 323-50	Additive seems to make for a better structured electrode.
(5) Hg on the Grid	Embrittles the grid - but embrittlement seems to go through a maximum with time.
(6) Cell Pack Tightness	Not very critical but a value of about 3 mils per separator layer is recommended.
(7) Pressed Powder Negative	Capacity 0.32 AH/gm of Ag. No cycle data yet
(8) MPR Negative Electrode	Sterilization and formation is feasible, no cycle data yet.
(9) Shape of Cell Case	Three shapes  , after 100 cycles at 100% d.o.d no difference has been detected.

* This table refers to heat sterilizable, high impact cells studied for long cycle life characteristics during the second quarter 1969.

From this experiment it is concluded that floating is less detrimental to cycle life than standing, but even floating may detract greatly from subsequent cycle life.

B. Pressed Powder Negatives

Thirteen cells have been constructed and are being cycled to determine the effect of a powdered Teflon binder on cycle life in pressed powder negative electrodes. The first three cells constructed were 11-plate cells and did not contain Teflon. They were made as similar to the standard "bomb cell" as possible. The only change was the substitution of a PPO case in place of a Teflon insert and nickel pipe so that the effect of a PPO case could be evaluated also.

Therefore, these cells were assembled using 281 size plates and a negative mix containing 4 percent Compound 323-43. The negatives were wrapped with eight layers of SWRI-GX. These packs were very difficult to insert into the PPO cases because of the plate width and the number of layers of separator.

Accordingly, five more cells were built, but all electrodes were cut down by 0.075 inches in width and only 9 plates were used. These packs slipped easily into the cases.

Both sets of cells were sterilized open in separate groups in large bombs. At the end of sterilization, the latter set of five cells was observed to have lost electrolyte, possible by wicking over the braided silver leads which had been bent over in order to accommodate all five cells in one bomb. (The first set of three cells did not have the leads bent over and did not show a lowered electrolyte level.). Electrolyte was added to the second set of five to bring the level up to the top of the plates. All cells were sealed with covers and then over-potted.

Table II shows cycling results for these 8 cells, and the first set of three are clearly superior. It is also notable that the second set of cells accepted a smaller percent of charge and delivered a smaller percentage of discharge in the first stages of those operations than did the first set. Subsequently, it was found that the second set of cells had about ten times the internal impedance that the first set had.

Thus, the performance of cells in PPO cases was equal to that of cells constructed in bombs, but there is no explanation for the smaller silver utilization of cells with cut-down plates.

TABLE II

Initial Cycles of Ag-Zn Cell for Long Cycle Life Test

	11-Plate Reg. Size Plates			9-Plate "Cut-Down" Plates				
Cycle #1	566-17-5	566-17-6	566-17-7	566-43-8	566-43-9	566-43-10	566-43-11	566-43-12
1st/Chg. Cap. (pre. form. incl.)	9.78	9.57	9 25	5.97	6.34	6 60	6 65	6 34
2nd/Chg. Cap.	.39	.98	.32	1.33	1 33	1 16	86	1 70
Net Chg. Cap.	9.89	9.85	9.43	6.62	6 97	6.95	6.91	6 99
1st Dischg. Cap.	7.05	7 00	6.65	3 86	4 81	4 64	4 45	5 14
Midvoltage	1.42	1.42	1.42	1.40	1.42	1.42	1 43	1 42
2nd Dischg. Cap.	1.55	1.45	1.31	1 58	1.16	1 51	1 64	93
Total Dischg. Cap.	8.60	8.45	7 96	5.44	5.97	6 15	6 09	6 07
Output/Input	87%	86%	85%	82%	86%	88%	88%	87%
Cycle #2								
1st/Chg. Cap.	8.51	8.40	8.32	5.49	5 90	5.86	5 76	5 89
2nd/Chg. Cap.	1.54	1.39	1.59	1.57	1.67	2.12	1.93	2 24
Net Chg. Cap.	8.64	8.66	8.50	6.16	6.42	6.57	6 45	6 63
1st/Dischg. Cap.	7.75	7.61	7.95	4.32	4 99	4.84	4.45	5 14
Midvoltage	1.42	1.42	1.42	1.40	1 42	1.42	1 42	1 42
2nd/Dischg. Cap.	.88	.67	.72	.98	.81	1.12	96	.93
Total Dischg. Cap.	8.63	8.28	8.17	5.30	5.80	5 96	5.41	6 07
Output/Input	100%	96%	96%	86%	90%	91%	84%	92%
AH/gram Ag	.39	.37	.37	.30	33	.33	.30	.34

The five other cells with cut down electrodes were 9-plate cells but containing 8 percent Compound 323-43 and 2 percent Teflon powder. These cells should yield additional information on the effect of Compound 323-43 and Teflon on cycle life and cell pressure. The data at the end of one cycle are shown in Table III and indicate an average capacity of about 0.32 AH/gram Ag. This capacity is somewhat low but comparable to that of the other cut down cells.

C. MPR Negative Electrodes

The past performances of sterilized cells made with MPR electrodes were unsatisfactory. However, because of the recent requirements for a long cycle life, high impact battery, the MPR electrode is being studied further.

In previous experiments, MPR electrodes which were heat-sterilized in KOH were seen to change to a gray color. Observation under a microscope indicated that the gray looking electrodes contained beads of mercury. The presence of Hg suggested the possibility of Hg damage to the positive plates. Six 7-plate cells were constructed to determine the capacity of sterilized MPR electrodes. The parameters of the cells were as follows:

(1) 2 grids per (-) electrode

(2) 8 layers of SWRI separator

(3) Electrolyte level at 80 percent of plate height

(4) A "U" fold layer of irradiated EM-476 around each electrode

Three of the cells (#4, 5, and 6) were unsterilized whereas the other three cells (#1, 2, and 3) were sterilized at 135 °C for 72 hours, and then sealed and overpotted.

The capacity data at the end of the first cycle are shown in Table IV. Even though two of the three sterilized cells had poor capacities (less than 0.3 AH/gm Ag), the best capacity (0.36 AH/gm Ag) for all 6 cells was obtained from one of the sterilized cells. This was the first time that a sterilized cell using MPR electrodes performed well. The fact that one cell could give such a good performance is encouraging and indicates that the MPR electrode should be studied further. The two MPR cells that failed will be postmortemed and the electrodes cycled against dummy electrodes. Among other things, the Ag electrodes will be examined for Hg damage.

TABLE III

Cycle Data of Sterilized Then Sealed Ag-Zn Cells *

	566-47-13	566-47-14	566-47-15	566-47-16	566-47-17
First Stage Charge Capacity (pre. form. incl.) (AH)	5.91	6 77	6.89	4.26	5 94
Second Stage Charge Capacity (AH)	2.68	1.38	1.01	3.75	1.68
Net Charge Capacity (AH)	7.18	7.08	7 15	6 90	6.76
First Stage Discharge Capacity (AH)	5.07	4.75	4.80	4.85	3.42
Midvoltage	1.40	1.40	1.40	1 40	1.36
Second Stage Discharge Capacity (AH)	78	1.15	1.16	.89	1.82
Total Discharge Capacity (AH)	5.85	5.90	5.96	5.74	5.24
Output/Input	81%_	83%	83%	83%	77%
AH/gram Ag Discharge	.32	.33	33	.32	29

* Cells contained 8% Compound 323-43, 2% Teflon, and 8 layers of SWRI.

TABLE IV
Capacity of MPR Electrodes

	Capacity (AH)					
	Sterilized				Unsterilized	
	1	2	3	4	5	6
Preformation at 9 mA	0.133	0.136	0.127	0.122	0.130	0 139
Total Chg. Cap.	-	6.00	5.87	6.22	5.71	5.65
1st Stage Dischg. at 1.68 A	0.168	0.336	4.20	3.36	2.86	2.86
2nd Stage Dischg. at 335 mA	1.61	2.80	0.737	1.09	1 31	1 12
Total Dischg Cap.	1.78	3 14	4.94	4.45	4.17	3.98
Wt. of ZnO/Cell (gms)	13.58	13.84	13.87	12 53	12.70	13.59
AH/gm Ag	0.13	0.23	0.36	0.32	0 30	0 29
Net Wt. of Ag	13.57	13.72	13.84	13.78	13 68	13.93
AC Impedance (ohm) at end of dischg.	0 387	0.188	0 064	0.081	0 054	0 056

* This includes preformation capacity.

Included in Table IV are the AC impedance values of each cell. The two cells that failed had unusually high impedance values (0.188 and 0.387 ohm), and this may account for their poor results.

D. Separators, Absorbers, and Cell Pack Tightness

As part of our usual procedure, all new separator material is given a functional test by determining the capacity obtained when the separator is used in cells of standard construction. Recently, the evaluation of data for cells constructed with a new formulation of SWRI separator has revealed some discrepancies. The discrepancies may be related to the non-uniformity of the separator which uses a new DOW polyethylene. In order to evaluate this new separator, the performance of two cells made with the old SWRI separator was compared with the performance of two cells made with the new SWRI separator. The four cells were constructed in the Ni bomb arrangement which permits sealing before sterilization and eliminates the effect of any other organics (as demonstrated in earlier reports). As shown in Table V, the capacities of the cells with the DOW type SWRI were 0.25 and 0.36 AH/gram Ag, whereas the capacities of 0.30 and 0.31 AH/gram Ag for the cells made with the old SWRI were much more uniform. Because the capacities of the cells made with the old SWRI were somewhat low, more data would be desirable. However, included in Table V are some impedance values. It is interesting to note that the order of increasing capacity is the order of decreasing impedance. Usually, the impedance for cells with good capacity (about 0.35 AH/gram Ag) is about 0.03 ohm. The fact that the cells with the old SWRI gave only about 0.30 AH/gram Ag correlates well with the high impedance value of 0.68 ohms. The data suggest the new SWRI material suffers from a lack of uniformity. Additional evidence supporting this contention was found independently in a study of pack tightness.

The tightness of the cell pack can influence performance of a cell and consequently considerable time has been spent in reviewing cell pack tightness. In this work, for the most part, cell pack tightness was based on separator thickness. The data for the following discussion will found in Tables VI, VII, and VIII.

Since good data had been obtained for cells having a separator thickness allowance of 3 mils per layer of separator, no cells were constructed more loosely. Generally, a tighter pack favors cycle life. Also included in the test was evaluation of the use of an absorber adjacent to the silver electrode. At the start, only EM 476 was available, but later, PELLON W and P 476-22 became available. All cells had negatives

TABLE V

Cycle Data of Cells Used to Evaluate SWRI Separator Containing Dow Polyethylene

	Usual SWRI		Dow Type SWRI	
	566-49-S-1	566-49-S-2	566-49-S-3	566-49-S-4
Open Circuit Voltage After Sterilization	-0.030	-0.034	-0.031	-0.026
A. C. Impedance After Sterilization (ohm)	.069	.066	.083	.035
Pre-formation at 8.5 ma Capacity (AH)	.194	.194	.195	.189
A. C. Impedance After Pre-formation (ohm)	.068	.101	.091	-
Pressure	no gauge	0 psi	no gauge	1" Hg vac.
First Stage Charge at 8.5 ma Capacity (AH)	4.45	5.24	4.02	6.01
Mid-Stage Discharge at 1,695 ma Capacity (AH)	.68	.34	.30	.32
Second Stage Charge at 9.5 ma Capacity (AH)	1.18	.53	.56	.34
Net Charge Capacity (AH)	5.14	5.62	4.47	6.22
A. C. Impedance After Charge (ohm)	.146	.118	.275	.459
First Stage Discharge at 1,695 ma Capacity (AH)	2.39	2.46	1.95	3.07
A. C. Impedance During First Stage Discharge (ohm)	.080	.082	.072	.057
Midvoltage	1.35	1.35	1.33	1.37
Second Stage Discharge at 340 ma Capacity (AH)	1.51	1.69	1.36	1.87
Total Discharge Capacity (AH)	3.90	4.15	3.31	4.94
Output/Input	76%	74%	74%	79%
AH/gram Ag Discharge	.30	.31	.25	.36
Pressure at End of Cycle	no gauge	1" Hg vac	no gauge	2" Hg vac

* Discharge was stopped when cells reached 1.55 volts.

TABLE VI

Performance of Silver-Zinc Cells Containing Compound 323-50

Cell Number	85-1	92-1	92-2	86-2	89-1
Grams of Silver	14.7	14.7	14.7	14.7	14.7
Grams of ZnO	19.8	19.1	19.1	19.6	19.6
Percent Compound 323-43	3	3	3	3	3
Percent Compound 323-50	7	7	7	7	7
Electrolyte Concentration, % KOH	44	44	44	44	44
Number of layers of separation	8	9	9	8	9
Identity of Separation	GX-115	GX-115	GX-115	GX-115	GX-115
Absorber	none	none	none	EM 476	EM 476
Thickness allowance per separator layer	0.0030	0.0030	0.0030	0.0030	0.0030
Rate for conversion of Compound 323-43	8 ma	50 ma	9 ma	8 ma	8 ma
Amp-hrs to convert Compound 323-43	0.143	0.140	0.141	0.156	0.156
Amp-hrs, theoretical	0.160	0.160	0.160	0.166	0.166
Formation charge - amp-hrs	6.23	6.26	6.39	6.15	6.25
Formation Discharge - amp-hrs	5.91	5.11	6.00	5.50	5.73
Sterilization - 135°C for 72 hours					
Performance - First Cycle					
Charge - amp-hrs - Step 1	5.43	4.60	5.16	4.40	5.03
" " - Step 2	0.78	0.64	0.87	0.60	1.50
" " - Total	6.21	5.24	6.03	5.00	6.53
Discharge - amp-hrs - Step 1	5.64	4.62	4.80	4.53	5.10
" " - Step 2	0.34	0.40	0.85	0.55	0.60
" " - Total	5.98	5.02	5.65	5.08	5.70
amp-hrs/gm Ag	0.406	0.341	0.384	0.345	0.387

Performance of Silver-Zinc Cells Containing Compound
323-50

Cell Number	85-1	92-1	92-2	86-2	89-1
Load voltages after:					
60 min.	1.463	1.434	1.460	1.427	1.421
90 "	1.449	1.430	1.434	1.411	1.391
120 "	1.435	1.406	1.413	1.397	1.383
Performance - Second discharge					
amp-hrs, Step 1	5.46	4.92	5.52	4.98	5.31
amp-hrs, Step 2	0.51	0.43	0.49	0.26	0.34
amp-hrs, total	5.97	5.35	6.01	5.24	5.65
amp-hrs/gm Ag	0.406	0.365	0.408	0.356	0.384
Performance - Third discharge					
amp-hrs, Step 1	6.06 (1)	4.68	5.64	5.01	5.58
amp-hrs, Step 2	0.18	0.40	0.43	0.45	0.38
amp-hrs, total	6.24	5.08	6.07	5.46	5.96
amp-hrs/gm Ag	0.424	0.345	0.412	0.371	0.405

NOTES: (1) Current density 66 ma/sq. in.; for others, current density for Step 1 of discharge was 100 ma/sq. in. and for Step 2, 20 ma/sq. in.

TABLE VII

Evaluating Parameters Affecting Cycle Life of Ag-Zn Cells

Cell No.	96.1	96-2	97-1	100-1	98-1	99-1	10-1	13-1	12-1
grams silver	14.7	14.7	14.7	14.7	14.7	14.7	14.7	14.7	14.7
grams zinc oxide	19.6	19.6	19.6	21.1	19.6	21.1	22.0	22.0	19.0
grams Compound 323-50	1.7	1.7	1.7	0	1.7	0	0	0	2.2
Per cent Compound 323-43	3	3	3	3	3	3	3	3	3
Separator roll number	3-356	3-356	3-356	3-356	3-356	3-356	3-356	3-356	115
Number of layers of GX separator	8	8	8	8	8	8	8	8	8
Thickness allowance per layer (in mils)	2.0	2.4	2.0	2.5	2.5	3.0	2.8	3.0	2.2
Absorber	EM 476	EM 476	EM 476	EM 476	Pellon 2530	Pellon 2530	P-476-22	P-476-22	P-476-22
Formation charge-amp-hrs	6.04	6.04	6.11	6.05	5.41	5.53	6.23	6.46	6.26
Formation discharge - amp-hrs.	5.48	5.64	5.89	5.91	4.80	5.02	5.86	6.16	5.68
Sterilization 72 hrs at 135°C									
First Cycle- charge-amp-hr	4.20	4.65	4.30	4.58	3.61	3.71	4.60	4.66	5.14
Step 1									
Step 2	1.00	0.90	1.00	0.84	0.66	0.69	1.16	1.21	0.93
Total	5.20	5.65	5.30	5.42	4.27	4.40	5.76	5.87	6.07
Discharge-amp-hrs									
Step 1	3.75	3.00	2.67	1.92	3.30	3.15	4.30	3.90	5.07
Step 2	0.96	1.92	2.18	3.04	0.52	0.84	1.09	1.48	0.52
Total	4.71	4.92	4.85	4.96	3.82	3.99	5.39	5.38	5.59
amp-hrs/gm Ag	0.318	0.338	0.329	0.337	0.260	0.271	0.366	0.366	0.380

TABLE VII (continued)
Evaluating Parameters Affecting Cycle Life of Ag-Zn Cells

Cell No.	96-1	96-2	97-1	100-1	98-1	99-1	10-1	13-1	12-1
Load voltage after:									
60 min.	1.330	1.334	1.322	1.300		1.340	1.366	1.331	1.450
90 min.	1.328	1.310	1.298		1.340	1.315	1.357	1.317	1.431
120 "	1.310						1.347	1.305	1.424
Second Cycle-discharge									
amp-hrs, Step 1	3.78	3.60	3.33	3.12	2.81	3.12	3.51	3.60	5.13
amp-hrs, Step 2	0.87	1.20	1.77	1.72	0.90	0.75	1.82	1.95	0.57
Total	4.65	4.80	5.10	4.84	3.70	3.87	5.33	5.55	5.60
amp-hrs/gm Ag	0.316	0.326	0.347	0.329	0.252	0.263	0.362	0.377	0.380
Third Cycle-discharge									
amp-hrs, Step 1	3.96	3.78	2.28		3.00		4.50	4.02	5.25
amp-hrs, Step 2	0.97	0.82	2.51		0.60		1.00	1.48	0.45
Total	4.75	4.60	4.79		3.60		5.50	5.50	5.70
amp-hrs/gm Ag	0.323	0.312	0.326		0.245	0.374	0.374	0.386	
Fourth Cycle-discharge									
amp-hrs, Step 1	3.75	3.81	3.03				4.32	4.32	5.37
amp-hrs, Step 2	0.90	0.73	1.71				1.08	1.38	0.36
Total	4.65	4.54	4.74				5.40	5.70	5.73
amp-hrs/gm	0.316	0.309	0.322				0.367	0.387	0.389

TABLE VIII

Performance of Secondary Silver-Zinc Cells Sterilized After One Electrical Cycle

Cell Number	79-1	80-1	81-1	82-1	83-1	83-2	84-1
gms of silver in pos. elec.	14.7	14.7	14.7	14.7	14.7	14.7	14.7
gms of zinc oxide in neg. elec.	21.4	21.4	22.2	23.0	22.0	22.0	20.0
per cent Teflon in " "	9	9	6	9	9	9	9
density of negative elec. (1)	45, 42	43, 44 (1)	43, 44 (1)	45, 45 (2)	45, 45 (2)	45, 45 (1)	38, 39
primary seal-resin/catalyst	100/3	100/1	100/1	100/1	100/8	100/8	100/1
electrolyte conc. - before addition of ZnO	44	44	44	44	44	43	44
no. of separator layers	8	8	8	8	8	8	8
Formation charge - total amp-hrs	5.97	6.04	6.07	5.90	6.02	6.15	6.02
Formation discharge -							
amp-hrs at 100 ma/sq. in	5.28	5.37	5.28	5.25	5.25	5.43	5.37
amp-hrs at 20 ma/sq. in.	0.41	0.44	0.43	0.48	0.49	0.38	0.48
total amp-hrs	5.69	5.81	5.71	5.73	5.74	5.81	5.85
amp-hrs/gm Ag	0.387	0.395	0.388	0.389	0.390	0.395	0.397
60 min. volts	1.469	1.459	1.456	1.454	1.459	1.460	1.456
90 " "	1.456	1.433	1.432	1.424	1.425	1.427	1.439
120 " "	1.441	1.419	1.407	1.404	1.409	1.414	1.421
Sterilization - 72 hrs at 135°C (3)							
First Charge - amp-hrs, step 1	5.82	5.53	5.45	5.33	5.02	5.02	5.02
amp-hrs, total	6.32	6.21	5.96	5.94	5.66	5.81	5.57
First Discharge -							
amp-hrs at 100 ma/sq. inc.	5.13	5.19	5.19	5.16	5.19	5.16	5.22
amp-hrs at 20 ma/sq. in.	0.65	0.73	0.57	0.47	0.39	0.45	0.37
amp-hrs, total	5.78	5.92	5.76	5.63	5.58	5.61	5.59
amp-hrs/gm Ag	0.393	0.402	0.391	0.382	0.379	0.381	0.380
60 min. volts	1.458	1.451	1.440	1.446	1.442	1.449	1.450
90 min. volts	1.422	1.420	1.413	1.423	1.429	1.429	1.432
120 min. volts	1.411	1.408	1.400	1.410	1.411	1.414	1.420

TABLE VIII (continued)

Performance of Secondary Silver-Zinc Cells Sterilized After One Electrical Cycle

Second Charge (4)							
amp-hrs, step 1	5.22	5.34	5.12	5.19	5.05	5.18	4.92
amp-hrs, total	5.75	5.96	5.66	5.78	5.63	5.73	5.30
Second Discharge							
amp-hrs at 100 ma/sq. in.	5.40	5.16	5.16	5.40	5.28	5.10	5.19
amp-hrs at 20 ma/sq. in	0.61	0.81	0.64	0.54	0.46	0.64	0.37
amp-hrs, total	6.01	5.97	5.80	5.94	5.74	5.74	5.56
amp-hrs/gm Ag	0.408	0.405	0.399	0.404	0.390	0.390	0.378
Third Charge (3)							
amp-hrs, step 1	5.68	5.67	5.40	5.62	5.34	5.34	5.16
amp-hrs, total	6.08	6.10	5.69	6.02	5.83	5.77	5.78
Third Discharge							
amp-hrs at 100 ma/sq. in.	5.40	5.40	5.40	5.40	5.31	5.22	5.55
amp-hrs at 20 ma/sq. in.	0.55	0.73	0.52	0.61	0.61	0.56	0.28
amp-hrs, total	5.95	6.13	5.92	6.01	5.92	5.78	5.83
amp-hrs/gm Ag	0.404	0.417	0.402	0.408	0.402	0.393	0.396

NOTES: (1) DEN438 EK85/DMP30
(2) Epocast 221/927
(3) Charge rate 100 ma, approx. 5.6 ma/sq. in.
(4) Charge rate 120 ma, approx. 6.6 ma/sq. in.

containing 9 percent Teflon in the zinc electrodes. Simultaneously, with the start of this test, a new batch of SWRI-GX separator became available. When the test results of the first cells of the series became available, the poor performances, both in respect to capacity and voltage, were associated with pack tightness. The even poorer capacities of cells 98-1 and 99-1 containing PELLON 2530 were not unexpected in view of the very muddy characteristics of the electrolyte removed from these cells at the time of adjusting their electrolyte levels. At this point, a series of three cells; 10-1, 13-1, and 12-1 was constructed. In cells 10-1 and 13-1, Compound 323-50 was eliminated on the possibility that the prior data indicating its presence is not harmful was in error. Also, pack tightness allowance was increased to 2.8 and 3 mils per separator layers, the latter being the value that has been consistently used here. For cell 12-1, the pack tightness allowance was decreased to 2.2 mils per layer of separator and the percentage of Compound 323-50 increased to 12 percent, both of these changes calculated to be detrimental to performance. However, separator material from Roll 115 was used instead of that from Roll 3-356, the latter roll being from the new batch mentioned above. As shown in Table VII, the performance of Cell 12-1 is the only one having both satisfactory capacity and voltage. Cells 10-1 and 13-1 have passable capacities but low voltages. Indications are that approaching a more loosely packed cell resulted in improvement of capacity (if one is to assume that the different capacities of Cells 96-1, 96-2, 97-1, and 100-1 on one hand and 10-1 and 13-1 on the other were not due to the use of EM 476 instead of P 476-22. If, however, pack tightness alone were responsible for the poor performance of these cells, the question that arises immediately is why did Cell 12-1 with a very tight pack perform adequately. Incidentally, it should be added that, with the exception of Cells 98-1 and 99-1 containing the PELLON 2530 W which had reduced capacities before sterilization, the poor voltages and capacities occurred only after sterilization.

Examination of the components of some of these cells after cycling revealed no dry areas of separator and considerable expansion of the negatives possibly due to the high percentage of Teflon. Also, single layer resistances were not extremely high. If one assumes that a looser pack tightness design is necessary because of the expansion of the zinc electrode, the question again arises as to why this was not necessary when separator from Roll 115, and negative electrodes having the same percentage of Teflon were used.

Reviewing prior data, the following interesting observation was made. Prior to the construction of Cell 79-1, included in Table VIII, poor load voltages resulted in a considerable number of cells, and the cause of this was not established. From Cell 79-1 through 92-2 (twelve in all), cell-to-cell capacity uniformity was very high and none had unsatisfactory voltages. All of these cells had separator from Roll 115; none of the others did. The difference between Roll 115 and the others used is that Roll 115 has a cloudy rather than clear appearance. This has been attributed to excess homopolymer on its surface resulting from temperature conditions existing during manufacture (refer to W. von Hartmann of JPL). This may be an area warranting further study.

E. Performance of Ag-Zn Cells, Before and After Sterilization

The capacity of cells after sterilization (0.35 AH/gm Ag) has not been quite as good as before sterilization (0.40 AH/gm Ag) as shown in Table IX. The load voltage of 1.42 before sterilization is much better than the voltage of 1.35 after sterilization. Nevertheless, both the capacity and the load voltage are acceptable.

The construction parameters for the above-mentioned cells are as follows: These cells contained three silver electrodes having densities of 69 gm/in^3 and total active material weights of 14.7 gm. The two center negative electrodes had 6.8 gm of mix and were 0.063 in. thick, and the outside ones had 4.6 gm of mix and were 0.044 in. thick with the exception that the 19-series had 6.3 and 4.4 gm, respectively. Calculated powder density for all except the 19-series was 40 gm/in^3, and for the 19-series, it was 38 gm/in^3. All except 16-series had no absorber. Allowance for separator was 0.0028 in/layer. All cells had negative wrap construction. Electrolyte for all was 44% KOH containing 110 gm ZnO/l. Negative electrode mixes all contained 3% Compound 323-43, and 9% Teflon. For the 16 and 17 series, the negative electrode mix contained 7% Compound 323-50 and for the 18 and 19 series, 12%Compound 323-50.

These cells will be life tested and it will be interesting to note if the load voltages increase with cycling as did Cells 10-1 and 13-1 (see D. Separators, Absorbers, and Cell Pack Tightness). If so, then the lower load voltage after sterilization might be related to the separation which was from the same roll.

TABLE IX

Performance Data on Silver-Zinc Cells, Before and After Sterilization

Cell Number Book No. 123	gms electrolyte filled	gms electrolyte sealed	Formation Charge amp-hr/gm Ag	Formation discharge amp-hr/gm Ag	Volts after 90 min. load	Post Sterilization Charge amp-hr/gm Ag	Post Sterilization Discharge amp-hr/gm Ag	Volts after 90 min. load
15-1	32.3	22.8	0.44	0.40	1.42	0.38	0.35	1.35
15-2	32.8	25.1	0.41	0.38	1.40	0.37	0.34	1.33
15-3	32.3	24.5	0.43	0.40	1.40	0.39	0.36	1.37
15-4	32.6	23.3	0.45	0.40	1.42	0.39	0.35	1.35
15-5	32.6	25.3	0.42	0.41	1.40	0.39	0.37	1.31
15-6	32.0	25.1	0.40	0.38	1.40	0.35	0.32	1.35
16-1	32.6	25.4	0.44	0.40	1.42	0.40	0.36	1.32
16-2	33.0	25.4	0.42	0.39	1.41	0.32	0.33	1.30
16-3	32.1	25.5	0.43	0.40	1.41	0.40	0.35	1.36
16-4	32.2	25.9	0.45	0.39	1.41	0.40	0.34	1.33
16-5	31.8	25.2	0.40	0.37	1.42	0.37	0.33	1.32
16-6	32.4	25.5	0.42	0.40	1.42	0.39	0.34	1.33
17-1	32.0	24.0	0.42	0.40	1.42	0.38	0.35	1.33
17-2	32.1	24.0	0.42	0.40	1.42	0.37	0.35	1.34
17-3	32.1	24.0	0.43	0.40	1.41	0.39	0.35	1.33
17-4	31.1	24.4	0.43	0.40	1.40	0.38	0.34	*
17-5	32.1	25.8	0.42	0.40	1.40	0.40	0.34	*
17-6	32.0	-	0.42	0.40	1.41	0.42	0.34	1.32

(continued)

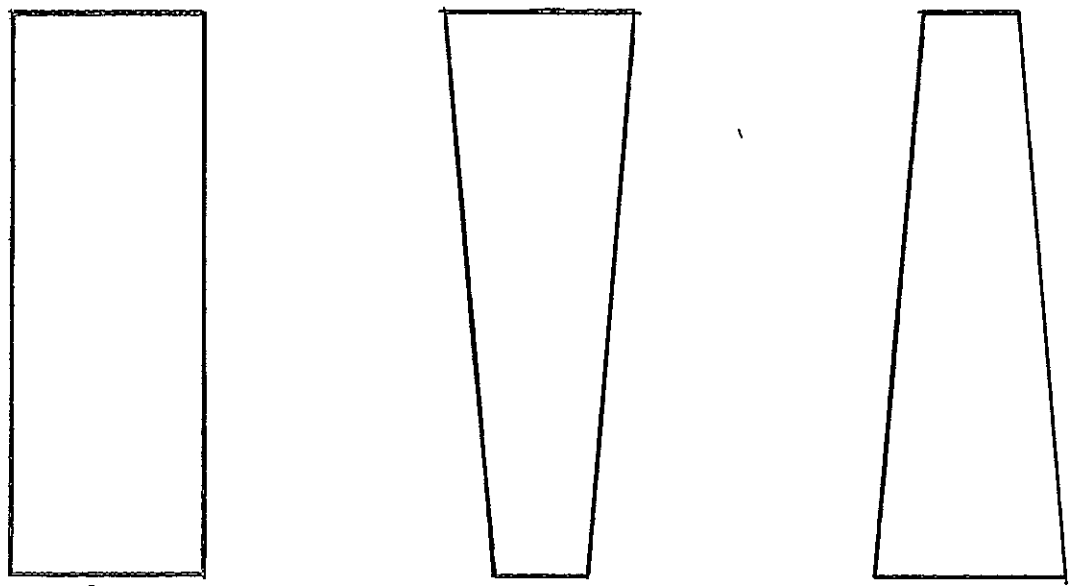
TABLE IX (continued)
Performance Data on Silver-Zinc Cells, Before and After Sterilization .

Cell Number Book No. 123	gms electrolyte filled - sealed		Formation Charge discharge amp-hr/gm Ag		Volts after 90 min. load	Post Sterilization Charge Discharge amp-hr/gm Ag		Volts after 90 min. load
18-1	34.0	24.9	0.43	0.41	1.43	0.43	0.37	1.36
18-2	33.4	24.4	0.43	0.41	1.42	0.47	0.35	1.37
18-3	33.5	24.6	0.43	0.40	1.42	0.41	0.36	1.34
18-4	33.3	24.4	0.43	0141	1.43	0.44	0.36	1.36
18-5	33.2	25.9	0.42	0.39	1.42	0.44	0.35	1.32
18-6	34.2	24.6	0.44	0.41	1.43	0.46	0.36	1.37
19-1	35.1	25.5	0.42	0.38	1.43	0.40	0.36	1.39
19-2	34.7	23.8	0.42	0.40	1.42	0.37	0.36	1.35
19-3	34.8	25.9	0.44	0.41	1.43	0.41	0.39	1.38
19-4	34.1	25.8	0.45	0.40	1.43	0.41	0.36	1.36
19-5	34.1	26.3	0.43	0.41	1.43	0.40	0.36	1.35
19-6	34.1	25.3	0.45	0.41	1.43	0.41	0.38	1.38

Note: * Cut off voltage 1.25

FIGURE 1

TAPERED CELL CAVITIES



F. Cells with Tapered Cell Cavities

Six 7-plate cells were constructed in PLEXIGLAS cases to study the effect of the shape of the case on cycle life. All electrodes were of the normal 281 dimensions. The cells numbered 1 and 1' (Figure 1) were of rectangular cross-section perpendicular to the width of the plates, 2 and 2' were short at the bottom but long at the top, and 3 and 3' were short at the top but long at the bottom. It was expected that 3 and 3' would have higher current densities at the top than the other cells and thereby offset to some extent the shape change believed to be due to gravity. The cells were not sterilized but were over-potted. The cells have completed 31 cycles of 100 percent d.o.d. The capacity of all the cells was around 0.33 AH/gm Ag. For cycling purposes, a nominal capacity of about 0.21 AH/g Ag was chosen and the discharge rate was 94 ma/sq.in. These cells will be cycled until failure but, at this time, no significant difference has been observed.

G. The Effect of Compound 323-43 on Cycle Life

Data shown in Table X indicate the probability that the presence of the ion of Compound 323-43 is desirable for extending cycle life. Thus it was decided to increase its amount by introducing another compound containing it. This compound, identified as 323-50, had been used earlier in Ag-Zn cells but its use led to gassing during formation. However, now that cells can be formed open to vent gas pressure and then sealed and sterilized, no difficulty in the use of Compound 323-50 has been encountered.

As shown by the data in Table VI, cells containing Compound 323-50 performed satisfactorily with respect to both load voltages and capacities. The rate for conversion of Compound 323-43 in Cell 92-1 was at 50 ma and for its duplicate, 92-2, 9 ma. Whether this resulted in the lower capacity of the former cell has not been established, but in the absence of data to the contrary, the lower rate previously recommended remains so. No reason is apparent for the lower capacity of Cell 86-2, but, as noticed by the data, it increased with cycles but that for Cell 92-1 did not. These cells are being life cycled to determine the effect of Compound 323-50 on cycle life.

TABLE X
Life Cycle Study - Ag-Zn Cells

Cell Numbers	gms Ag	gms ZnO	Percent 323-43	Sterilization (before, after) 1st cycle	Orig. Cap. amp-hrs	Cap. at __th cycle amp-hrs		Cycles to Failure	Cause of Failure
132-14-1	14.7	14.6	7	before	3.60	1.41			
					0.80	0.99			
					4.40	2.40	189	189	Low capacity
132-27-2	14.7 (1)	11.9	5	after	4.86	N.A.			
					0.42				Ag penetration
					5.10			202	shorted
132-59-1	14.7	14.0	5	before	4.32	1.83			
					0.84	0.90			
					5.16	2.73	156	160	Low capacity
132-73-2	14.7	13.8	5	before	4.80	2.10			
					0.53	0.66			Ag penetration
					5.33	2.76	142	146	shorted
132-77-1	18.5	18.0	4	before	4.92	2.91			
					1.14	1.98	(2)		
					6.06	4.89	128	185	
132-77-2	18.5	18.0	4	before	4.41	1.89			
					1.14	1.93			
					5.56	3.82	128	175	Low capacity
147-6-1	14.7	18.2	0	after	3.99	N.A.			
					0.90				Ag penetration
					4.89			83	shorted
147-6-2	14.7	18.2	0	after	3.75	N.A.			
					1.12				Ag penetration
					4.87			82	shorted
147-6-3	14.7	18.2	0	after	3.51	N.A.			
					0.96				Ag penetration
	(3)				4.47				shorted
147-6-4	14.7	18.2	0	after	3.99	N.A.			
					0.90				
					4.89			90	Low capacity

TABLE X (continued)
Life Cycle Study - Ag-Zn Cells

Cell Numbers	gms Ag	gms ZnO	Percent 323-43	Sterilization (before, after) 1st cycle	Orig. Cap. amp-hrs	Cap. at __th cycle amp-hrs		Cycles to Failure	Cause of Failure
147-6-5 (3)	14.7	18.2	0	after	3.66	N.A.		90	shorted
					1.59				
					5.25				
119-93-4	18	18.2	7	none	5.65	2.82			
					0.91	1.81			
					6.56	4.63	306	352	shorted

NOTES: (1) Compound 323-43 tank converted at low rate in very low KOH conc. prior to construction.

(2) as of 6/2/69

(3) Positive electrodes impregnated with a compound similar to 323-43.

H. Life Testing of Cells and Batteries

Approximately two years ago, two batteries of six cells each were life tested at a cycle depth of approximately 60 percent of their nominal capacity based on 0.25 amp.hr. per gram of silver. These were cells which had been sterilized as cell packs and then inserted into jars and sealed. From the parameters tested, the results indicated generally longer life resulted with increasing electrolyte concentration and when a polypropylene absorber (EM 476) was located adjacent to the silver electrodes. With the advent of the capability for constructing cells that could be sterilized after sealing, testing continued. The cycle consisted of 21 hours charge using a modified constant potential source set at 11.60 volts for 6 cells (1.93 volts per cell) with a current limit of 0.25 amp. for cells with nominal ratings of 3.7 amp. hrs. The discharge was for 3 hours through a 10-ohm load and removed approxomately 2.7 amp. hrs. per cycle. Some cells had nominal ratings of 4.5 amp. hrs. as a result of silver electrodes of different weights. Most of the cells were those which had not been constructed with cycle life determination the principal concern, but were selected from those studied during the cell development study which was being done.

The summary of the data on the sealed-sterilized cells are included in Table X. All cells had 8 layers of GX separator with the exception of 119-93-4 which had 9 and was unsterilized. Some observations follow: (1) the failure mode was either low capacity or "silver" penetration; (the latter determination is based on cell behavior during charge and open circuit periods, zinc penetration giving a different behavior pattern than "silver" penetration and on the fact that evaluation of the separator showed extensive "silver" penetration through all layers); (2) substitution of mercuric oxide for Compound 323-43 resulted in considerably reduced cycle life which was slightly improved for cells which had their silver electrodes impregnated with a compound similar to Compound 323-43, (3) data for only one cell containing Compound 323-43 which was sterilized after cycling is included, the others having been sterilized before cycling, but results were not unfavorable for the former procedure, (4) the unsterilized cell gave 175 percent as many cycles as the best sterilized cell, (5) all cells but one had sintered Teflon negative electrodes and these did not eliminate erosion of active material.

III. GRID STUDIES

In a cell, the grid is responsible for carrying current and forming a structure to retain the active material. Strength, overvoltage, and chemical surface of the grid are factors which affect its ability to function, and in the case of the negative grid, these factors, in turn, can be modified by the silver grid interacting with the negative mix. Thus, studies have been conducted on the effects of mix components on grid properties.

A. Grid Embrittlement

Foremost among the components affecting silver grids of Ag-Zn cells is mercury. Mercury is usually added to the negative mix to reduce gassing of the zinc electrode. However, it has been observed and reported previously that grids which had been used in cells containing mercury in the negative mix were weaker than the original grids. Actually, the strength of the grid seems to be a function of time and appears to pass through a minimum. Observations indicate that cells which stood for less than three months were very brittle whereas those that stood for a year or more were strong. More recent data as discussed in the following experiment indicate that zinc also may be responsible for the embrittlement of the grid.

Two silver grids were examined to determine the reason why one was ductile and the other very brittle. The silver grids had been taken from two different silver zinc cells whose histories were as follows:

Grid 41 - Cell assembled, then sterilized. Cycled four times and fully discharged to zero volts. Resterilized, charged, and then discharged to 1.55 volts. This grid was ductile and showed little corrosion.

Grid 42 - Cell assembled, then sterilized. Cycled four times and discharged to 1.55 volts. This grid was very brittle and showed a substantial amount of corrosion.

Both grids were examined under the mixroscope, X-rayed, and chemically analyzed. The following results were obtained:

Grid 41 (Ductile) - A polished and etched cross section of Grid 41 was observed with the microscope and found to consist of an outer reaction zone surrounding an unaltered silver core. The grain structure of the core is comparable to

that occurring in an unused silver grid. A distorted silver pattern was obtained from an X-ray diffraction analysis of the surface of the grid. This indicates that the outer grid is a solid solution of silver and mercury. Chemical analysis of the total grid showed the presence of 94.80 percent Ag, 0.21 percent Zn, and 5.21 percent Hg.

Grid 42 (Brittle) - A polished cross section of Grid 42 was observed with the microscope and showed two distinct zones. Neither zone reacted with the silver etchant[1]. The polished section was treated with a dilute (1·1) HCl solution while being observed with the microscope. It was noted that the outermost zone reacted vigorously with the acid and became pitted. The entire grid was ground and then treated with NH_4Cl solution to eliminate the adhering ZnO and X-rayed. The following pattern was obtained

d Å	I/I_1
2.43	40
2.19	32
2.13	100
1.63	18
1.41	20
1.258	15
1.185	16
1.175	15
1.066	2

Although an exact match could not be found in the ASTM file, this pattern resembles zeta Ag Zn. Chemical analysis of of the entire grid shows the presence of 78.57 percent Ag, 15.97 percent Zn, and 7.17 percent Hg.

The X-ray pattern obtained from Grid 42 is identical to one previously obtained from the silver grid of the negative electrode from a Leesona Moos cell. Chemical analysis of that grid showed it to be composed of 92.8 percent Ag, and 7.1 percent Zn. Mercury was also present but insufficient sample was available to do a quantitative determination.

It should be noted that the Leesona Moos grid had been formed but not cycled. It is thus possible that the zinc was introduced into the silver grid during formation with mercury acting as the transporting medium. Moreover, resterilization may lower the zinc content of the grid. Experiments will have to be designed to verify these hypotheses.

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[1] silver etchant is 1 part KCN (5 percent solution) plus 1 part $(NH_4)_2S_2O_8$ (5 percent solution)

B. Overvoltage Study

In making electrodes stronger for high impact cells, high strength metals or massive amounts of silver are required to reinforce the electrode. In the negative electrode, the strengthening member must have a hydrogen over-potential equal to or greater than that of the usual thin amalgamated silver grid. If this be not so, then the lower overvoltage surface of the reinforcing metal becomes a site for the possible evolution of hydrogen during charge. (see report for the First Quarter of 1968, JPL Contract 951296, p. 9).

When massive silver sheet or grids are used to strengthen the negative electrode, the normal amount of mercury in the negative mix (Ca. 4%) may be inadequate to properly amalgamate the reinforcing mass of silver and charged zinc. Gassing may then occur. Furthermore, it is conceivable that amalgamation of the mass of silver would occur first on its surface, and if by chance the concentration of mercury was just sufficient to control gassing, then after sterilization when the mercury had diffused throughout the mass, the surface concentration might again be too low to have an adequately high overvoltage. High gas pressure would then develop on charge.

To insure sufficient mercury for the massive silver, the reinforcing member could be preamalgamated. While this approach should control hydrogen evolution, it could lead to low strength embrittled grids. Clearly, data are lacking on these systems and it is proposed to investigate the effect of various concentrations of mercury on the over-potential of silver and the effect of sterilization on both the overpotential and brittleness of the grid.

As a preliminary experiment, the effect of sterilization on overpotential of silver was determined for one level of mercury. The data in Table XI show that the overvoltage of amalgamated and unsterilized silver is higher than that of the unamalgamated. But surprisingly, the overvoltage of the amalgamated and sterilized silver was on either side of that of the untreated silver depending on the time of observation. This could be the effect of a film formed during sterilization which was subsequently reduced during the experiment. If the phenomenon is real, it could account for gas observed during cell formation. This observation will be followed in later experiments at other concentrations of mercury.

TABLE XI
Effect of Sterilization and Amalgamation on Hydrogen Overvoltage

Treatment		Voltages (v) at Two Currents					
		10 (ma)			80 (ma)		
Amalgamated *	Sterilized **	6/30 9 AM	6/30 2 PM	7/1 9 AM	6/30 9 AM	6/30 2 PM	7/1 9 AM
No	No	1.51	1.54	1.54	1.64	1.64	1.68
Yes	No	1.82	1.82	1.82	1.90	1.98	1.96
Yes	Yes	1.39	1.68	1.76	1.47	1.90	1.94

* 2% of Hg by weight

** 72 hrs. at 135°C

C. Cells with Lead-Plated Grids

Four 7-plate cells, two of which were controls, were prepared to test the possible effects of using lead in the negative plates. These cells have completed four cycles. By plating the Ag grid with lead, it was hoped that the effect of mercury on the strength of the grid would be minimized. These cells were sealed in nickel bombs and sterilized at 135 °C for 72 hours. The data shown in Table XII indicate that none of the cells increased in pressure. However, the two cells which contained 0.001 inch of lead on the negative grid did not perform as well as the two control cells which contained no lead. Because the Pb-plated cells seem to be improving in capacity, all of the cells will be cycled further before being taken apart for analysis. Note that the rate of charge and discharge was varied slightly for the various cycles.

TABLE XII
Capacity, Voltage, and Pressure Data for Cells With Lead Plated Negative Grids

	Control		Pb-Plated	
	58	59	60	61
Cycle #1				
First Stage Charge Capacity (Preformation incl.)	5.23	5.29	4.42	4.37
Second Stage Charge Capacity	.61	.60	1.31	1.40
Net Charge Capacity	5.44	5.45	4.89	4.91
First Stage Discharge Capacity at 2.00 A	2.68	2.74	2.80	2.50
Midvoltage	1.39	1.39	1.39	1.39
Second Stage Discharge Capacity at 200 ma	1.89	1.68	1.18	1.30
Total Discharge Capacity	4.57	4.42	3.98	3.80
Output/Input	84%	81%	81%	77%
AH/gram Ag Discharge	.34	.33	.29	.30
Pressure Change at end of Cycle	none	none	none	none
Cycle #2				
First Stage Charge Capacity	4.71	4.36	3.79	3.49
Second Stage Charge Capacity	.57	1.12	1.81	1.74
Net Charge Capacity	4.94	5.01	4.91	4.52
First Stage Discharge Capacity at 1,690 ma	3.99	3.87	3.35	2.96
Midvoltage	1.40	1.40	1.42	1.41
Second Stage Discharge Capacity at 338 ma	.84	.60	.55	.74
Total Discharge Capacity	4.83	4.47	3.90	3.70
Output/Input	98%	89%	80%	82%
AH/gram Ag Discharge	.36	.33	.28	.29
Pressure Change at end of Cycle	none	none	none	none
Cycle #3				
First Stage Charge Capacity	4.71	4.35	4.02	3.68
Second Stage Charge Capacity	.86	.86	1.66	1.73
Net Charge Capacity	5.01	4.82	4.31	4.04
First Stage Discharge Capacity at 1,690 ma	4.40	4.15	3.74	3.50
Midvoltage	1.40	1.41	1.42	1.42

TABLE XII (continued)
Capacity, Voltage, and Pressure Data for Cells With Lead Plated Negative Grids

	Control		Pb-Plated	
Cycle #3 (continued)	58	59	60	61
Second Stage Discharge Capacity at 338 ma	.71	.47	.35	.51
Total Discharge Capacity	5.11	4.62	4.09	4.01
Output/Input	102%	96%	95%	99%
AH/gram Ag Discharge	.39	.34	.30	.30
Pressure Change at end of Cycle	none	+1.0 psi	+2.0" Hg	+2.0" Hg
Cycle #4				
First Stage Charge Capacity	4.52	4.19	4.07	3.88
Second Stage Charge Capacity	.86	.81	1.24	1.26
Net Charge Capacity	4.96	4.54	4.70	4.53
First Stage Discharge Capacity at 1,690 ma	4.30	4.35	3.90	3.80
Midvoltage	1.40	1.41	1.41	1.41
Second Stage Discharge Capacity at 338 ma	.71	.44	.37	.54
Total Discharge Capacity	5.01	4.79	4.27	4.34
Output/Input	101%	105%	91%	96%
AH/gram Ag Discharge	.38	.35	.31	.33
Pressure Change at end of Cycle	none	none	none	-1.0" Hg

NOTE: The mid-charge discharge for some cells at times exceeded 20%, but the cell voltage never went below 1.55 volts.

FABRICATION AND TESTING OF CELLS

I. DEVELOPMENT OF HEAT STERILIZABLE - HIGH IMPACT 5 0 AH CELLS, TASK 9

A Objective and Past Work

This task requires the development of cells meeting the requirements of JPL Specification GMP-50437-DSN-C, high impact of 2,800 ± 200 g at 115 ± 3 ft/sec , and JPL Engineering Memorandum 342-70 Thirty (30) cells of 5 AH nominal capacity are to be delivered in December 1969. Non-high impact test cells have delivered 11.0 AH at 3 3 amperes to 1.25 volts per cell, 16.4 watt-hours at an average voltage of 1.49 volts, and 43 watt-hours per pound of cell after 72 hours wet heat sterilization at 135 C. One high impact version of this cell constructed in the same cell case was assembled into a 12-cell battery and after heat sterilization survived tests in the C-SAD experimental spacecraft at a shock level estimated to be 2400 "g" (1)

Component evaluation tests were performed on 10 AH test cells to determine the change in performance after heat sterilization upon incorporation of -

- Epoxy platelock to increase plate pack structural strength
- Sand blasting of cell sealing surfaces
- RNF tubing on plate leads as insulation
- Zirconium sheet cores in positive plates

RNF irradiated polyolefin tubing interacted with negative plates giving high hydrogen gassing rates and was replaced by heat shrinkable teflon Zirconium sheet cores were found electrochemically safe but required redundant Ag lead wires for conductivity. Other effects were within experimental error.

B Model 281 Cell Automatic Cycling

Six 10 AH cells were assembled in series array and cycled at 50% depth of discharge on a 21 hour charge/3 hour discharge routine at room ambient Cycling was begun at a charge level of 20% of full charge, first charging 21 hours at a modified CP of 1 94 volts per cell and a limiting current of 0.21 ampere. End of discharge voltages for the six cells varied within the range·

Cycle No	End of Discharge Voltage Range (Volts)
1	1 520 - 1.540
8	1.511 - 1.536
13	1 510 - 1.528
30	1.496 - 1.518
1-30	Mean decrease in EDV = 27 mv

On the 49th cycle capacity was measured by a two-step discharge: first at 3.3 amperes, and then 0.7 ampere to 1.25 volts per cell.

Capacity had decreased from an initial range of 9.5 - 10.6 AH to 8.6 - 10.6 AH, an average decrease of 0.17% per cycle. The cells were then returned to the auto-cycling regime. Including previous wet life and heat sterilization of 72 hours at 135°C, the age of the cells was 6 months on the 50th cycle. Cycling to failure will provide a measure of the wet life of 6 layers GX membrane separator under anticipated mission conditions at 75 ± 5°F and the cycle life of sintered teflonated negative plates on this charge/discharge profile.

C. Model 361 5.0 AH High Impact Cell Design

Initial cell design concepts for a 5.0 AH cell capable of surviving 4,000 g's were described in reference (2). Shock tests of non-heat sterilizable 5.0 AH cell packs based on this design (see Task 12 of this report) showed lateral movement of the plates was still sufficient at 4,000 g's to permit buckling to begin at the juncture of plate tab and active material. Primary failure site was the 17-mil sheet zirconium positive plate core. Assumptions in the stress analysis prior to shock did not adequately cover the physical system of parallel columns each successively stressed just beyond its own buckling strength during 4,000 g's shock. Application of the Euler equation to correct the design then predicted the need for a zirconium core thickness increase from 17 to 31 mils minimum and 39 mils for a safety factor of 2.0. Appendix I gives the calculation. The redesigned positive strut thickness will be 0.037 inch. In addition, plastic shims will be installed between the plate struts to prevent lateral motion in the buckling direction. Both changes should eliminate the buckling failure mode at 4,000 g's.

D. Future Work

Plastic cell case and cover parts are being molded by Servtech Plastics, Monrovia, California. Chemically etched negative grids are on order from Glar Ban Corporation, Buffalo, New York. Prototype 5 AH cell assembly is scheduled for November 1969.

II. DEVELOPMENT OF HIGH CYCLE LIFE 48 AH CELLS TASK 10

A. Objectives and Past Work

This task requires development of wet heat sterilizable 48 AH cells meeting the requirements of JPL Specification 50436-DSN-B and delivery of 100 cells in April 1970. Operational requirements include:

- One year prelaunch storage followed by 72 hours heat sterilization at 135°C;
- Charge, 9-month interplanetary travel;

- Environmental shock 200 "g" for 0.7 ± 0.2 msec, 100 "g" deceleration for 10 minutes, and 35 "g" rms maximum vibration 100 to 2000 cps; plus after landing;

- 400 cycles, 50% depth, 12-hour maximum charge time and discharge rates of C/10 to C/3 from 10°C to 50°C.

Half size 24 AH cells, cycled on a 10 hour charge/2 hour discharge after heat sterilization for 100 hours at 135°C, failed by Ag penetration after 84 cycles in a total wet charged life of 5-6 months for a separator system of 6 layers Southwest Research Institute GX membrane. Negative plate capacity loss rates was 0.33 AH/cycle.

B. Factorial Cells

A factorial experiment has been initiated to investigate 3 levels each of teflonation in sintered teflonated in sintered teflonated negatives, electrolyte composition, wet membrane thickness, and zinc oxide to silver active material weight ratio. Twenty-seven 16 AH cells have been constructed, sterilized, and subjected to formation charge. Design factors for each of the 27 cells were described in reference (3). The same number and type of positive plates was used in each cell so that the nominal capacity at 0.25 AH/gram of Ag is the same value (16 AH) for all cells. Negative plates are of 3 thickness groups depending upon the variable ratio ZnO/Ag (0.9, 1.2, and 1.5) but have a common density (45 gm/in^3). Electrolyte volume in each cell was controlled within 0 to 3 cc of the calculated volume of all voids in plates and the 8 layer GX membrane. Calculated and actual volumes ranged from 48 cc to 65 cc and increased uniformly with increasing cell pack thickness: i.e. increasing plate thickness or increasing wet membrane thickness allowance (2.0, 2.4, and 2.8 mils per layer).

After preformation and hermetic seal the cells were clamped (simulated battery chassis), heat sterilized 100 hours in N_2 at 135°C, and then leak checked. No leakage was observed although crazing of the DOW DEN438EK85/DMP30 sealing epoxy was apparent in some cells. This epoxy has since been replaced by a non-crazing type in newer cells.

Post-heat sterilization discharge capacities at C/3 rate are given in Table XIII by cell design factors for the first three cycles at 100% DOD. Cells S/N 4, 22, and 23 performed poorly and were replaced. Post-mortems are scheduled.

Cells are now on 100% depth cycling tests: charging at 0.76 ±.01 amp to 2.03 ±.02 volts per cell, and discharging at 5.3 ±0.1 amp to 1.25 ±.03 volts per cell.

TABLE XIII

FACTORIAL CELL DISCHARGE CAPACITIES
FIRST THREE CYCLES

Design Factors				Discharge Capacity - AH (1) 5.3 Amp to 1.25 V		
KOH %	ZnO/Ag Weight Ratio	Membrane Wet Thickness Mils	Teflon Additive %	Formation Cycle 1	Cycle 2	Cycle 3
41	0.9	2.0	5	24.4	20.9	18.9
"	"	2.4	9	18.4	15.4	13.8
"	"	2.8	7	24.2	21.2	20.8
"	1.2	2.0	9	21.0	16.8	17.8
"	"	2.4	7	16.2	14.3	13.3
"	"	2.8	5	19.8	15.0	16.8
"	1.5	2.0	7	17.8	14.6	13.6
"	"	2.4	5	20.2	18.8	18.1
"	"	2.8	9	22.5	20.1	20.1
43	0.9	2.0	9	18.8	15.3	14.4
"	"	2.4	7	24.7	21.2	18.8
"	"	2.8	5	23.0	19.6	18.8
"	1.2	2.0	7	20.3	18.0	17.5
"	"	2.4	5	19.2	15.2	16.0
"	"	2.8	9	15.4	14.2	12.3
"	1.5	2.0	5	25.3	14.1	12.1
"	"	2.4	9	22.1	20.3	19.3
"	"	2.8	7	19.1	18.5	17.3
45	0.9	2.0	7	16.0	13.7	11.6
"	"	2.4	5	21.1	18.5	17.0
"	"	2.8	9	25.9	22.4	21.6
"	1.2	2.0	5	21.3	18.6	17.2
"	"	2.4	9	21.5	20.0	20.3
"	"	2.8	7	21.1	19.8	17.3
"	1.5	2.0	9	16.0	16.4	14.3
"	"	2.4	7	20.4	18.2	17.6
"	"	2.8	5	28.5	14.1	8.7

(1) All cells cycled 100% DOD after charge at 0.76A to 2.03 V/C.

Cycling data will be analyzed at 16 and 35 cycles by statisticians of the N. C. State University.

III. DEVELOPMENT OF RECHARGEABLE PRIMARY 70 AH CELLS TASK 11

A. Objectives and Past Work

In this task wet heat sterilizable 70 AH cells are being developed to meet the requirements of JPL Engineering Memorandum 342-71 summarized previously[4]. One-hundred cells are presently scheduled for delivery in late August 1969. The Model 364 cell has demonstrated after heat sterilization a mean 4 cycle discharge capacity of 89 AH at the C/4 rate, 133 watt-hours at an average voltage of 1.49 volts, an energy density of 52 WH/lb. of cell, and a wet cycling life to date of 14 months. During vibration tests at JPL positive plates buckled in the vertical test plane in the active material below the tab-plate spot weld. Several plate tab designs were then tested in a fatigue tester until the prototype positive and negative plate designs were selected. Each plate is now framed by a Ag channel and has a massive tab welded to the channel. Fatigue test time to failure was at least tripled in both plates by the redesign.

B. Prototype Cell Design and Prototype Cell Tests

A prototype design review approved the redesigned Model 364 cell and nine cells were released for construction. Table XIV compares the new and old cell designs. The negative plate process was changed to a sintered teflonated active material process to increase cycle life, and the separator wet thickness was increased from six to eight layers of Southwest Research GX membrane (18 mils total) to increase wet charged stand life from 14 to 18 months after heat sterilization.

Four epoxy case to cover seals were tested through sterilization of 72 hours at 135°C, thermal shock to 0°C, and then hydrostatically burst. Five of 6 specimens sealed with DOW DEN438EK85/DMP30 (100:3 with 5-7 minute vacuum) leaked through craze cracks in the epoxy during sterilization. One survived thermal shock and burst at 90 psi unsupported. The best epoxy seals survived both tests with no crazing (6 of 6) and burst at 60, 70, 70, 75, 125, and 135 psi. In the cases with lowest burst pressures the edges at the break site varied in color from white to amber, a possible molding fault. Production cells should have cases pressure checked at 50% mean burst pressure to find and reject imperfections in the molded material.

The massive negative plate tabs required insulation to prevent zinc growth up the tabs on charge. Epoxy coatings, and sleeves of TFE and FEP were sterilized in 45% KOH. FEP and TFE materials passed the test. FEP sleeves were selected for use in the prototype cells.

Nine Model 364 cells were constructed. Six have successfully passed heat sterilization and are now on formation charge with three non-sterile control cells. Table XV summarizes the maximum to minimum weights of the nine cells through processing steps leading up to formation charge as typical control on the 70 AH cells. Electrolyte height was observed through

TABLE XIV

PROTOTYPE 70 AH CELL DESIGN

Design Parameter		Unit	Previous Design	New Design
1.	Capacity, rated @ C/4	AH	80	70
2.	Plates/cell	+/-/-1/2	9/8/2	Same
3.	Active material/cell, Positive	g Ag	286	248
	Negative	g ZnO	198	187
4.	ZnO: Ag ratio, wt.		0.69:1	0.75:1
5.	Active area/cell	in^2	186	164
6.	Plate grid type and weight	die and g/in^2	2/0 - 0.448 expanded interrupted	3/0 - .224 expanded, double with 0.010" Ag channel frame.
7.	Positive process	type	Sintered Ag	Same
8.	Negative process and composition active material: ZnO, 323-43, teflon	type	Pressed powder 91-7-2	Sintered teflonated 91-4-5
9.	Plate thickness and weight	mils/g		
	• Positive		48 / 43.7	43 / 42.4
	• Center negative		56 / 33.0	55 / 37.0
	• End negative		33 / 20.9	29 / 25.6
10.	Separation SWRI-GX			
	• Negative retainer	No. layers	1	None
	• Negative wrap	No. layers	6	9
	• Wet thk. W & W/O overlap	Mils	2.33 / 2.48	2.26 / 2.40
11.	Jar height (PPO 534-801)	in.	4.82	4.92
12.	Cover (PPO 534-801	type	Machined	Molded
13.	Weight sealed cells	lb.	2.53	2.74

TABLE XV

PROCESS WEIGHT CONTROL 70 AH MODEL 364 CELLS

Process Step	Weight - Grams (n = 9 Cells) Minimum	Median	Maximum
Dry Weight of Cell	975	980	992
Flooded Wet Weight	1216	1225	1239
Filled Electrolyte Weight*	227	239	262
Adjusted Electrolyte Weight	227	227	227
Sealed Weight			
Before HS	1202	1210	1219
After HS**	1201	1208	1218
Loss in Weight in HS (As Water)	1		2

* Level at ~86% plate height before formation charge.

** n = 6; 72 hours 135°C

a clear polysulfone window installed in one cell. After heat sterilization there was no evidence of KOH leakage at terminals or case to cover seal. Weight loss (1-2 grams) is assumed to be water diffusion through PPO jar walls at 135°C.

During formation charge pressures were monitored on gages installed after cooling down from sterilization. Vacuums were observed in the cells when the seals were broken. Charge pressures averaged 8 psi with 15 psi maximum.

C. Future Work

- Install six sterile cells in an aluminum chassis and ship to JPL for vibration tests.
- Cycle non-sterile cells, let-down, then HS 72 hours at 135°C, and cycle again to prove pre-test capability on 70 AH cells.

IV. DEVELOPMENT OF HEAT STERILIZABLE HIGH IMPACT 25 AH CELLS TASK 12

A. Objectives and Past Work

This task requires the development of wet heat sterilizable 25 AH cells capable of surviving 4,000 "g" shocks in any axis and meeting the requirements of JPL Engineering Memorandum 342-68. A lot of 100 cells is to be delivered in December 1969.

B. Experimental Nine Plate Cells

Four non-sterile high impact 9-plate cells were constructed for design verification tests at 4,000 "g" in thick walled Lucite jars. The cells contained 4 positive plates with 17-mil zirconium cores, 5 negative plates reinforced by etched Ag grids, and 7 layers GX membrane. All parts except the case met the requirement of the high impact 25 AH Model 362 cell drawings.

All cells developed excessive hydrogen pressure on formation charging requiring continuous venting. The diagnosis was hydrogen gassing at the Ag grid to zinc metal couple in the negative plates, accelerated by the massive etched Ag grid structure. Input was 94% of theoretical Ag capacity; output at 2.4 amps (C/2 rate) was 5.9 AH minimum equivalent to 1.06C. On second cycle recharge gassing continued at a lesser rate. Three cells were then shipped to JPL for shock tests.

C. Shock Tests on Model 362X Cells

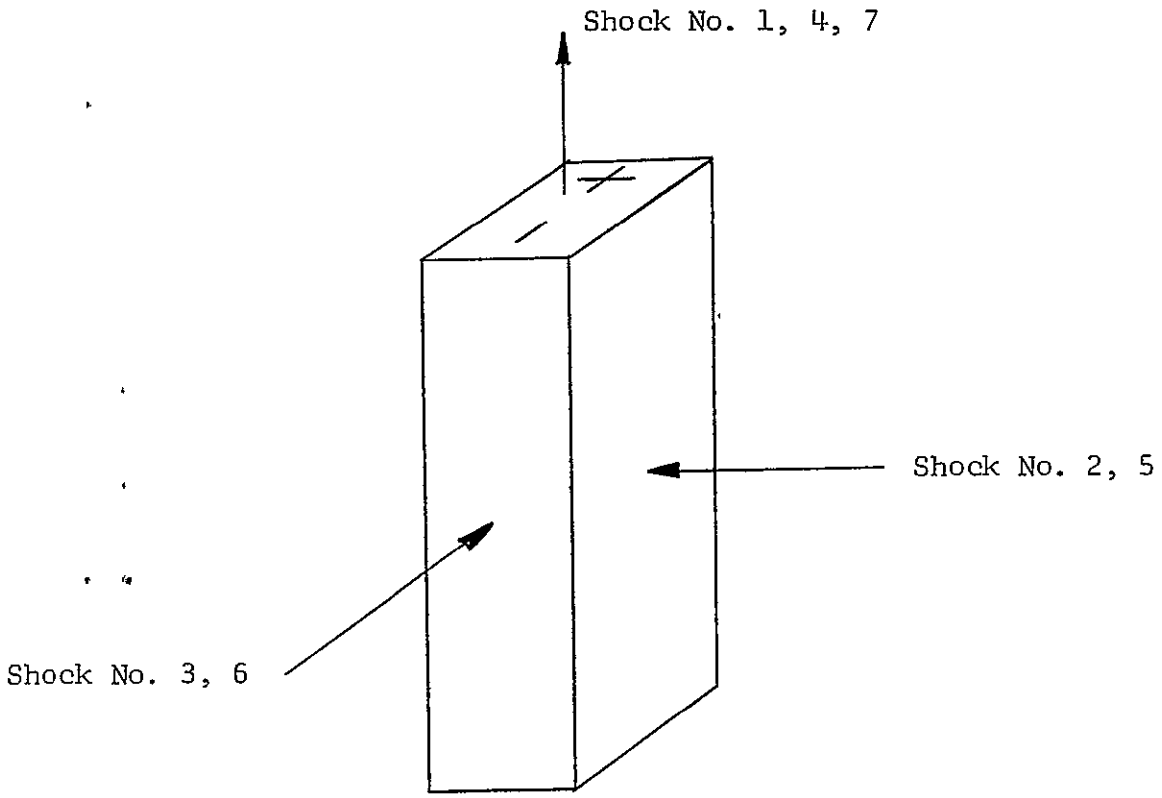
Shock levels ranged from peak levels of 2100 g's up to 4200 g's with pulse durations of approximately 1 msec. Table XVI presents the impact data for the seven shocks performed. High speed motion pictures were made during each shock to show the movement of the cell pack in the critical area of the plate struts. The effects of the shocks on each cell is given in the following discussion.

TABLE XVI

SHOCK DATA ON MODEL 362X CELLS

Shock No.	Cell S/N	Impact Velocity (fps)	Measured Peak "g"	Stopping Distance (in.)	Calculated Average "g"	Pulse Duration (Msec.)
1	2	94.5	2,250	.785	2,190	1.1
2	3	93.0	2,100	.803	2,000	1.1
3	1	93.0	2,100	.790	2,040	1.1
4	2	102.0	2,900	.740	2,400	1.1
5	3	101.0	4,200	.530	3,600	1.0
6	1	101.0	4,000	.515	3,700	1.0
7	3	101.0	4,000	.538	3,520	1.0

Velocity vectors at impact



S/N 2

This cell was shocked in a terminals forward attitude at 2200 g's and 2900 g's. Although plate strut instability was seen at the lower shock level, there was no apparent damage. The positive plate struts clearly buckled at the higher shock level (see Figure 2). There was no damage to the negative plate struts; however, there was damage to the upper unsupported portion of the negative plates adjacent to the positive plates which suffered the greatest movement due to positive strut buckling (see Figure 3). Clearly, additional support is needed to prevent positive plate buckling. This added support to prevent positive plate movement will also offer additional support to the negative. The only evidence of shock damage to the separator was at the tops of the plates where buckling occurred.

S/N 1

This cell was shocked with the plates hitting edgewise on the positive terminal side. Shock levels were at 2100 g's and 4000 g's. There was no visible damage to any plate struts. The cell maintained a fully charged open-circuit voltage throughout the shock tests and was capable of discharge following the tests. The only evidence of any damage was loosening and movement of some active material from the etched silver structure of one of the end negatives. Discharge capacities for the two cycles following the shock tests yielded AH/gAg efficiencies of 0.140 and 0.184. However, since the negative plates of these cells have gassed continuously, the low capacities are probably due to self-discharge of the negatives on open-circuit stand. This supposition is further substantiated by the charge characteristics of the cell which show more than 90% of the recharge capacity being accepted on the upper voltage plateau. Therefore, the loss in capacity cannot necessarily be attributed to the high impact exposure.

S/N 3

This cell was shocked with the plates hitting flatwise at 2100 g's and 4200 g's after which an additional impact test was performed at 4000 g's in a terminals forward attitude. There was no observable damage due to the flatwise shocks. The high speed films showed the expected bending characteristics for the slot supported negative plates. The terminals forward condition resulted in damage identical to that observed for S/N 2 (see Figures 4 and 5).

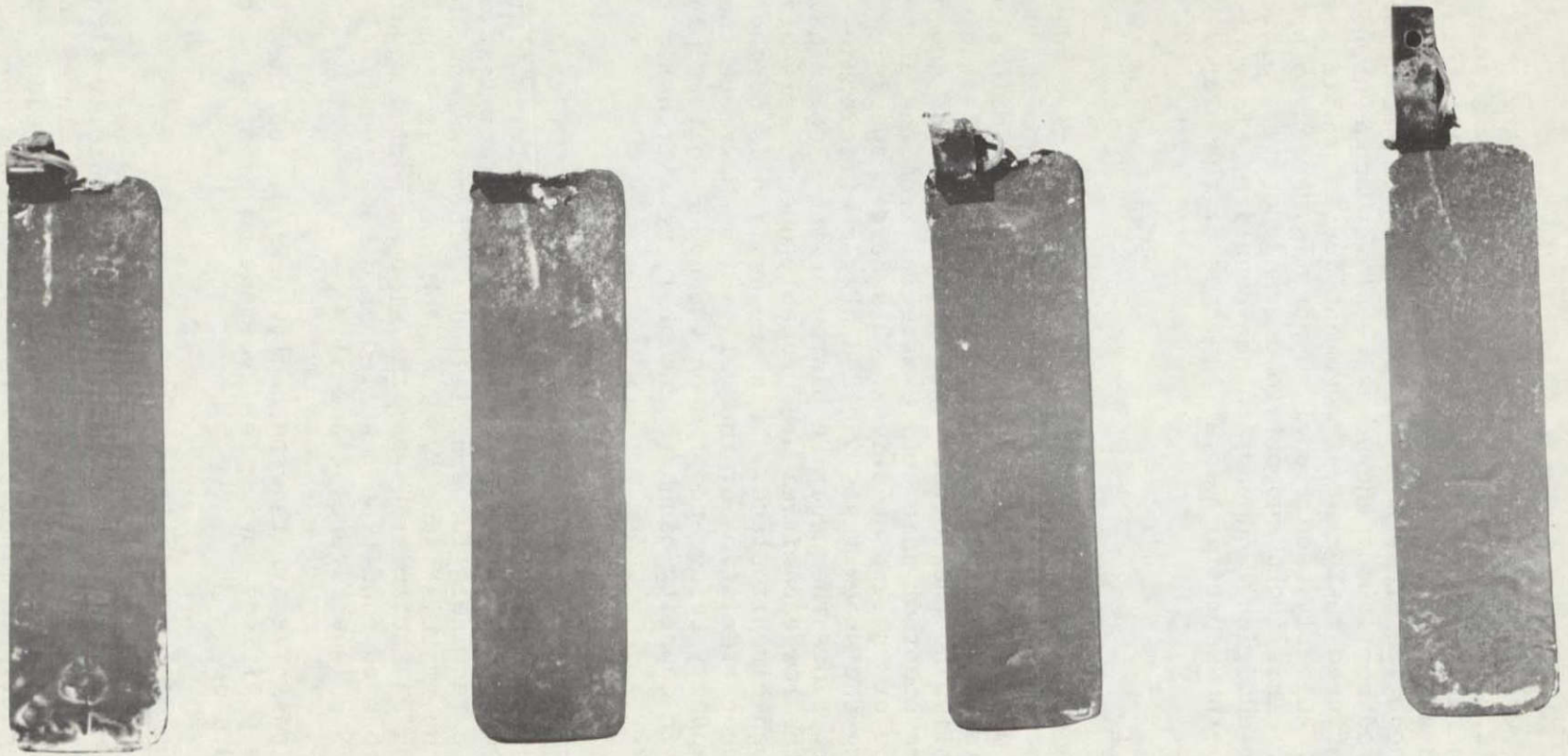
The positive struts were badly buckled, and the negative plates adjacent to the positives having the greatest movement suffered damage on the unsupported side.

Discussion of Results

The Model 362 configuration will successfully withstand shocks in directions (1) perpendicular to the plane of the plates and (2) with the plates hitting edgewise on the positive terminal side. Since the shock on the negative terminal side should not be any more severe than shock on the positive side, high impact in this direction should be

FIGURE 2

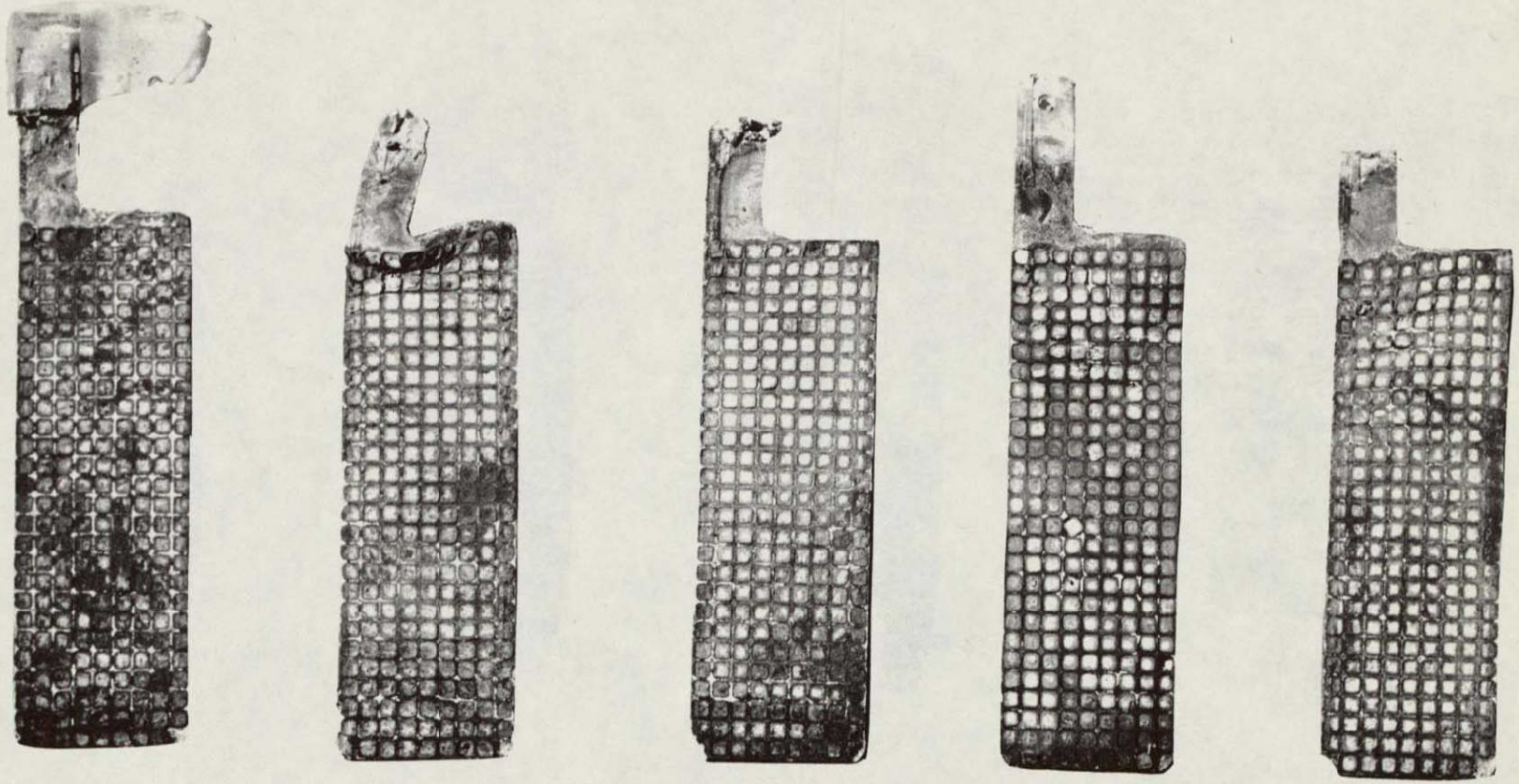
POST SHOCK POSITIVE PLATES OF MODEL 362X CELL - S/N 2



Velocity Vector 2900 g's

FIGURE 3

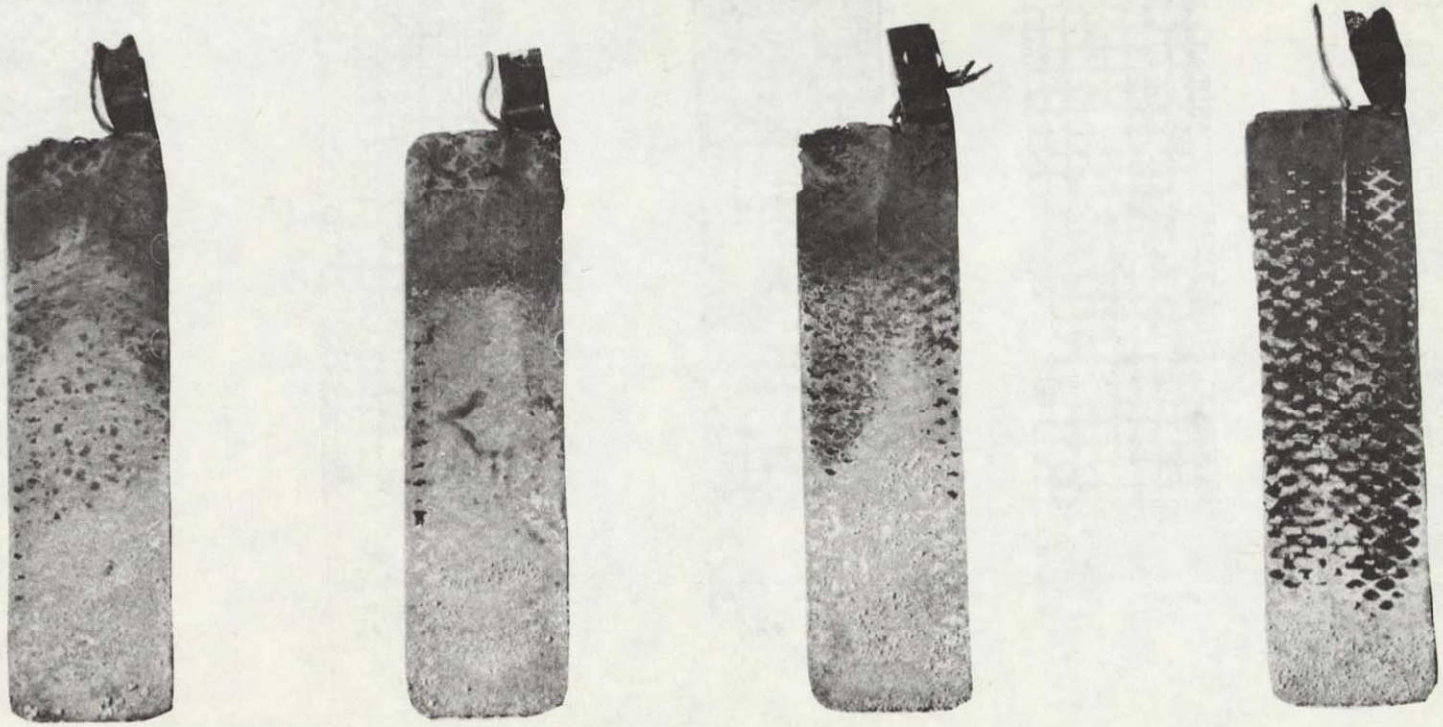
POST SHOCK NEGATIVE PLATES OF MODEL 362X CELL - S/N 2



Velocity Vector 2900 g's

FIGURE 4

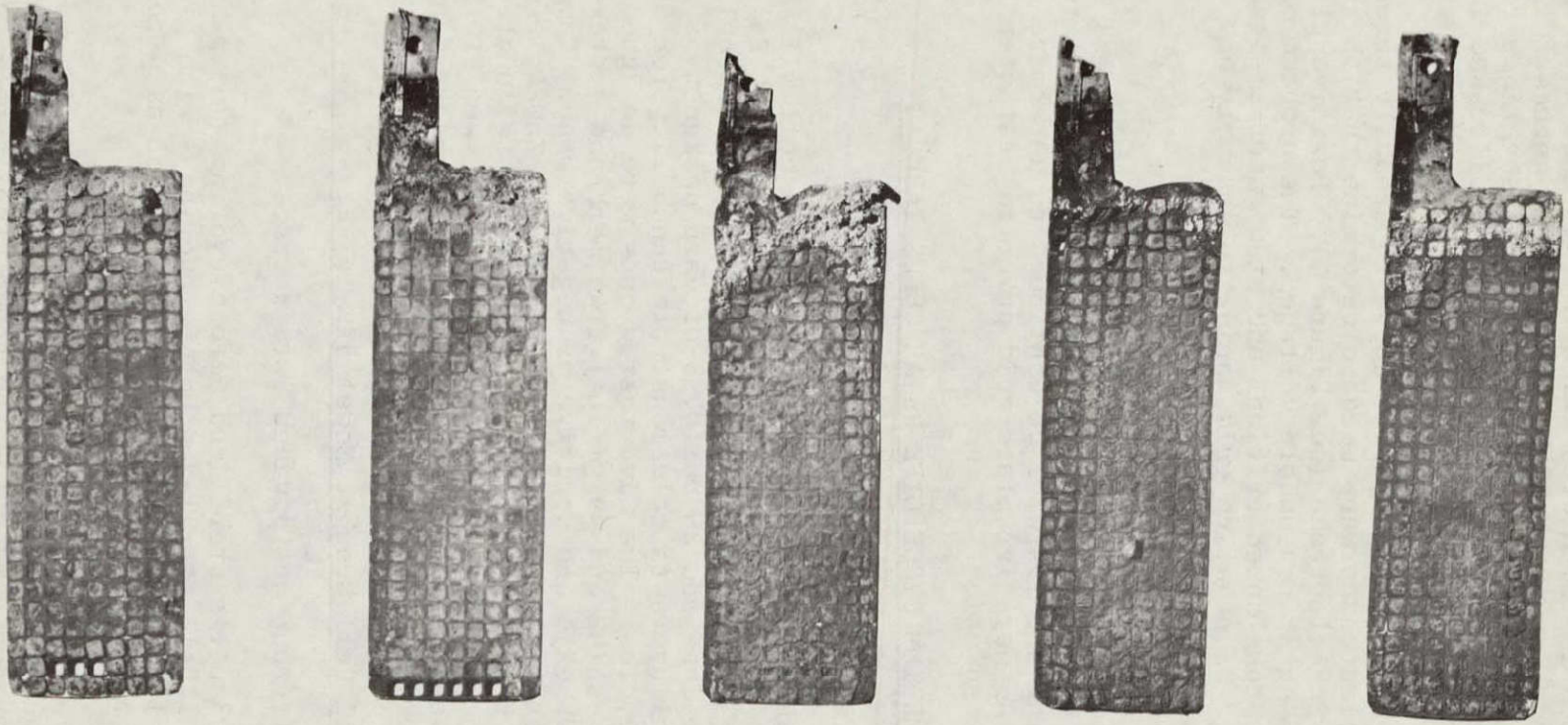
POST SHOCK POSITIVE PLATES OF MODEL 362X CELL - S/N 3



Velocity Vector at 4,000 g's

FIGURE 5

POST SHOCK NEGATIVE PLATES OF MODEL 362X CELL - S/N 3



Velocity Vector at 4,000 g's

successfully withstood. Furthermore since shock tests with terminals trailing create forces in the plates which the plate structures are best designed to withstand, impact at 4000 g's should be successfully withstood in this direction. The only direction presently susceptible to damage is with terminals leading on impact. The redesign discussed in Task 9 will permit impact in all directions.

The cell remaining at ESB lost capacity steadily through 5 cycles. Reference electrodes were used to determine that the negative was indeed the limiting electrode (see Figure 6). Positive plates delivered 0.41 AH/gm Ag at reasonable voltages. The problem of gassing and capacity loss is considered critical and studies of amalgamation techniques to be used on negative grids prior to assembly are in progress.

D. Future Work

Positive plate struts will be increased in thickness to 0.040 inch and shims will be added to prevent lateral motion of plate struts at 4,000 g's. Gassing studies will be continued to determine whether amalgamation of the Ag negative plate grid prior to heat sterilization will be an effective solution.

V. DEVELOPMENT OF MEDIUM CYCLE LIFE 25 AH CELLS TASK 13

A. Objectives and Past Work

In this task a 25 AH wet heat sterilizable cell will be designed, developed, and tested to the requirements of JPL Engineering Memorandum 342-68 less the 4,000 g's shock. ESB Model 379 cells were designed in five versions and 25 cells, 5 of each design type were manufactured for cycling tests to demonstrate capability for 90 50% depth of discharge cycles. The five test groups were designed to evaluate two negative densities (42 and 49 gm/in^3), two membrane systems (1L Pellon 2530W and 7L GX vs 9L GX), and positive or negative wrap. Common to all cells were the design factors: 69 gm/in^3 positives; ZnO/Ag weight ratio of 0.8; twin 3/0 Ag grids in each negative; sintered teflonated negative containing 5% teflon and 4% compound 323-43; and the same PPO 534-801 jar. Table XVII gives a summary of group cell performance during activation, heat sterilization, and initial cycles.

B. Experimental Cell Groups, Model 379-1, -2, -3, -4, -5

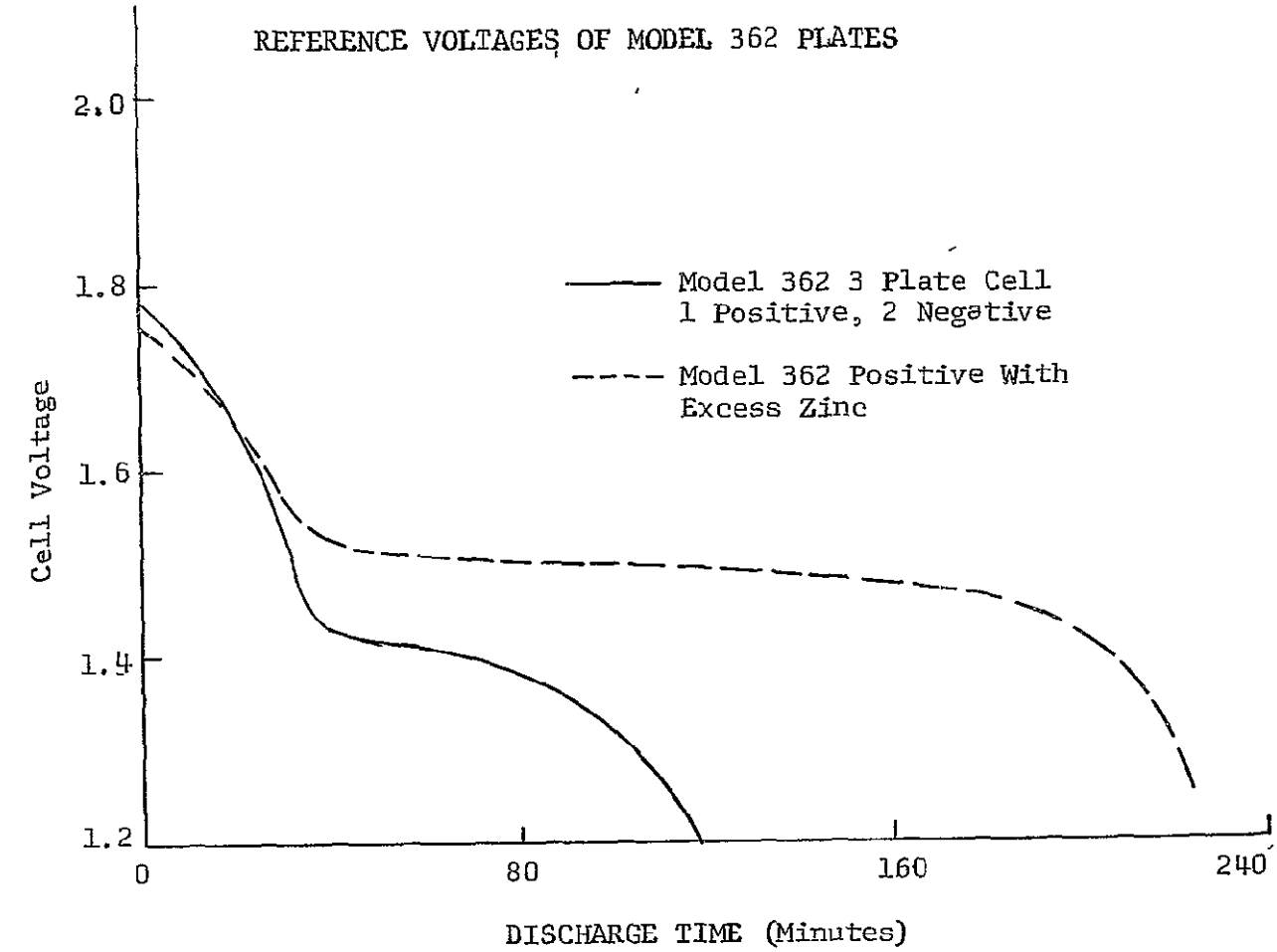
Each 5 cell group was divided into 3 tests -

Test 1 - 3 cells sterilized before cycling - no platelock
Test 2 - 1 cell sterilized before cycling - with platelock
Test 3 - 1 cell cycled before sterilization as a control and as a pretest group.

Table XVII gives data for the Test 1 and 3 cells through 3 cycles at 8A, 16A, and 2A discharge rates at 75 ±5°F. Figures 7 - 11 present voltage versus capacity discharge curves for the three sterile cells of each of

FIGURE 6

REFERENCE VOLTAGES OF MODEL 362 PLATES



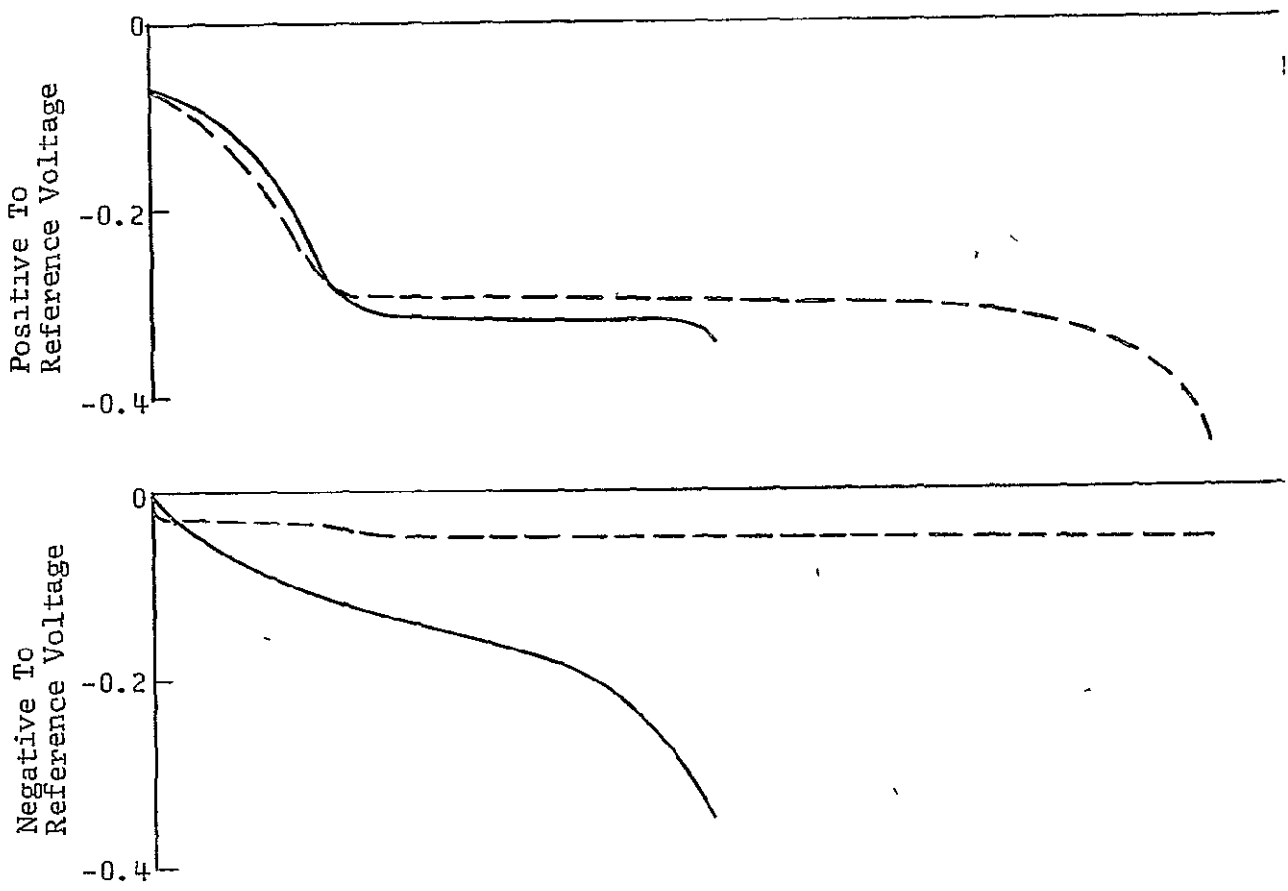


TABLE XVII

STERILE MODEL 379 CELL PERFORMANCE

Cell P/N	Design Factors: Plates Wrapped (+)or(-)	Separator System L/Type	Negative Density gm/in3	Electrolyte Weight gm	Cycle 1 Input AH	Cycle 1 Output (8A) AH	Cycle 2 Input AH	Cycle 2 Output (16A) AH	Cycle 3 Input AH	Cycle 3 Output (2A) AH	Net Input All Cycles AH
1	+	1L Pellon	49	122.7							
2*		2530W		123.5	34.5	33.6	32.4	30.6	26.5	27.5	1.7
3		7L GX		122.7	34.3	31.5	27.9	26.6	26.5	27.5	3.1
4				122.7	34.2	31.6	28.9	26.9	26.5	27.5	3.6
5	+		42	123.9	33.6	30.6	27.6	26.6	26.5	27.0	3.5
6		Same		125.4	39.2	35.4	31.3	29.6	31.1	30.9	5.7
7				124.2	37.4	33.4	29.9	29.6	27.5	28.1	3.7
8*				124.7	37.5	36.0	32.8	30.9	29.1	29.9	2.6
9	+	9L GX	42	124.9	36.2	34 0	31.3	29.3	27.3	27.7	3.8
10				124.9	33.1	30.6	28.9	26.9	25.3	27.1	2.7
11*				128.8	35.4	34.4	29.7	28.0	31.1	29.7	4.1
12				124.9	34 7	31.8	28.9	26.4	26.8	27.1	5.1
13	-	Same	42	123.7							
14				123.3	39.6	36.0	33.4	31.4	33.5	34.0	5.1
15*				123.9	37.4	36.6	34.2	32.2	33.5	32.6	3.7
16				123.9	38.0	35.6	31.9	29.3	31.6	33.0	3.6
17	-	Same	49	117.7	40.8	37.1	37.3	33.6	34.9	38.4	3.9
18*				118.2	44.3	43.5	36.9	34.1	41.8	43.4	2.0
19				117.7	41.2	37.2	38.1	35.0	35.4	41.8	0.7
20				119.4	41.1	38.0	38.1	37.3	37.1	40.7	0.3

(*) Non-sterile control cells.

FIGURE 7

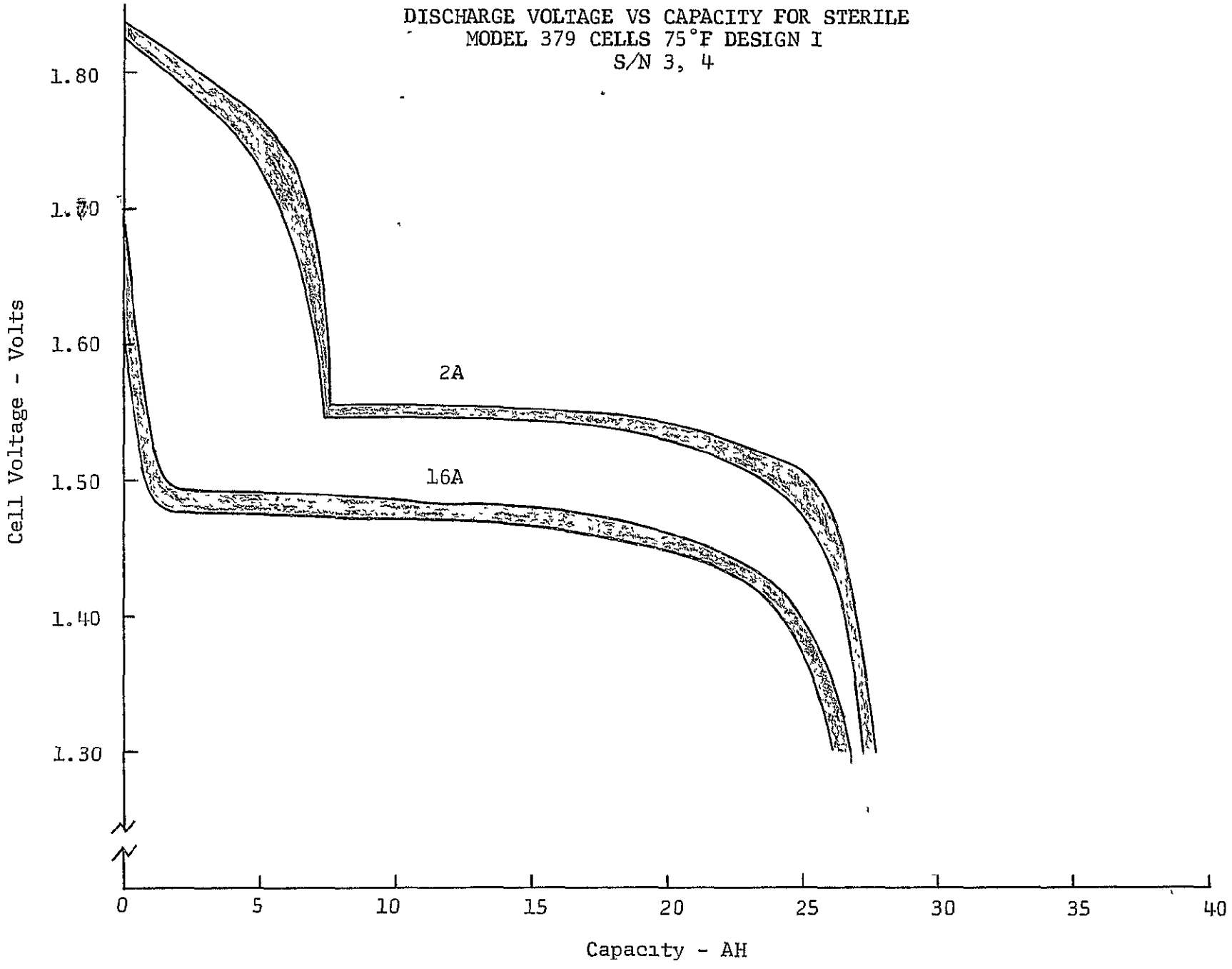

DISCHARGE VOLTAGE VS CAPACITY FOR STERILE
MODEL 379 CELLS 75°F DESIGN I
S/N 3, 4
Cell Voltage - Volts
1.80
1.70
1.60
1.50
1.40
1.30
2A
16A
0
5
10
15
20
25
30
35
40
Capacity - AH

FIGURE 8

DISCHARGE VOLTAGE VS CAPACITY FOR STERILE
MODEL 379 CELLS 75°F DESIGN 2
S/N 5, 6, 7

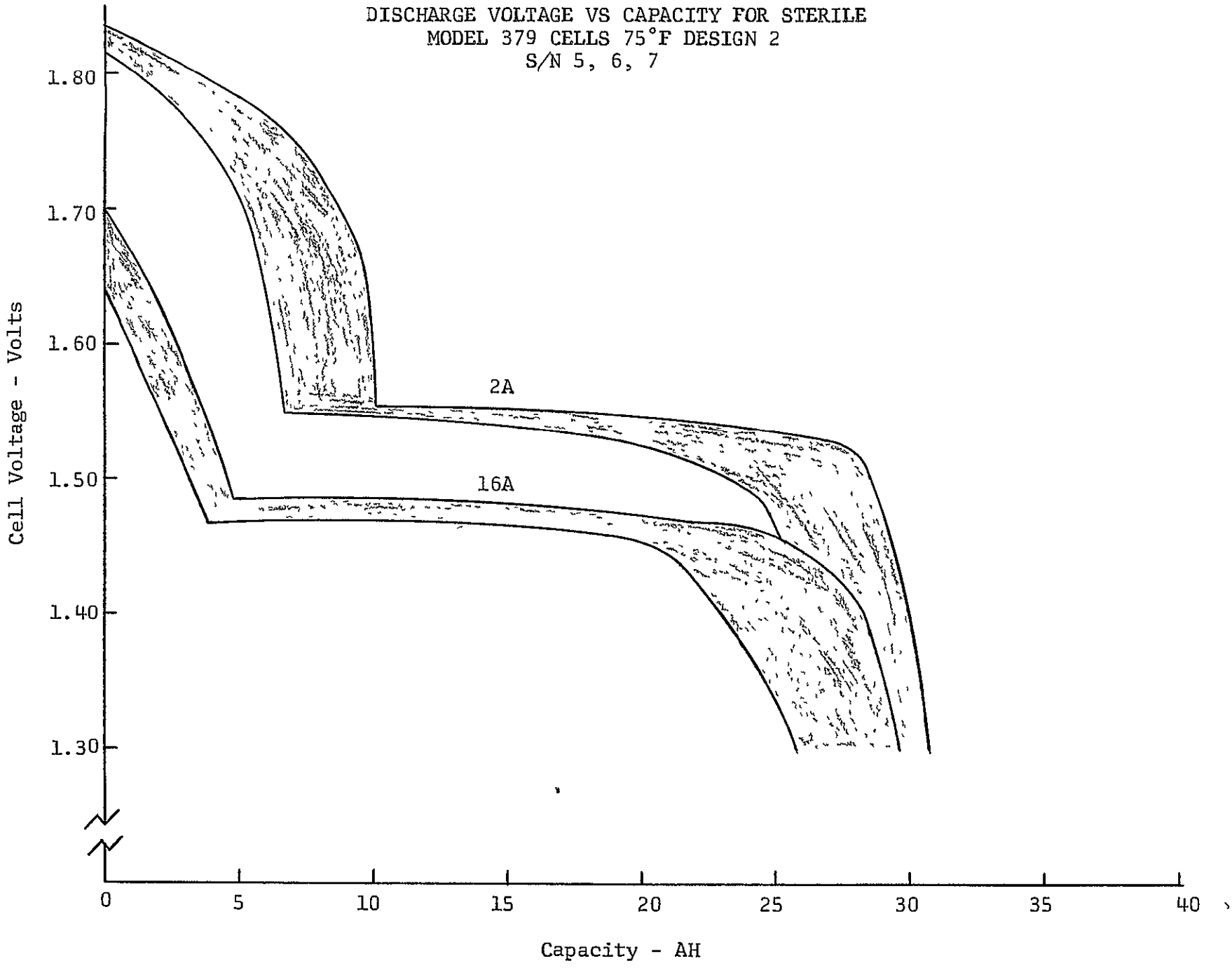


FIGURE 9

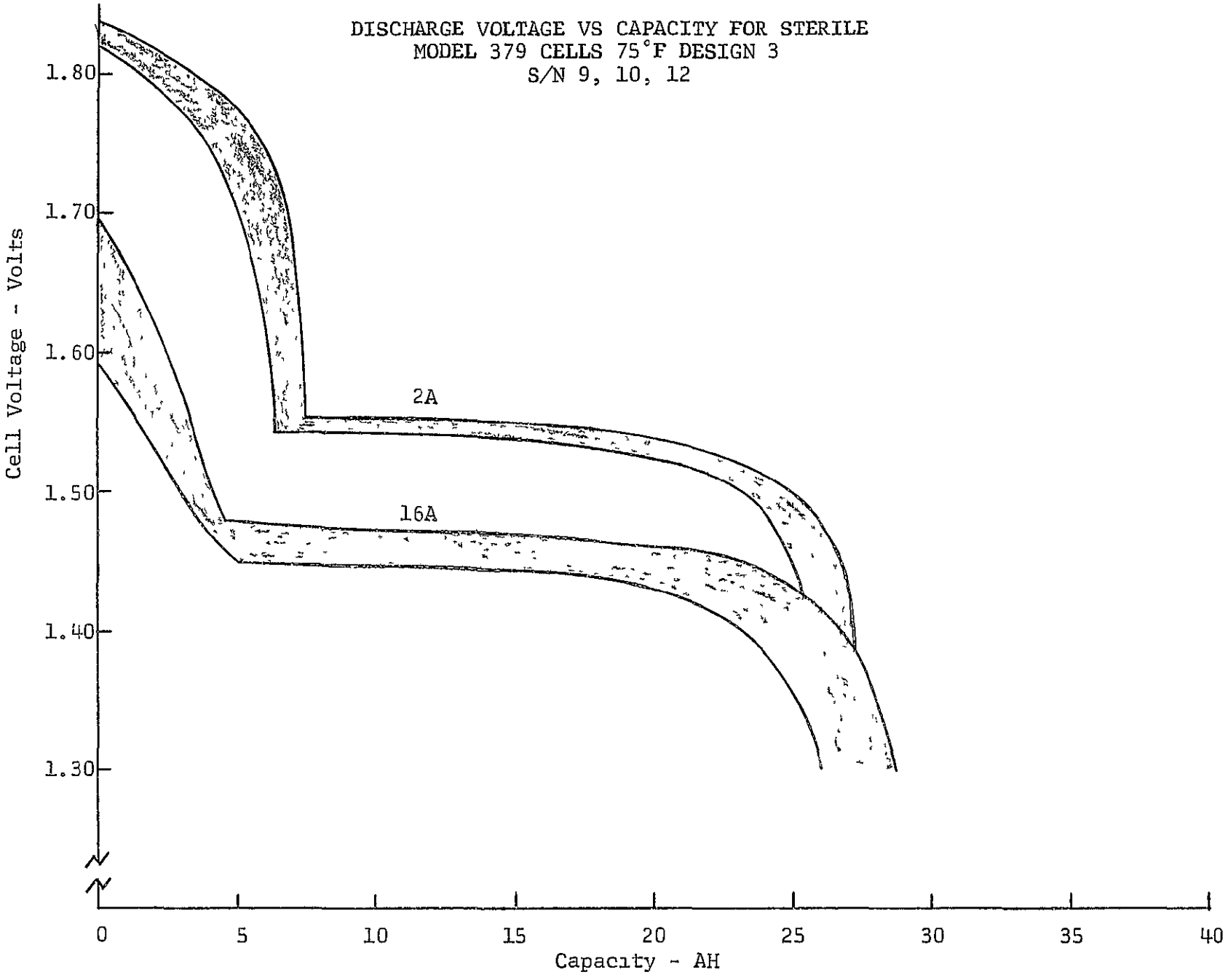

DISCHARGE VOLTAGE VS CAPACITY FOR STERILE
MODEL 379 CELLS 75°F DESIGN 3
S/N 9, 10, 12
Cell Voltage - Volts
1.80
1.70
1.60
1.50
1.40
1.30
2A
16A
0
5
10
15
20
25
30
35
40
Capacity - AH

FIGURE 10

DISCHARGE VOLTAGE VS CAPACITY FOR STERILE
MODEL 379 CELLS 75°F DESIGN 4
S/N 14, 16

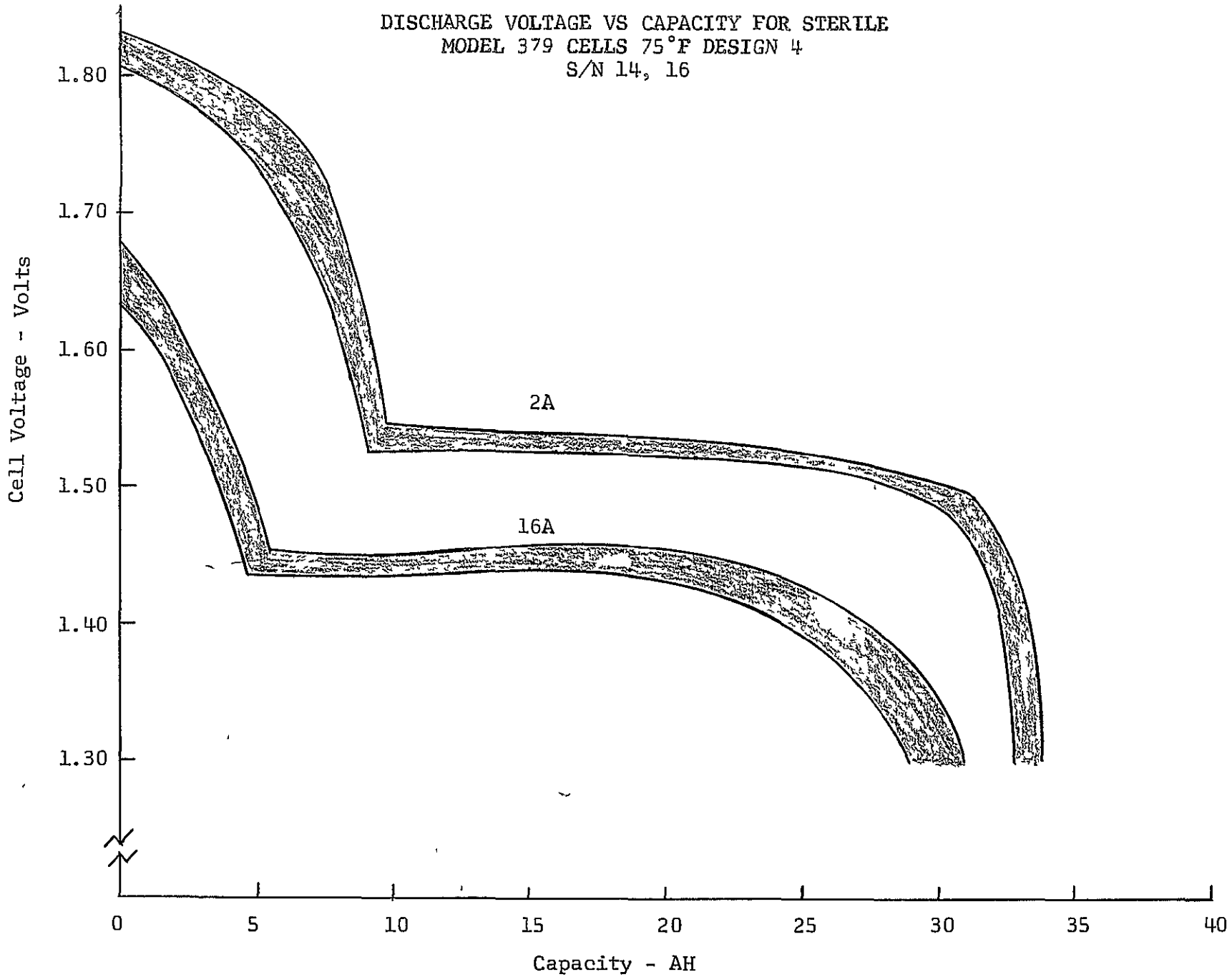
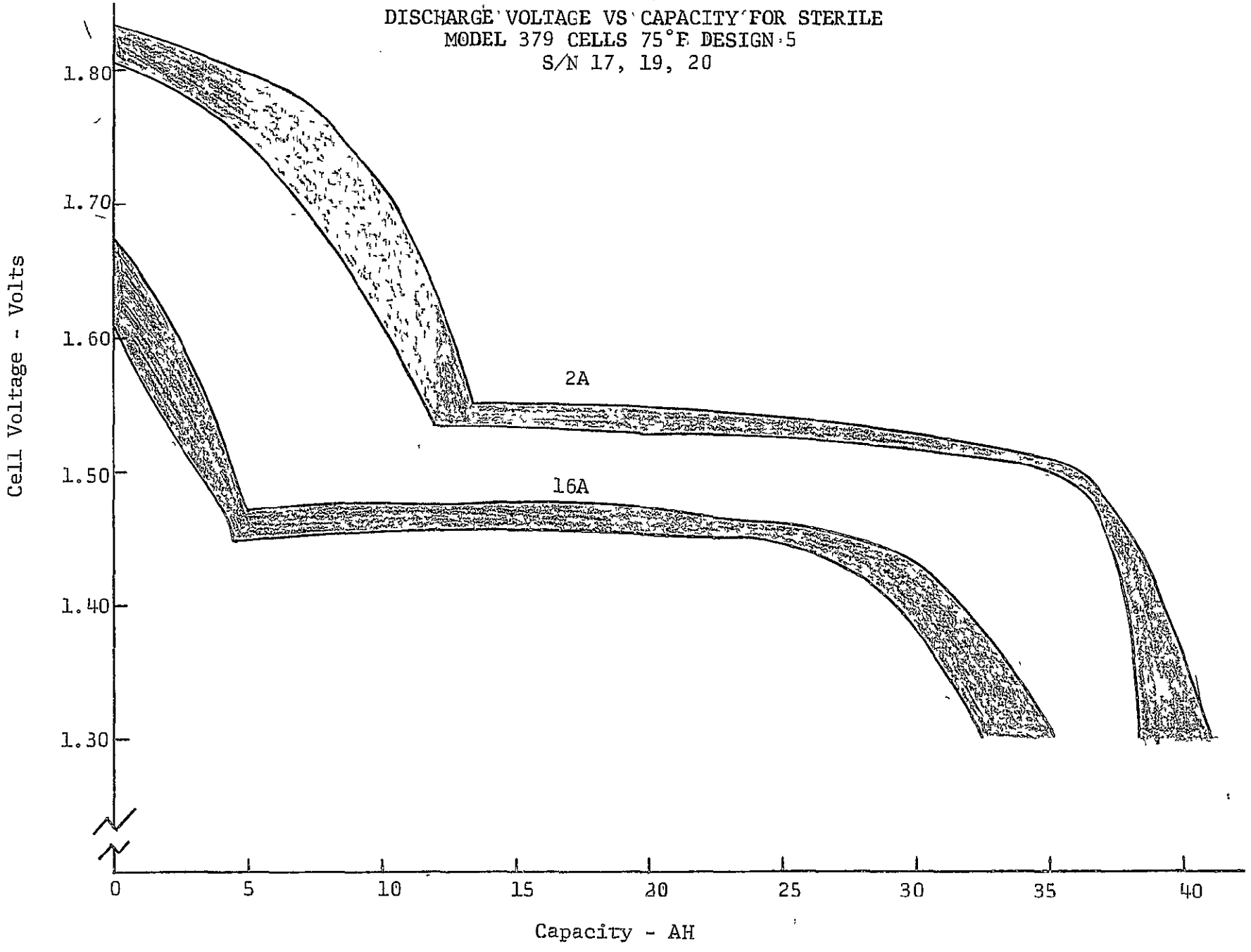


FIGURE 11


DISCHARGE VOLTAGE VS CAPACITY FOR STERILE
MODEL 379 CELLS 75°F DESIGN 5
S/N 17, 19, 20
Cell Voltage - Volts
1.80
1.70
1.60
1.50
1.40
1.30
2A
16A
0
5
10
15
20
25
30
35
40
Capacity - AH

the five designs. Mean discharge efficiencies over the 3 cycles varies from a minimum of 0.33 AH/gm Ag for Design 1 to a maximum of 0.39 AH/gm Ag for Design 2. Non-sterile cells exhibit values of 0.35 AH/gm Ag minimum to 0.41 AH/gm Ag maximum on the same test.

The three cell groups were then placed on automatic cyclers operating two 50% depth of discharge cycles per day on a modified CP 10 hour charge - 2 hour constant load discharge. Rated capacities, discharge loads, limiting currents and actual capacities observed on the 5th and 25th cycle were: -

Design No.	Rated Capacity (4 gm Ag/AH)	Load Resistance (ohms)	Limiting Charge Current at 1.94 V/C (C/20) Amps	Observed Capacities, AH 5th	25th
1	22	0.817	1.14	11 3	11.4
2	20	0.895	1.04	9.9	9 7
3	20	0.883	1.06	9.6	9.7
4	24	0.766	1.22	11.8	11.8
5	26	0.700	1.34	12.2	12.2

After completing 28-36 cycles (varied by group) on the single load test, the cells were transferred to a Data Acquisition System (DAS), and cycling was continued on a 2-step discharge routine: high rate for 48 minutes, low rate for 72 minutes.

Cycling parameters then became:

Design No.	Discharge Rate-Amps High	Low	Capacity - AH High	Low	Total	Actual Energy W-Hr.
1	12.2	1.13	9.8	1.4	11 2	16.6
2	10.9	1.13	8.7	1.4	10.1	15.4
3	11.2	1.13	9.0	1.4	10.4	14.9
4	13.1	1.13	10.5	1.4	11.9	17.6
5	11.5	3.00	9.2	3.6	12.8	19.3

Cycling was continued at 75 ±5°F. As of June 30, 1969 the cycles accumulated ranged from 78-95 including 4 initial cycles at 100% depth. Table XVIII summarizes failure modes by design type and cell serial number. Designs 1 and 2 have completed 90 cycles successfully, but total wet life is 4 months and not the required

2 wet uncharged
9 wet charged; float at 1.93 V/C
3 cycling
14 months total life.

Designs 1 and 2 have common 1L Pellon 2530W positive absorbers, and 7L GX membrane, while the failing designs have 9L GX only. The design factors in order of importance then became:

Absorber > positive wrap > layers GX (7L minimum) > negative density.

TABLE XVIII

LOW IMPACT 25 AH CELL CYCLING TEST - CYCLES TO JUNE 30

Plate Wrap	Separator System L/Type	Negative Density g/in^3	Electrolyte Weight g	C Rating AH	No. of Cycles, 50% DOD Single Step	Two Step Discharge	Total	Failure Mode
+	1L Pellon 7L GX	49	123	22	36	55	91	Cycling
+	Same	42	124	20	36	55	91	Cycling
+	9L GX	42	125	20	30	54	84	(1)
-	Same	42	124	24	30	50	80	(1)
-	Same	49	118	26	28	46	74	(1) (3)

NOTES: (1) End of discharge voltage below 1.25 V.

(2) All cells sterilized 72 hours at 135°C wet sealed.

(3) Cell S/N 17 shorted by Ag penetration on cycle 78.

(4) Wet life of cells = 4 months.

Energy delivered on each DAS cycle varied by design group. Figure 12 shows cycle 45 mean wattages by design group during the 2-step discharge. Designs 1 and 2 are rated 3 and 4 respectively in energy output per cycle amont the 5 test groups. Figures 13 through 17 show end of charge and end of discharge voltages for the five 3-cell groups. End of charge and discharge current was also monitored. Designs 1 and 2 reveal least scatter of the data as would be expected if end of life is not near. Cycling tests will be continued during the next quarter to failure of the first cell in each group.

C. Pretest Capability

One cell of five in each of the five design groups was selected as a non-sterile control test cell and to measure the loss in capacity, if any, caused by heat sterilization after initial pretest cycles. These cells were discharged at 8A, 16A, and 2A rates to 1.25 volts, then let down using an 8.2 ±0.8 ohm resistor across the terminals of each cell to a voltage of 0.10 volt per cell in a 40 hour period. Open circuit voltages ranged from 0.02 volt to 0.18 volt 30 minutes after removing the shorting load. During heat sterilization for 72 hours at 135°C cells S/N 15 and 18 (groups 4 and 5) leaked through epoxy cover seal cracks losing 2 and 6 g's weight respectively. The lost electrolyte was restored and the cells were resealed. The three cycles before heat sterilization were then repeated after heat sterilization. Table XIX gives the resulting discharge capacities and mean 3-cycle AH/gm Ag efficiencies compared to the pre-heat sterilization data on the same cells and to the past heat sterilization data on 13 cells having no pretest. Losses in efficiency appear to be -

No HS	HS	Pretest & HS
0	- 5.4%	-7.3%

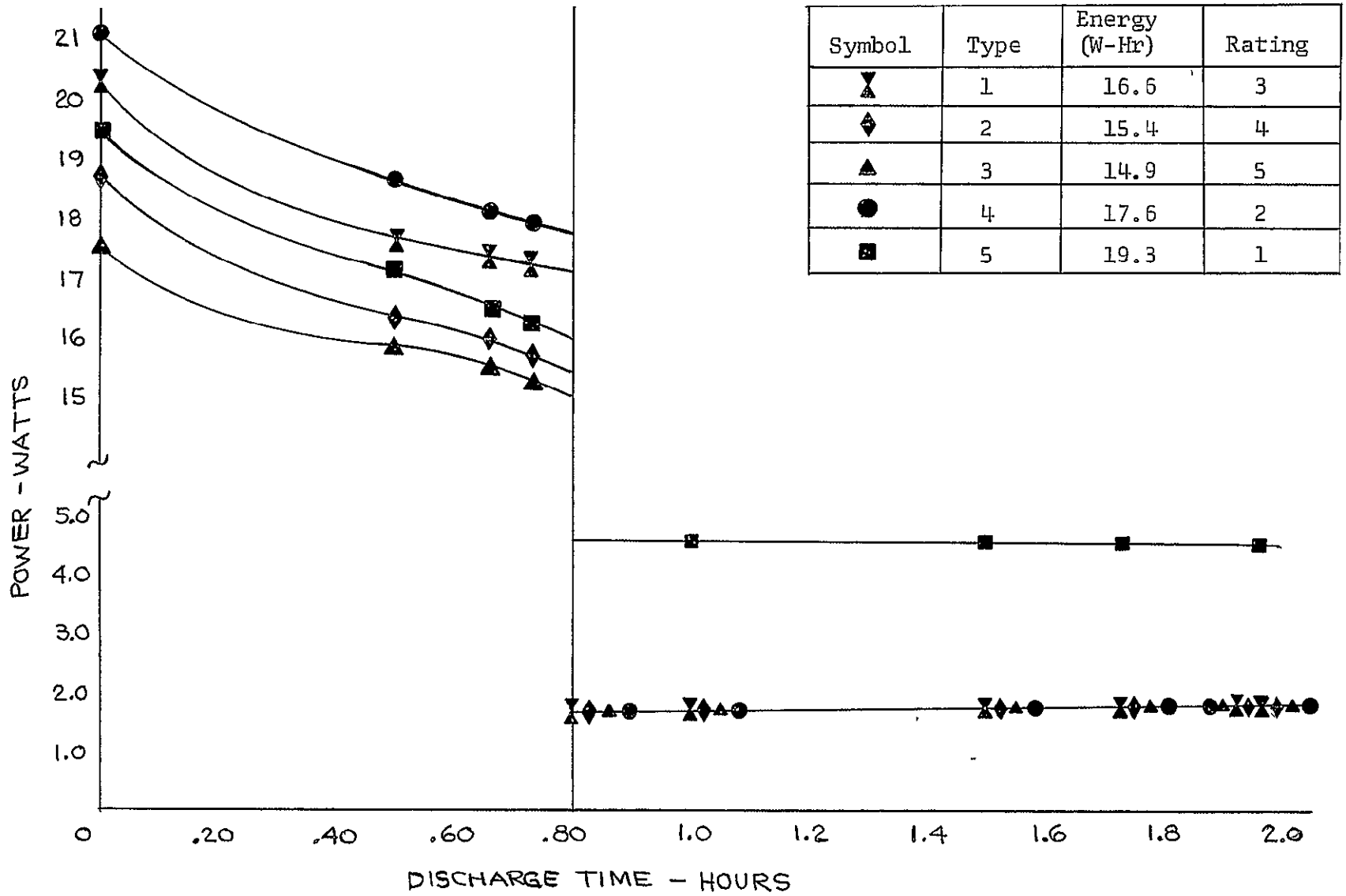
Leakage in two of the five cells has increased the loss rates in the latter group so that this estimate is a "safe" estimate. Improvements in the let down procedure so vital to pretest success are needed to decrease test time and to eliminate over discharge of some cells.

D. Plate-Lock Test Group

One cell of each design type was also selected to have an epoxy plate-lock added to bottom of plates to give support for vibration and shock. The cells were otherwise identical to the non-plate-lock cells. After sterilization sealed for 72 hours at 135°C three cycles were performed at discharge rates of 8, 16, and 2A to 1.25 volts giving the data of Table XX. The mean capacity response was -15% over 5 designs. Other responses were:

Design Comparison	Factor Under Test	Response (%)
1, 2, 3 vs 4, 5	Positive vs Negative Plate Wrap	-9.7 vs -23
1, 5 vs 2, 3, 4	High Density Negative vs Low Density Negative	-24 vs -9.0

FIGURE 12
MEAN POWER PER CELL VS DISCHARGE TIME
MODEL 379 STERILE 3-CELL GROUPS
50% DEPTH CYCLE NO. 45



Symbol	Type	Energy (W-Hr)	Rating
⧗	1	16.6	3
◆	2	15.4	4
▲	3	14.9	5
●	4	17.6	2
■	5	19.3	1

FIGURE 13

END OF CHARGE AND DISCHARGE VOLTAGE FOR 3-CELL
DESIGN TYPE 1 MODEL 379 50% DEPTH CYCLES
(10 HOUR CHARGE/2 HOUR DISCHARGE)

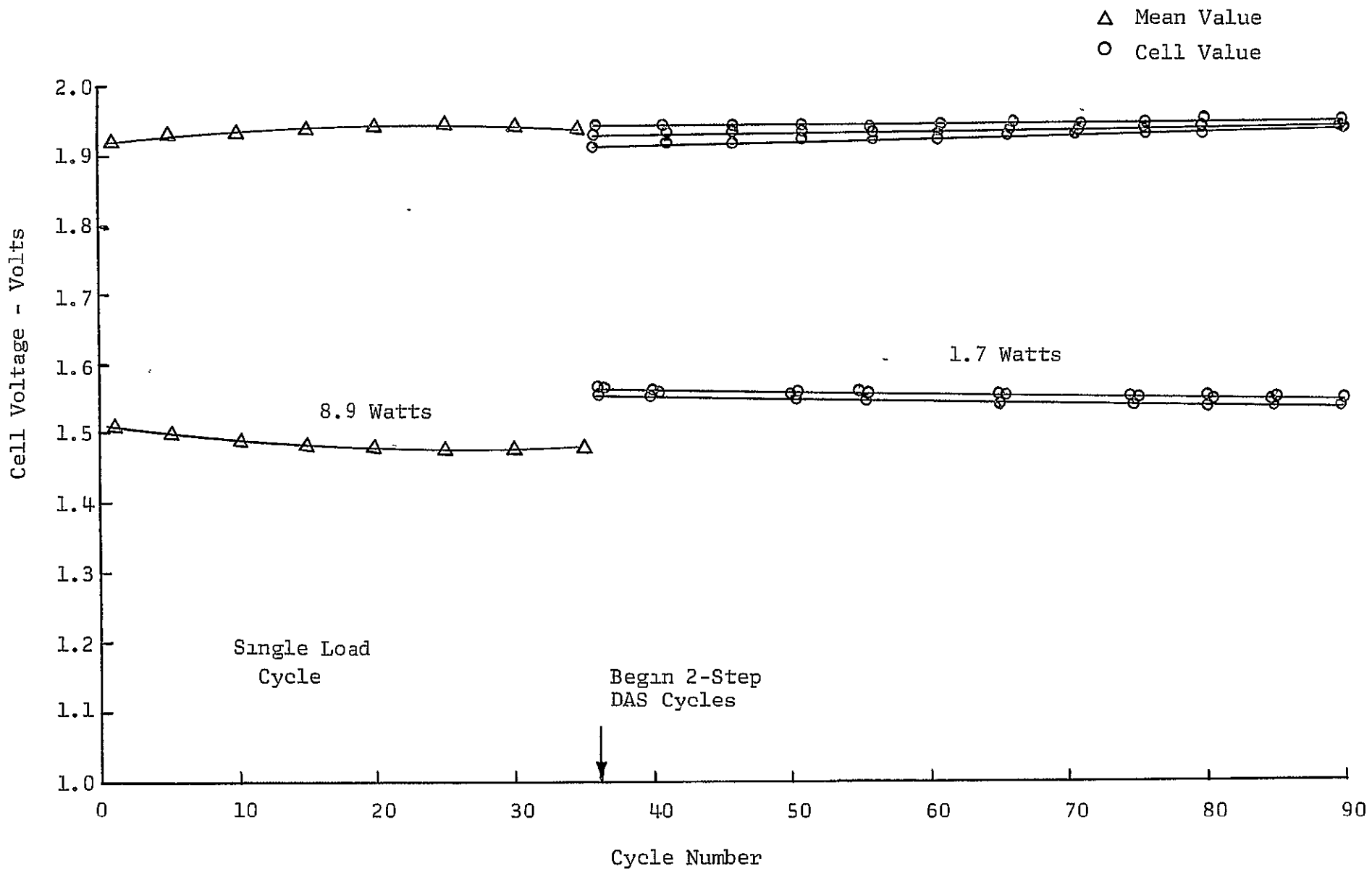


FIGURE 14

END OF CHARGE AND DISCHARGE VOLTAGE FOR 3-CELL
DESIGN TYPE 2 MODEL 379 50% DEPTH CYCLES
(10 HOUR CHARGE/2 HOUR DISCHARGE)

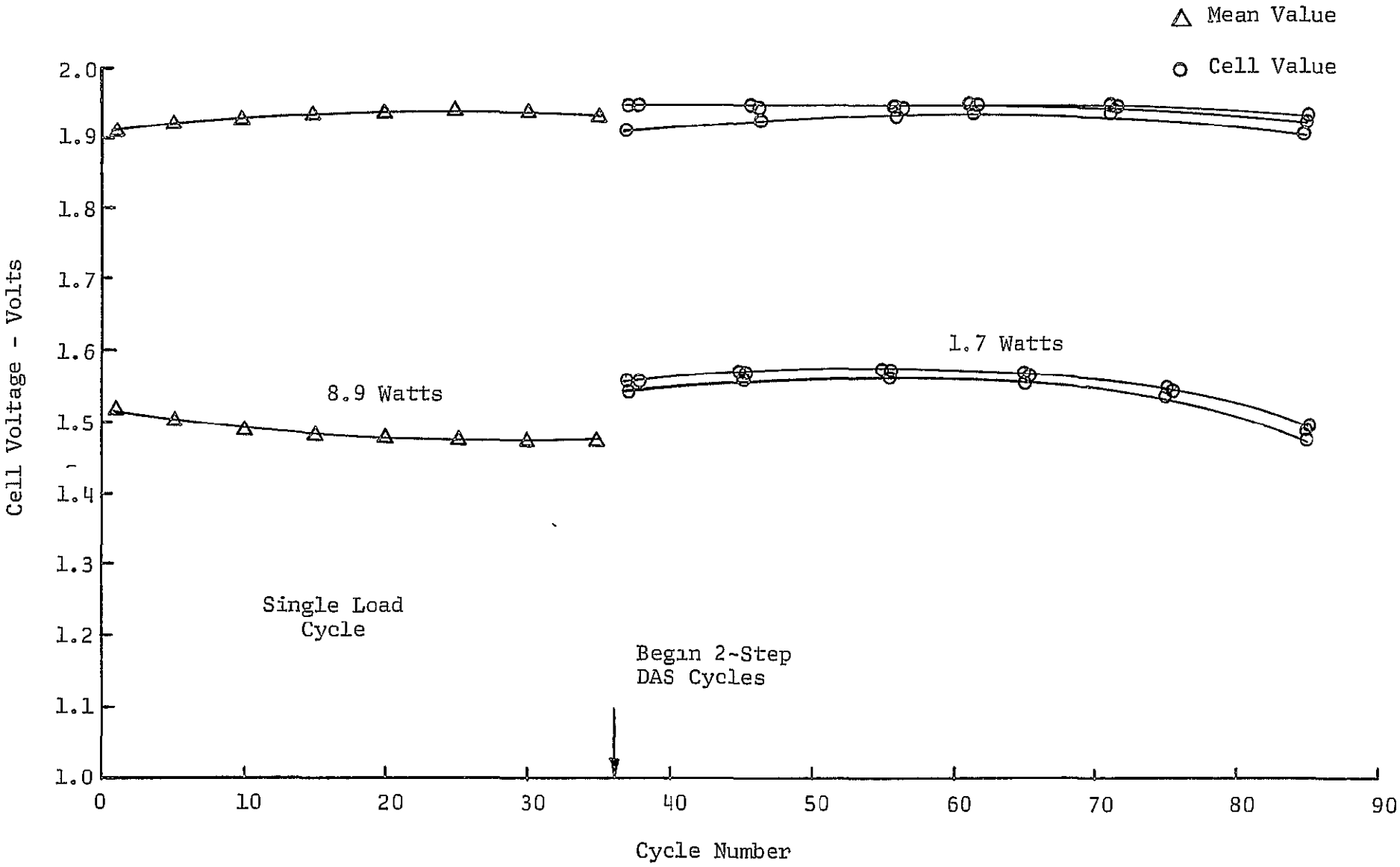


FIGURE 15

END OF CHARGE AND DISCHARGE VOLTAGE FOR 3-CELL
DESIGN TYPE 3 MODEL 379 50% DEPTH CYCLES
(10 HOUR CHARGE/2 HOUR DISCHARGE)

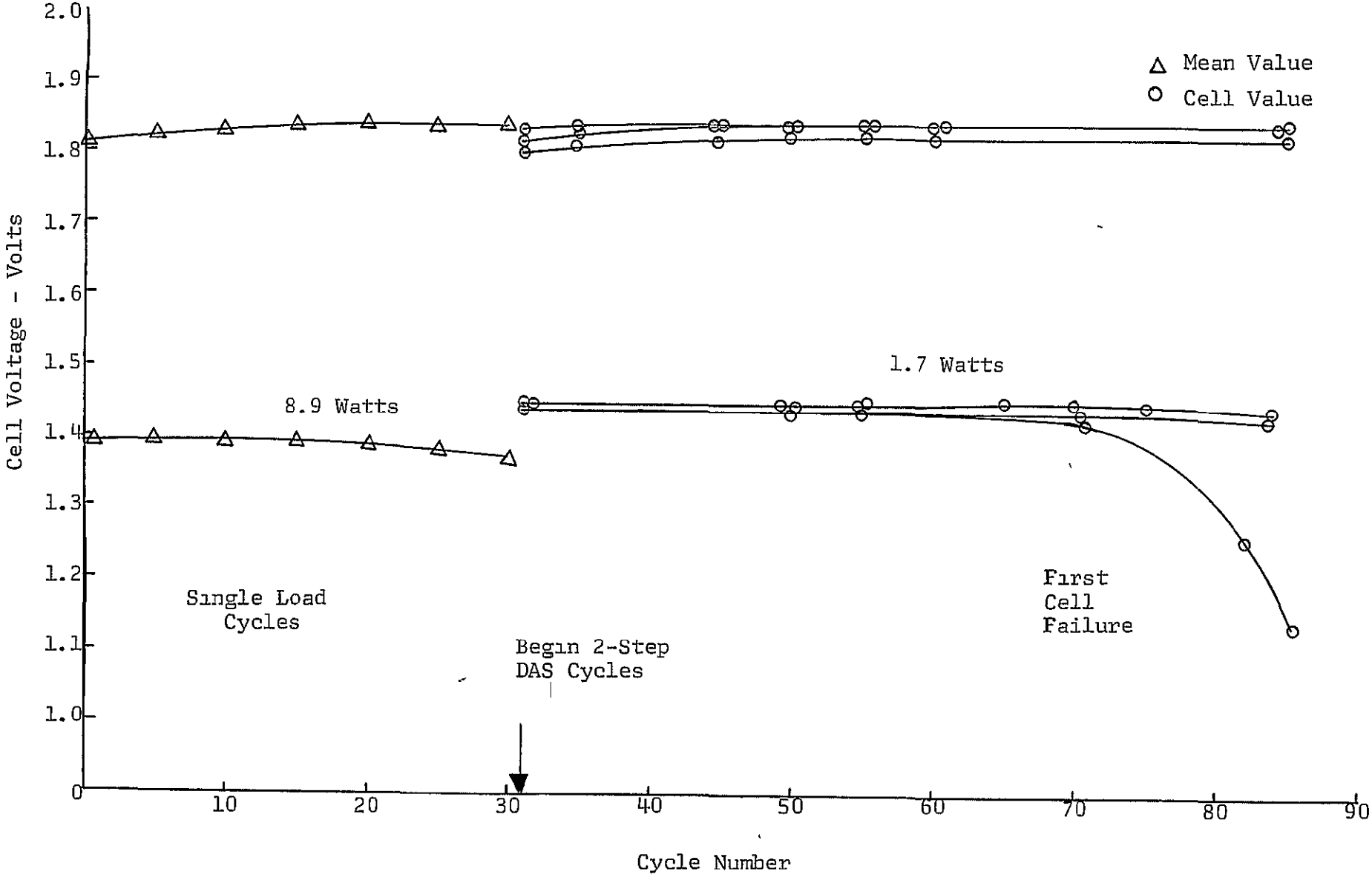


FIGURE 16

END OF CHARGE AND DISCHARGE VOLTAGE FOR 3-CELL
DESIGN TYPE 4 MODEL 379 50% DEPTH CYCLES
(10 HOUR CHARGE/2 HOUR DISCHARGE)

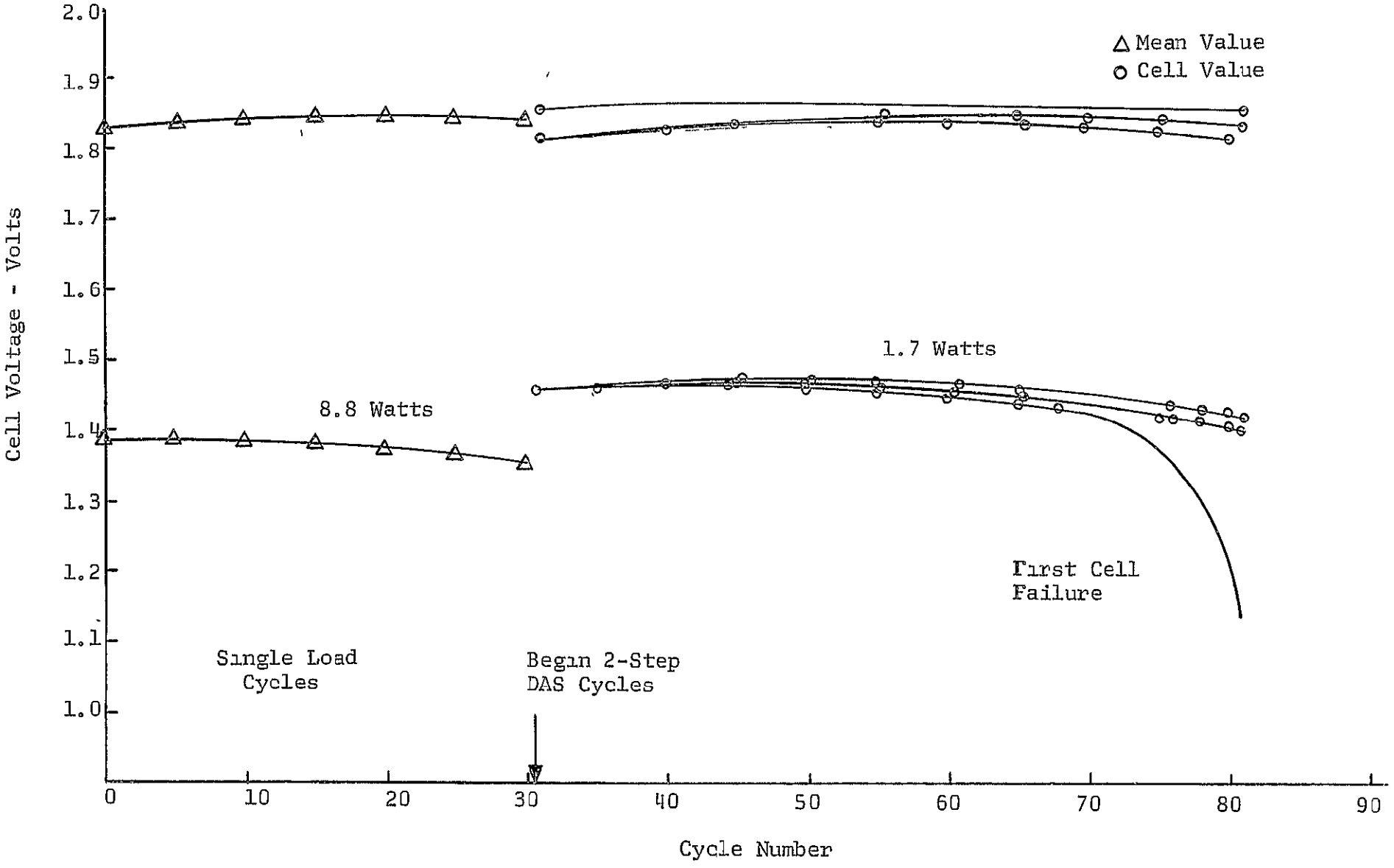


FIGURE 17

END OF CHARGE AND DISCHARGE VOLTAGE FOR 3-CELL
DESIGN TYPE 5 MODEL 379 50% DEPTH CYCLES
(10 HOUR CHARGE/2 HOUR DISCHARGE)

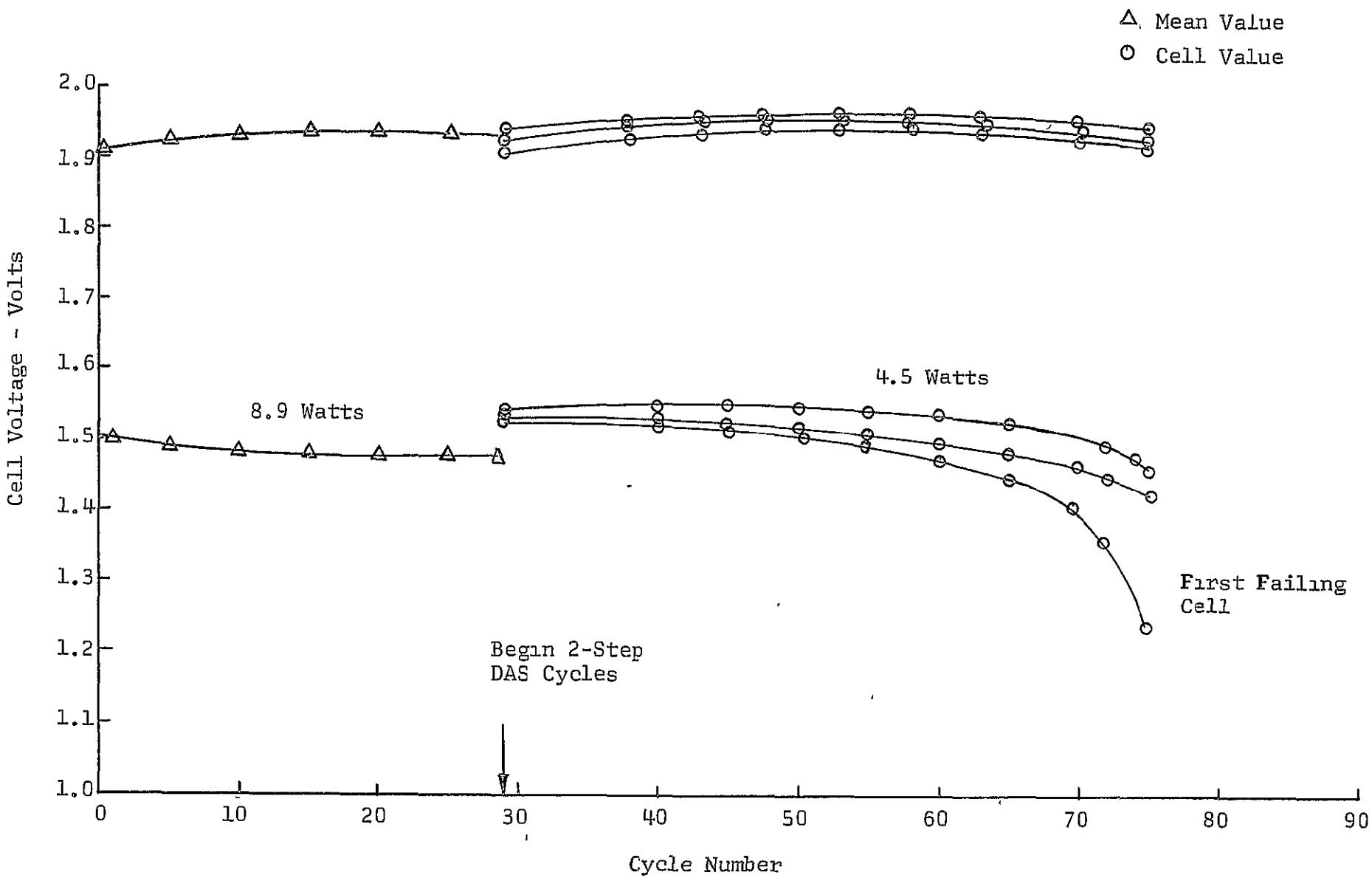


TABLE XIX

EFFECT OF CYCLING BEFORE HEAT STERILIZATION

Cell Design Type	Sterile Pre-Test Cell Discharge Capacities (Amp-Hr)			Discharge Efficiencies[1] (Amp-Hr/g Ag)		
				Pre-Test Cells		
	8 Amp	16 Amp	2 Amp	Pre-Sterilization	Post-Sterilization	Cells Not Pre-Tested
1	28.3	29.9	28.5	0.342	0.326	0.322 0.323
2	32.5	31.4	30.5	0.399	0.389	0.347 0.395 0.376
3	32.2	29.1	27.4	0.374	0.360	0.368 0.344 0.346
4	32.0	33.3	30.6	0.357	0.338	0.357 0.344
5	30.4	39.9	27.5	0.389	0.314	0.351 0.366 0.373
All Types	--	--	--	0.372	0.345	0.352

(1) Average over 3 discharges.

TABLE XX

EFFECT OF PLATELOCK ON DISCHARGE EFFICIENCY
MODEL 379 25 AH CELLS

Design Type	Mean Discharge Efficiency (Amp-Hr/g Ag)*		Response
	No Platelock	Platelock	
1	0.322 0.323	0.262	-18.6%
2	0.347 0.395 0.376	0.368	-1.3%
3	0.368 0.344 0.346	0.320	-9.4%
4	0.357 0.344	0.293	-16.3%
5	0.351 0.366 0.373	0.257	-29.2%
All Types	$\bar{X}_1$ = .352	$\bar{X}_2$ = .300	-14.8%

(*) Mean of 3 cycles at discharge rates 8A, 16A, and 2A to 1.25 volts.

On the basis of this data cell designs least effected by an epoxy platelock will have

- positive wrap
- low density negatives.

The capacity loss is reduced by a bake out process which was not performed on the above cells. Assuming the bake out to be an approved addition to the manufacturing process, plate-locks can be added to future cell designs without significant capacity loss. The effect on cycle life should be determined by future tests, however.

E Seal Development

Molded cell case covers were procured during the quarter for use on Model 379 prototype cells. Ten cell cases and molded covers were sealed with production sealant in the cover to jar seal, and Epocast 221/927 or Isochem 811B/A as the terminal sealant. Production electrolyte was added to each cell (80 cc), and the case was hermetically sealed After a post cure of 16 hours at 100°C, the cells were sterilized 72 hours at 135°C in air inverted for the last 24 hours. Weight loss was 1.0 - 1.5 gms water per cell with no visible leaks or cracks.in the epoxy seal. The coefficients of thermal expansion for these epoxy materials are reasonably well matched to PPO -

- Production Sealant 1 39 X 10^{-5} in/in°F
- PPO 534-801 2.9 X 10^{-5}
- Epocast 221/927 2.2 X 10^{-5}
- Isochem 811B/A 2 9 X 10^{-5}

and all have good tensile shear bond strength.

F Deliverable Cells

In accord with contract requirements 20 each type A, B, and C cells were manufactured and delivered to JPL for tests. The designs selected represented those giving the best discharge capacities during early 100% DOD cycles and may not reflect optimum cycle life designs

Cell Type	Design Type	Delivery Date or Schedule
A	3	4-18-69
B	4	5-15-69
C	5	7-23-69

G. Future Work

Cycling will be continued to failure of the second cell in each test group. Failing cells will be analyzed to determine mode of failure and degree and type of negative plate erosion.

V. QUALITY ASSURANCE

Quality Assurance activities for the Second Quarter of 1969 included a Design Review, a Field Trip, Weekly Meetings, completion of an IOS package, and the writing of a general Q.A. specification for factorial experiments.

In more detail, the design review was held on ESB Model 364, Task XI, at ESB. The minutes have been distributed. A Q.A. staff member traveled to The Carl F. Norberg Research Center to perform a final acceptance of the Data Acquisition System, that is now used for JPL cycling.

Weekly meetingswith all ESB project engineers were held to familiarize each other with progress of past week and schedule for upcoming week.

Quality Assurance Specification No. 251 (QAS 251) was written during this quarter. This specification is intended to provide Q.C. inspectors with a step-by-step inspection plan for factorial experiments. The specification details the requirements for traceability and identification of those factors under consideration in the experiment. This specification has been submitted.

An Inspection Operation Sheet package (IOS) was written for the Model 364 cell. This package has been submitted.

The Q.A. requirements for the Model 380 Factorial Test Plan was completed during this quarter. This portion was included on the plan submitted.

References: (1) E. K. Casani. Capsule System Advanced Development CSAD Mission Model, 6 May 1968, Jet Propulsion Laboratory Report 760-20

(2) First Quarterly Progress Report JPL Contract 951296, January 1 to March 31, 1969, Task 12, p38.

(3) IBID, Table XII, p31.

(4) Report for Fourth Quarter 1968, JPL Contract 951296, P25.

APPENDIX I

CALCULATION OF POSITIVE PLATE CORE THICKNESS BY EULER EQUATION

The Euler equation gives the critical elastic buckling load for a long, slender column axially loaded assumed to fail by buckling -

$$P_c = \pi^2 EI/\ell^2$$

where

P_c = critical buckling load in pounds

I = least moment of inertia of cross-sectional area, $in.^4 = 1/12\ wt^3$

E = Modulus of elasticity; for zirconium = 14×10^6 psi

L_e = Length of column (effective) = 2L for fixed end, free end condition = 1.13 in.

W = Width of column = 0.40 in.

t = Thickness of column

For 11.0 grams Model 381 positive plate assembly weight at 4000 g impact X 2 for safety factor

$$P_c = (11.0\ gm)(0.0022\ lb/gm)(8{,}000\ g) = 194\ lbs.$$

$$t = \left(\frac{12\ P_c \ell_e^{\ 2}}{\pi^2\ EW}\right)^{1/3} = 0.037 \text{ inch zirconium thickness.}$$