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987987**DEVELOPMENT OF LARGE SCALE ADVANCED
NI-CD BATTERIES EMPLOYING ROLL-BONDED
ELECTRODES**

BY E. FERREIRA AND A. CHARKEY
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FOR ADVANCED RESEARCH PROJECTS AGENCY AND
NAVAL SURFACE WARFARE CENTER
WEAPONS RESEARCH AND TECHNOLOGY DEPARTMENT

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EXECUTIVE SUMMARY

A 12-month, Phase II development effort was undertaken by Energy Research Corporation (ERC) to solve several technical issues remaining from the Phase I program. This work was necessary before an effective transition of the ERC roll-bonded battery technology to the Navy could occur.

The program was structured to proceed with the following tasks:

Task 1.0 - Continuation of Long-Term Float Testing of 2000-Ah Nickel-Cadmium (Ni-Cd) Cells from the Phase I Effort

Task 2.0 - Accelerated Cell Corrosion Study

Task 3.0 - Fabrication of Advanced 2000-Ah Ni-Cd Cells to Resolve Mechanical Shorting and Demonstrate A Minimum of 500 Cycles

The Phase II program was successfully completed with a demonstration of 34 months of continuous cell float and still yielding an output capacity of 2200 Ah or 110 percent of rated cell capacity.

It was established, through the accelerated corrosion study, that the estimated life of ERC's Ni-Cd cells exceeded eight years with cells still maintaining an output capacity of over 100 percent of rated capacity; extrapolated results indicated that at least a 10-year life is attainable.

Six advanced 2000-Ah Ni-Cd cells demonstrated a cycle life of 600 cycles at the 1C rate while yielding an output capacity of 2100 Ah without cell failure. In addition, the cells demonstrated an energy density of 19 Wh/lb at the 1-hr rate.

The approach taken under Task 1.0 consisted of testing ten 2000-Ah cells (Designs #1 and #2) from Phase I and subjecting them to a constant potential charge, (float) of 1.35 V/cell. Periodically, these were discharged at the 1-hr rate, (2000 Amps) to 0.8 V/cell, followed by a second capacity test discharge at the 1-hr rate to 0.8 V/cell. Cells were then recharged and returned to the float regime at 1.35 V/cell. These cells accumulated a total of 34 months on continuous float, yielding 2200 Ah or 110 percent of rated cell capacity.

In Task 2.0 an accelerated test program was performed to determine the ultimate life of ERC's roll-bonded, positive electrodes. Corrosion rates of graphite and current collector

oxidation where performed in the presence and absence of nickel hydroxide at various temperatures. To separate the effects of loss in capacity due to the "aging" of nickel hydroxide at various temperatures and capacity loss due to graphite oxidation (potassium carbonate formation) cells were also constructed and tested. In addition, cells using sintered electrodes were tested to determine how nickel hydroxide ages in the absence of graphite and the presence of large quantities of K_2CO_3 (potassium carbonate). The corrosion study consisted of three independent subtasks which proceeded in parallel. These subtasks were:

Subtask 2.1 - Graphite Corrosion

Subtask 2.2 - Simulated Cell Corrosion

Subtask 2.3 - Effects of K_2CO_3 (potassium carbonate) on cell capacity

A total of 300 cells, with electrodes measuring 3.875 inches x 2.875 inches, were built for the corrosion tests. The electrode composition was a formulation similar to that of the 2000-Ah Phase I cells. Cell assembly and formation was accomplished under subtasks 2.2 and 2.3.

The cells were divided into groups (3 cells each) and placed in designated temperatures of 20, 40, 50, and 60°C, respectively. At two-month intervals, one cell group at each temperature was removed and tested. This procedure was followed through 12 months. The percent carbon loss was measured in each case and related to an Arrhenius type accelerated lifetime condition. The equivalent life was assumed to double the real time exposure for each 10°C temperature increase. The cells accumulated a simulated life of about 8 years in the course of the test, while maintaining an output exceeding 100 percent of rated cell capacity.

Under Task 3.0, reproducibility of cell component was demonstrated by manufacturing six advanced 2000-Ah Ni-Cd cells. These were life tested in excess of 600 cycles with no failures. As was reported in the Phase I program, two of the original 2000-Ah cells developed internal shorts. Dissection of these cells revealed the current collector design, particularly at the edges of the electrodes, to be the cause of failure. A new current collector, employing modifications to eliminate the possibility of separator perforation by the grid projections, was designed for the new cell set. After completion of manufacturing and formation, each cell was life cycled. The Phase II ultimately demonstrated the capability of ERC's Ni-Cd cells to accumulate at least 500 cycles over the potential 10-year life.

Future work should address the following areas:

- Investigate the minimum percentage of graphite to permit extending beyond 10-year life
- Investigate the amount of collector corrosion a cell can tolerate (loss of cobalt, nickel plating and substrate foil) before it affects cell voltage and capacity drops below 80 percent of rated capacity

- Verify life extrapolation used in this program
- Long-term verification of separator systems
- Continuation of float testing to 48 months and test cycling to 1000/1500 cycles

It is felt that these steps should verify the life extrapolation used in this program. The resulting product will be a large capacity, manufacturable cell with long calendar (greater than 10 years) and good cycle life suitable for diverse applications.

FOREWORD

This Program is a continuation of earlier research and development efforts by Energy Research Corporation (ERC) on application of the roll-bonded process secondary nickel electrode by private funding and previous Government sponsored contracts. These include, among others: NASA NAS 3-19766 (June 1975), NAVSEA N00024-79-C-4546 (October 1979) and N00024-81-C-4217 (January 1981). The current contract N60921-C-89-0123 as amended and extended has enabled both fabrication and cycle testing of prototype cells containing large (12-inch x 20-inch) size electrodes as well as accelerated corrosion testing of the electrode substrate material.

This work was sponsored by the Advanced Research Projects Agency (ARPA), Undersea Warfare Office (Captain R. Lowell). Technical monitoring and contract administrative matters were carried out by the Naval Surface Warfare Center Dahlgren Division (NSWCDD) White Oak Detachment. While being primarily developed for military use, this technology is adaptable to numerous applications in the civilian sector.

The Final Technical Report on this Program has been received and accepted by both ARPA and NSWCDD. In recognition, however, of wider possibilities noted above, it was determined that this NSWCDD Technical Report should be produced. It will serve to establish a permanent public record of the effort and assure a broader dissemination of the results to DoD-wide entities, other Government agencies, their contractors and NATO Allies.

Approved by:


C. E. MUELLER, Head
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ABSTRACT

The roll-bonded fabrication of non-sintered nickel electrodes has been investigated by fabrication and testing of two 2000-Ah cell sets. The cells achieved at least 600 50 percent depth of discharge (DOD) 1C rate cycles. Sustained energy of 18-19 Wh/lb was delivered. A constant potential float of 34 months showed a modest decrease from initial capacity to 2200 Ah. A redesigned current collector in the second cell set eliminated all symptoms of internal shorting previously experienced.

An Arrhenius type elevated temperature accelerated corrosion test was performed on small cells having similar electrode compositions as those of the full size cells. These tests indicated substantial conversion of the electrode graphite component to carbonate in the electrolyte.

This oxidation results in a decrease in substrate conductivity and increase in electrolyte resistivity. In practice, however, relation of the data back to ambient temperature indicated at least a 10-year useful calendar cell life.

While the cell technology developed here was intended for military use, it has good potential for transfer to other Government and commercial applications, such as in industrial systems, load leveling, uninterruptible power sources and electric vehicles. It is with this additional perspective that the current report is presented.

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SECTION 1

INTRODUCTION

This final report presents the research and development work conducted by Energy Research Corporation (ERC) under Contract N60921-89-C-0123, Phase II, issued by Naval Surface Warfare Center Dahlgren Division (NSWCDD) White Oak Detachment and funded by ARPA for the Development of an Advanced Nickel-Cadmium Battery.

Under the Phase I program, several technical issues remained to be solved in order to instill confidence in the ERC battery Technology for military and civilian applications. These issues were: Reliable prediction of 10-year battery life through an accelerated cell corrosion study, long-term float testing, continuous cycling test with a minimum of 500 cycles and resolving transient internal mechanical shorts observed in Phase I through cell component reproducibility.

For the Phase II program these issues were divided into tasks as follows:

Task 1.0 - Continuation of Long-Term Float Testing of 2000-Ah Cells from the Phase I Effort

Task 2.0 - Accelerated Cell Corrosion Study

- 2.1 Graphite Corrosion
- 2.2 Simulated Cell Corrosion
- 2.3 Effect of K_2CO_3 (potassium carbonate) on Cell Capacity

Task 3.0 - Fabrication of Advanced 2000-Ah Ni-Cd Cells To Resolve Mechanical Shorting and Demonstrate A Minimum of 500 Cycles

- 3.1 Redesign and Reassemble Piercing Machine for Current Collector Manufacture
- 3.2 Design of a New Current Collector
- 3.3 Assembly of Test Equipment
- 3.4 Manufacturing of Six Advanced 2000-Ah Cells
- 3.5 Cycle Testing of Six 2000-Ah Cells
- 3.6 Post Cycling and Failure Analysis

Under Task 1.0, ten 2000-Ah cells remaining from Phase I were maintained on a float regime consisting of a constant potential charge of 1.35 V/cell. Periodic test discharges at the 1-hour rate were performed and after 34 months on float these cells were yielding about 2200 Ah.

Under Task 2.0, cells were built to establish the life of ERC's nickel-cadmium by determining the corrosion rates of graphite and current collector oxidation in the presence and absence of nickel hydroxide at various temperatures. Based on the percent carbon loss vs. accelerated estimated life, calculated as doubling for every 10°C temperature increase, the simulated cells accumulated about eight years of life, yet maintained an output capacity of over 100 percent of rated capacity. Although the final loss in carbon ranges from 12 percent to 46 percent, the cell capacities were excellent. The performance achieved is believed to be related to the increase of electrode porosity which allows extra electrolyte to penetrate the electrode, therefore making it more conductive.

Under Task 3.0, the fabrication of six advanced 2000-Ah Ni-Cd cells, was undertaken. It was necessary to develop a new current collector, which was the cause of the internal shorting encountered under Phase I. The piercing discs also needed repair so a new set of discs were designed, manufactured and assembled. The male and female discs in the existing machine were consumed during the manufacturing of the current collectors under Phase I. Furthermore, to prevent the recurrence of internal shorting, a new current collector design was initiated. This new design reduced the piercing projection heights and allowed the manufacture of collectors with a 1/4-inch wide flat salvage margin on each side of the collector. The existing 4000 Amp power supply and cycling equipment which was disassembled at the conclusion of Phase I was reassembled under this task. This equipment allowed the automatic cycling of the six advanced 2000-Ah Ni-Cd cells and also periodic test discharges on the remaining cells on float from Phase I.

ERC also established and electrochemical design for the 2000-Ah cells during this period. All of the cell components, such as case, cover, terminals, hardware and active materials were obtained and six 2000-Ah cells were assembled. Upon completion of the assembly, each cell was cycle tested. Individual cell voltages, temperatures and number of cycles were recorded. A total of 600 cycles were performed on these cells yielding a final output capacity of 2100 Ah without cell failure. A comparison of the cycle testing and float testing with corrosion data shows good agreement, as indicated in Table 1-1.

TABLE 1-1. LIFE COMPARISON OF NI-CD CELLS

Type of Test Regime	Cell N/C (Ah)	Time On Test	KOH Analysis		Output Capacity (Ah)	% Rated Capacity
			% KOH	% CO ₃		
Float	2000	34 Month (2.8 years)	21	11	2200	110
Cycling	2000	600 Cycles	25	11	2100	108
Float 50°C (Corrosion Study)	2.39	34 Month (2.8 years)	14.4	13.9	2.75	107
Float 50°C (Corrosion Study)	2.39	96 Month (8 years)	13.3	16.5	2.56	107

The following sections present the details of the work performed on each of the three tasks.

SECTION 2

TECHNICAL DISCUSSION

TASK 1 - LONG-TERM FLOAT TESTING OF 2000-Ah CELLS FROM PHASE I

ERC continued testing of ten 2000-Ah cells on a float regime during Phase II. These cells which were designed and constructed in Phase I consisted of two designs as follows:

Design No. 2001 - Six Cells Manufactured

Positive Plates:	40
Dimensions:	20-inch H x 12-inch W x .058-inch T
Mix Formula:	67 percent Ni(OH)_2 + 30 percent graphite + 3 percent TFE
Collector:	.003-inch thick pierced silver foil, nickel and cobalt plated
Nominal Capacity:	2000 Ah at 1C rate
Negative Plates:	44
Dimensions:	20-inch H x 12-inch W x .024-inch T
Mix Formula:	90 percent CdO + 8 percent Ni(OH)_2 + 2 percent TFE
Collector:	.004-inch thick perforated copper foil nickel plated
Theoretical Capacity:	4400 Ah
Separator:	Positive - Celgard
	Negative - 2 layers of Pellon FS2119, .005-inch thick
Electrolyte:	35: KOH + 1 percent LiOH

Design No. 2002 is identical to design No. 2001, except it contained 5 percent cobalt spinel coated on the graphite. Six cells were also manufactured. These cells were divided into two groups as follows:

Group 1 - Test Cycling Design No. 2001 - Cells No. 1, 2, 3 and 4
 Design No. 2002 - Cells No. 1, 2, 3 and 5

Group II - Float Testing Design No. 2001 - Cells No. 5 and 6
 Design No. 2002 - Cells No. 4 and 6

At the conclusion of Phase I, cells manufactured under Group I had been cycled through 500 cycles and cells under Group II had been on float for 9 months. During cycle testing cells No. 2 and 1 of Designs No. 2001 and 2002 developed internal shorts and were dissected.

The continuation of the float test regime on these remaining eight cells consisted of the following routine:

Float at a constant potential of 1.35 V/cell for a period of 60-90 days followed by a discharge at the 1-hour rate (2000 Amp) to 0.8 V/cell. At this point the cells were to receive a second capacity test discharge consisting of a charge at 500 Amps for 6 hours, followed by a discharge at the 1-hour rate (2000 Amp) to 0.8 V/cell. Each cell was then recharged at 500 Amps to 1.45 V/cell and returned to the float regime at 1.35 V/cell. Initially, these cells were only subjected to capacity test discharges at 500 Amps after 16, 20 and 24 months of float because the cycling equipment (4000 Amp power supply and cycler) were disassembled after completion of Phase I. Once the cycling equipment was assembled, cells were then discharged at 2000 Amps (1-hour rate).

Test Results

During this period each cell was connected to a power supply at a constant voltage of 1.35 V/cell. Capacity test discharges at 500 Amp were conducted at 16, 20 and 24 months. Cell capacities, float current, KOH analysis and water additions for 500 A capacity test discharges were recorded and are presented in Table 2-1.

Presented in Table 2-2 and 2-3 are the cell capacities, float currents and water addition for the 2000 Amp (1-hour rate) capacity test discharge performed after 22/30 and 26/34 months of float testing. Figure 2-1 presents the second capacity test discharge at the 1-hour rate (2000 Amp) after 34 months. Figure 2-2 shows the capacity maintenance of both designs during float after 34 months.

Analysis and Discussion of Results

As indicated in Table 2-1, the capacity test discharges performed after 16, 20 and 24 months of float show cell capacities of 2250 Ah with average cell voltages of 1.18 V. The float currents are 2.0, 2.5 and 2.75 Amps for the 16, 20 and 24 month periods to maintain 1.35 V/cell.

The water additions per cell have shown a slight increase from 575 to 700 cc. Cell No. 4 of Design No. 2002 which has been on float with a gas recombination module shows water addition of 100 cc to 135 cc. The electrolyte analysis shows average results of 23.8 percent KOH to 22.1 percent KOH and 10.6 percent to 10.9 percent K_2CO_3 . Although the cells yielded 2200 Ah at the 1-hour rate discharge, as can be seen from Tables 2-2 and 2-3 the float currents have increased to about 4.3 Amps average to maintain a 1.35 V potential per cell with water addition also increasing from 625 to 715 cc. Cell No. 4 of Design No. 2002 containing the recombination catalyst shows water addition of 165 cc for every 180 days.

TABLE 2-1. FLOAT TESTS - 500 AMP DISCHARGE TO 0.80 V
Float 1.35 V/cell - Minimum Acceptable Capacity 1600 Ah
Second Capacity Test Discharge

Cell Design No.	Cell Capacity (Average)	Average Voltage (V)	Average Float Current (A)	Average Float Current (A)		Water Addition (cc)*	Time of Float (months)
				%KOH	% K ₂ CO ₃		
1	2250	1.18	2.0	23.8	10.6	575	16
2	2250	1.18	2.0	23.8	10.6	575	16
1	2250	1.18	2.5	23.1	10.7	660	20
2	2250	1.18	2.5	23.1	10.7	660	20
1	2280	1.18	2.75	22.1	10.9	700	24
2	2280	1.18	2.75	22.1	10.9	700	24

* Every 60 Days

TABLE 2-2. SUMMARY OF RESULTS OF 2000-Ah cells ON FLOAT AT 22/30 MONTHS

2000 Amp Discharge To 0.8 V
Minimum Acceptable Capacity - 1600 Ah
Second Capacity Test Discharge

Cell Design No.	Float Cell Voltage (V)	Float Current (A)	KOH Analysis		Water Addition (cc) Every 60 Days	Capacity Test Discharge @ 26 Months		Time Of Float (Months)
			KOH	K ₂ CO ₃		Cell Capacity (Ah)	Cell Voltage (V)	
Cycler Design #2001								
Cell #1	1.35	3.8-4.0	21.0	11.2	670	2200	.790	22
Cell #3	1.35	"	21.2	11.4	710	"	"	"
Cell #4	"	"	21.0	11.2	660	"	"	"
Cycler Design #2002								
Cell #2	1.34	"	21.1	11.5	650	"	.810	"
Cell #3	1.35	"	"	11.0	700	"	.850	"
Cell #5	1.36	"	21.5	11.2	675	"	.840	"
Float Design #2001								
Cell #5	1.35	"	23.0	10.9	635	"	.850	30
Cell #6	"	"	23.1	10.7	660	"	.850	"
Float Design #2002								
Cell #4	1.35	"	23.9	9.7	135*	"	.890	"
Cell #6	1.36	"	23.7	10.0	625	"	.890	"

*Recombination Catalyst (Every 180 Days)

TABLE 2-3. SUMMARY OF RESULTS OF 2000-Ah cells ON FLOAT AT 26/34 MONTHS
 2000 Amp Discharge To 0.8 V
 Minimum Acceptable Capacity - 1600 Ah
 Second Capacity Test Discharge

Cell Design No.	Float Cell Voltage (V)	Float Current (A)	KOH Analysis		Water Addition (cc) Every 60 Days	Capacity Test Discharge @ 34 Months		Time Of Float (Months)
			KOH	K ₂ CO ₃		Cell Capacity (Ah)	Cell Voltage (V)	
Cycler Design #2001								
Cell #1	1.35	4.2	21.0	11.0	700	2200	.790	26
Cell #3	1.35	"	21.0	11.4	710	"	.800	"
Cell #4	"	4.3	21.0	11.2	660	"	.800	"
Cycler Design #2002								
Cell #2	1.35	4.2	21.0"	11.0	670	"	.810	"
Cell #3	1.35	"	20.0	11.0	715	"	.800	"
Cell #5	1.36	"		11.2	600	"	.800	"
Float Design #2001								
Cell #5	1.35	"	22.1	10.9	670	"	.800	34
Cell #6	"	"	21.5	10.7	700	"	.810	"
Float Design #2002								
Cell #4	1.35	"	22.0	9.7	165*	"	.810	"
Cell #6	1.36	"	22.2	10.0	625	"	.800	"

*Recombination Catalyst (Every 180 Days)

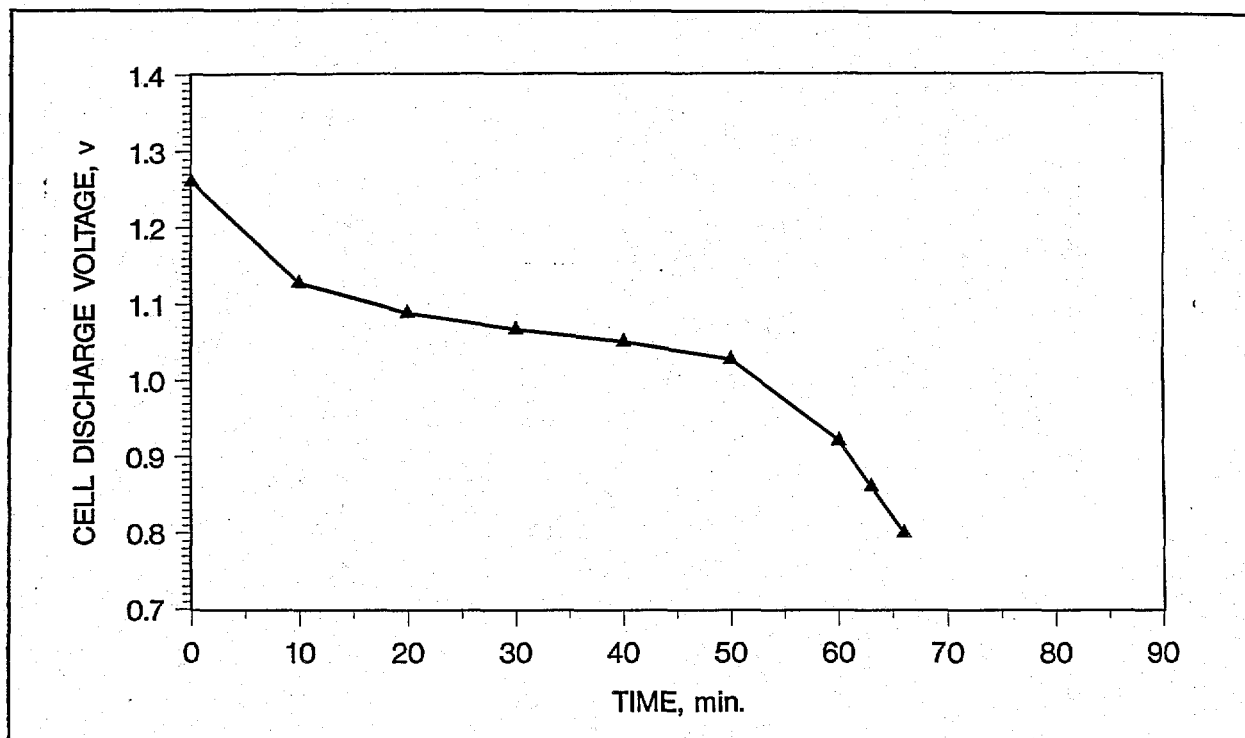


FIGURE 2-1. 2000-AH NI-CD 1-HOUR RATE
2000 Amp Discharge - Float Cell After 34 Months

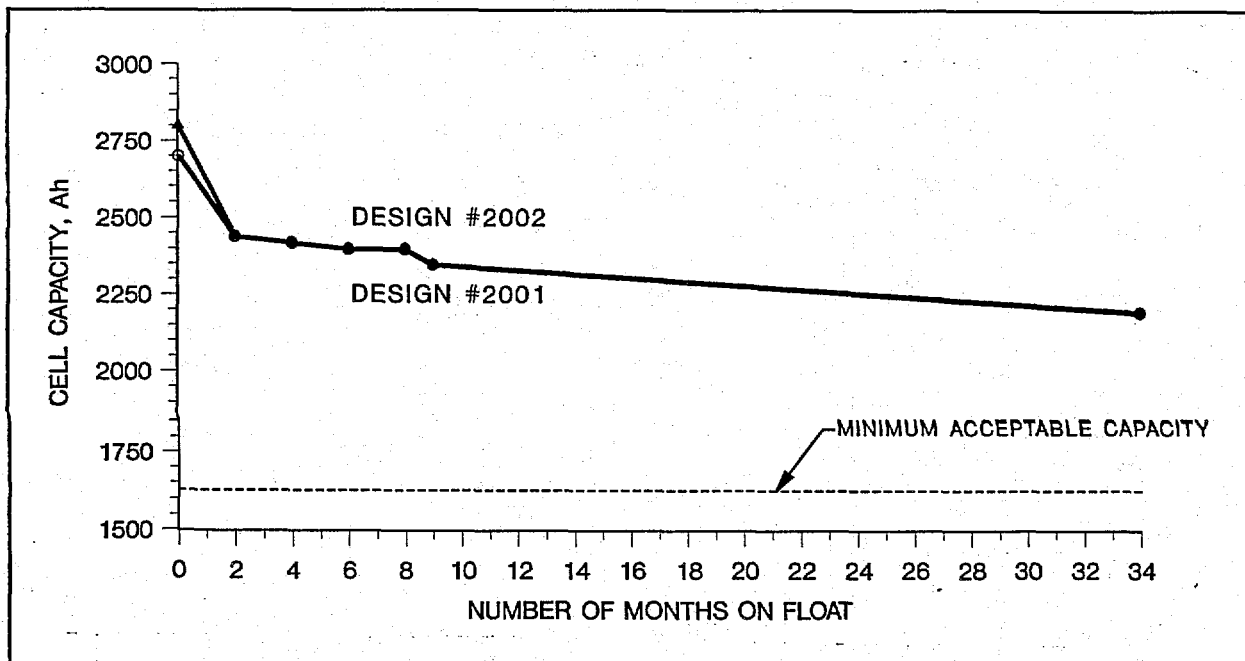


FIGURE 2-2. 2000-AH NI-CD LIFE CYCLE FLOAT
2000 Amp Discharge to 0.8 V

The increase in current to maintain 1.35 V could be an indication of small internal shorts in these cells. During the analysis conducted on cells under the corrosion study up to the 12th-month interval, no signs of cadmium shorting was observed. It can then be concluded that the small internal shorts detected in the float cells are due to mechanical shorts caused by the current collector. It is noted that the cells were assembled using the original current collector design from Phase I. It is recommended that in the future the cells exhibiting signs of soft shorting be dissected for analysis.

TASK 2 - ACCELERATED CORROSION STUDY

The main objective of this accelerated corrosion study performed on ERC's cells was to establish the ultimate life of the roll-bonded nickel-cadmium technology, through the corrosion rates of graphite and current collector oxidation in the presence and absence of nickel-hydroxide at various temperatures. The results demonstrated and established that ERC's Ni-Cd rolled, bonded electrode would provide a battery with at least a 10-year lifetime. For this a 14-month period was proposed, but because of contract schedules and limitations of funding, only 12 months of the study was concluded. Although extrapolation of the results proved a 10-year lifetime battery, the 12-month study demonstrated conclusively that the ERC Ni-Cd, roll-bonded electrode can provide a battery with at least an 8-year lifetime.

The corrosion study consisted of three independent subtasks which proceeded in parallel. These subtasks were:

- Subtask 2.1 Graphite Corrosion
- Subtask 2.2 Simulated Cell Corrosion
- Subtask 2.3 Effect of K_2CO_3 (potassium carbonate) on Cell Capacity

The cells were built, with electrodes similar to those of the 2000-Ah cells. A total of 300 cells were built and housed in polysulfone cases. Each cell was sealed with a polysulfone cover containing one terminal per polarity and fitted with a "one-way" valve to prevent ingress of CO_2 into the cell. After assembly completion and initial formation of cells under subtasks 2.2 and 2.3, each cell was placed in the proper testing temperature oven. To further prevent ingress of CO_2 , ovens were blanketed with a flow of dry nitrogen gas.

Presented below is the detailed testing conducted on each of the subtasks.

Subtask 2.1 - Graphite Corrosion - Cell Group No. 139 - No. 276

Graphite electrodes with and without cobalt spinel coating were fabricated using ERC's rolled-bonded technique. The graphite electrodes contained 9.1 percent Teflon and the graphite was either coated with 5 percent cobalt spinel or left uncoated. Each cell contained one graphite electrode laminated to a silver current collector which had been nickel and cobalt plated. Each electrode measured 3.875-inch H x 2.875-inch W and were assembled,

suspended vertically in a polysulfone case between two nickel foil counter electrodes. Blank cells were also fabricated using the same type of construction except no graphite was used. Three cells per variation were assembled along with one blank for each temperature and time variation. Three test temperatures of 20°C, 40°C and 60°C were used and after being placed in the ovens, cells were analyzed at each time period after 2, 4, 6, 8, 10 and 12 months of continuous float charge. Three identical cells together with one blank were opened after each time period at each temperature and the electrolytes analyzed for % KOH and %K₂CO₃. Prior to final cell assembly each electrode was weighed and recorded. At the end of each time period the graphite electrodes were washed free of electrolyte in a Soxhlet extractor and then dried. The electrodes were weighed and compared to the original weights.

A total of 126 cells and 12 blanks were fabricated for this subtask. Table 2-4 summarizes the test matrix for this task. Upon final assembly, each cell was filled with 43 cc's of 35 percent KOH + 1 percent LiOH by weight. Cell group No. 139 - No. 264 and blank cell group No. 265 - No. 276 were assigned to this task.

Subtask 2.2 - Simulated Cell Corrosion - Cell Group No. 1-138

These cells were built containing one positive and two negative electrodes with the same active material, capacity density and thickness as in the 2000-Ah cells, except the dimensions were 3.875-inch H x 2.875-inch W. Cells were constructed with unprotected and protected cobalt oxide spinel coated graphite. The positive electrode was wrapped in a separator consisting of one layer of Celgard 3400 and the negatives wrapped in two layers of Pellon FS2119, .005-inch thick.

Prior to cell assembly, each positive electrode was weighed and its thickness measured. The Pellon and Celgard layers were also weighed and recorded. Positive and negative electrodes were assembled, and suspended vertically in a polysulfone case. Blank cells were also fabricated in a similar manner without active materials. Three cells per variation were assembled along with one blank for each temperature and time variation. Three test temperatures of 20°C, 40°C and 50°C were used and after being placed in the proper ovens, cells were analyzed at each time period of 2, 4, 6, 8, 10 and 12 months of continuous float charge.

At the end of each time period of continuous float at each temperature, three identical cell units together with one blank were removed from each oven. A capacity test discharge at the 1C rate followed by a charge at C/5 and a second capacity test discharge at the 1C rate to a cutoff cell voltage of 0.80 V was performed. Test results were compared to those obtained initially on the formation cycle at the 1C rate. Electrolyte samples from each cell were removed and analyzed for %KOH and %K₂CO₃, were conducted and compared to the initial results. The positive electrodes were then removed, washed in a Soxhlet extractor and dried. Electrode and separator thicknesses and weights were recorded and compared to the initial results. Porosity tests were also performed on the electrodes. The current collectors were also examined and preserved for SEM and optical microscope analysis. A total of 126 cells and 12 blanks were also fabricated for this subtask. Table 2-5 summarizes the test

matrix for this task. Upon final assembly each cell was filled with 40 cc's of 35 percent KOH + 1 percent LiOH by weight. Cell group No. 1 - No. 126 and blank cell group No. 127 - No. 138 were assigned to this task.

TABLE 2-4. GRAPHITE CORROSION TEST MATRIX

Current Collector	Silver Foil, Nickel and Cobalt Plated
Graphite Type	a) Unprotected b) Cobalt Spinel Coated
Temperature	a) 20°C b) 40°C c) 50°C
Test Intervals	a) 2 months b) 4 months c) 6 months d) 8 months e) 10 months f) 12 months
No. of Cells	3 Replicates x 2 Variations x 3 Temperatures x 7 Intervals = 126
No. of Blanks	12

Subtask 2.3 - Effect of K_2CO_3 On Cell Capacity - Cell Group No. 277 - No. 300

To separate the effects of loss of capacity due to "aging" of $Ni(OH)_2$ at elevated temperature and capacity loss due to graphite oxidation, (K_2CO_3 formation) cells identical to those under Subtask 2.2 were constructed. In addition cells were also constructed using sintered electrodes to determine how nickel hydroxide ages in the absence of graphite and presence of large quantities of K_2CO_3 . The sintered electrodes were manufactured by Eagle Pitcher Corporation and measured .021-inch thick, having a capacity density of 6.75 Ah/in³. The cells were assembled with a sintered plate wrapped in a layer of Celgard 3400, and two CdO electrodes each wrapped in two layers of Pellon .005-inch thick.

TABLE 2-5. SIMULATED CELL CORROSION TEST MATRIX

Current Collector	Silver Foil, Nickel and Cobalt Plated
Graphite Type	a) Unprotected b) Cobalt Spinel Coated
Positive Negative Active Material and Electrolyte	Similar to 2000-Ah cells
Temperature	a) 20°C b) 40°C c) 50°C
Test Intervals	a) 2 months b) 4 months c) 6 months d) 8 months e) 10 months f) 12 months
No. of Cells	3 Replicates x 2 Variations x 3 Temperatures x 7 Intervals = 126
No. of Blanks	12

Prior to cell assembly, each positive electrode was weighed and its thickness recorded. Three cells of each design were assembled per every concentration of carbonate. Cells were placed in an oven at 50°C and after two months of continuous float charge they were removed from the oven for capacity performance. This procedure consisted of a test discharge at the 1C rate followed by a charge of C/5 and a second capacity test discharge at the 1C rate to a cutoff cell voltage of 0.80 V. The results were then compared to those data obtained on the initial cell formation. Electrolyte samples from each cell were removed and analysis for %KOH and % K₂CO₃ were performed and compared to the initial formation results. Positive electrodes were removed, washed in a Soxhlet extractor and dried. Electrodes and separator thicknesses and weights were recorded and compared to the initial results. A total of 24 cells were constructed and tested. Table 2.6 summarizes the test matrix for this task. Upon final assembly each cell was filled with 40 cc's of 35 percent KOH + 1 percent LiOH by weight. Cell group Nos. 279 - Nos. 307 was assigned to this subtask.

TABLE 2-6. EFFECT OF K_2CO_3 ON CELL CAPACITY TEST MATRIX

Positive Electrode Type	a) Roll-Bonded Cobalt Spinel Coated Graphite b) Sintered
K_2CO_3 Content	a) 0 percent By Weight b) 10 percent By Weight c) 15 percent By Weight d) Percent By Weight
Test Conditions	a) 1C Rate Discharges - Initial Performance b) 1C Rate Discharges - After 2 Months Storage At 50°C
No. of Cells	3 Replicates x 2 Electrode Types x 4 K_2CO_3 Concentrations = 24

TEST RESULTS

Initial Formation and Long-Term Testing

After filling each cell with 35 percent KOH + 1 percent LiOH, a soaking period of 72 hours was allowed before formation. Cell groups No. 1 - No. 126 and No. 277 - No. 300 were then subjected to a formation procedure consisting of 3 cycles as follows:

Charge at .31 Amp for 16 hours

Discharge at 1.16 Amp to a cutoff voltage of 0.80V/cell

The last discharge was conducted at the 1C rate of 2.32 Amp to a cutoff voltage of 0.80V/cell. Presented in Table 2-7 is a summary of the initial cell capacity baseline data, which includes the average initial cell capacity (Ah) at the 1C rate, the average cell voltage at the 1C rate for every 21 cells of group No. 1 - No. 126 and every 3 cells for group No. 277 - No. 300. It can be seen from this table, that at the 1C rate of discharge, cells No. 277 - No. 300, with added carbonate to the electrolyte shows a decreasing average voltage with increasing concentration of carbonate. This is true for cells with both sintered and rolled, bonded positive electrodes. This is to be expected, since the higher percent of carbonate increases the electrolyte resistance and at the same time reduces the KOH concentration.

TABLE 2-7. CORROSION CELL INITIAL FORMATION CAPACITIES AND VOLTAGES

Cell Group No.	Average Initial Cell Capacity 1-Hr Rate, Ah	Average Voltage 1-Hr Rate, V
1-21	2.39 $\pm$.02	1.166
22-42	2.39 $\pm$.02	1.123
43-63	2.39 $\pm$.02	1.133
64-84	2.43 $\pm$.02	1.144
85-105	2.43 $\pm$.02	1.140
106-126	2.39 $\pm$.02	1.140
277-279	2.53 $\pm$.03	1.154
280-282	2.53 $\pm$.03	1.127
283-285	2.47 $\pm$.11	1.100
286-288	2.43 $\pm$.08	1.090
289-291	3.29 $\pm$.04	1.153
292-294	3.20 $\pm$.14	1.130
295-297	2.97 $\pm$.17	1.112
298-300	2.82 $\pm$.06	1.097

Upon completion of the formation procedure, three samples of electrolyte were removed from every group of 21 cells and two samples from every group of three cells, and were analyzed for %KOH and %K₂CO₃. Table 2-8 summarizes the electrolyte analysis results, and presents the cell group number, cell construction, temperature regime and electrolyte analysis after formation for cell group No. 1-126 and No. 277-300. The graphite and blank cells were not formed and the results are the initial filling. This table is the baseline data for the electrolyte results. Each group was then placed into the designated test temperature for the start of the long-term continuous float corrosion study. To prevent ingress of CO₂ from the air, the ovens were blanketed with a continuous flow of dry nitrogen gas.

To determine the charge current for these cells on the long-term float and to compensate for self-discharge under different temperatures, studies were initially conducted on 20-Ah cells at various temperatures. The 20-Ah Ni-Cd cells were given a C/5 charge, a C/2 discharge followed by a C/5 full charge. Capacities were recorded and each cell was then stored at 20°, 40°, 50° and 60°C for three days. Following the storage temperature test, cells were once again discharged at C/2. To check for capacity, the cells received the same C/5 charge and C/2 discharge and the data compared with the initial results to determine the percentage capacity loss per day at each given temperature.

From these results, an Arrhenius plot was developed which is presented in Figure 2-3 and shows the loss of charge per day vs. storage temperature. Also included is published data for sintered and pocket plate electrodes. Also determined from the self-discharge data were the float currents (mA) and current densities (mA/in₂) at various temperatures which were to maintain the cells at full potential. These results are presented in Table 2-9.

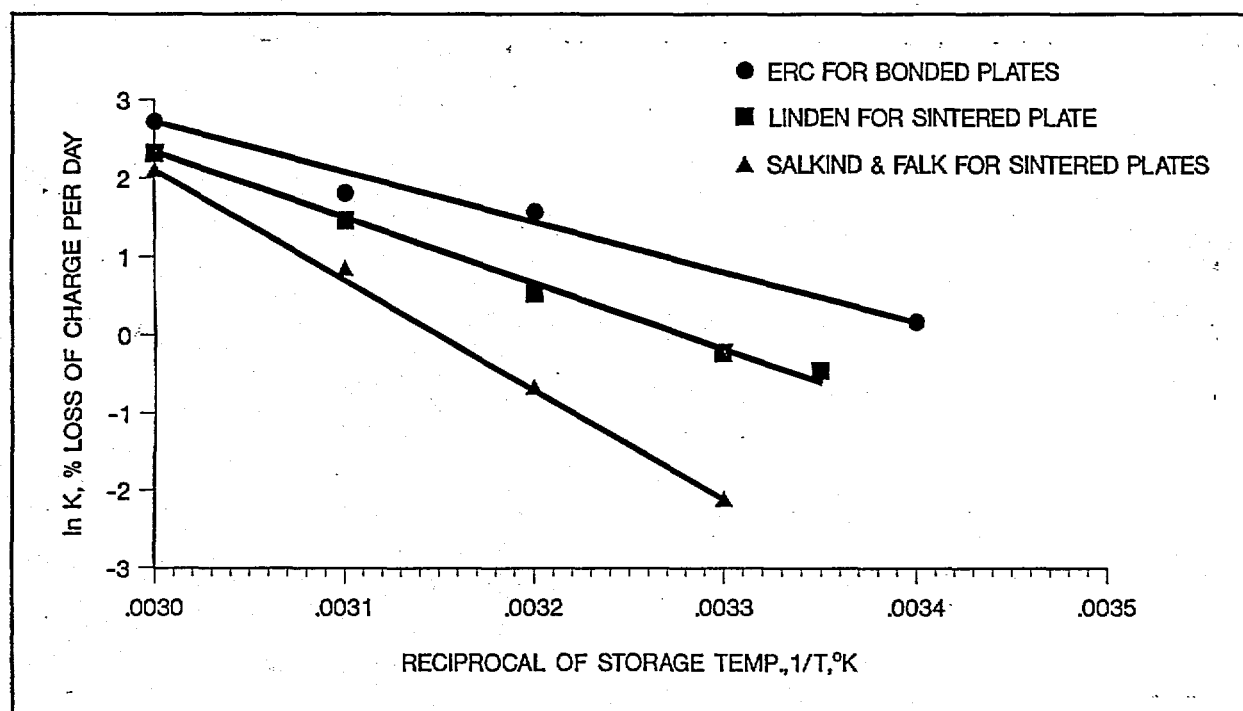


FIGURE 2-3. ARRHENIUS PLOT OF CHARGE LOSS IN NICKEL-CADMIUM CELLS

TABLE 2-8. SUMMARY OF CELL CONSTRUCTION & ELECTROLYTE ANALYSIS

Cell Group Number	Construction	Temp. °C	Electrolyte Analysis After Formation & Initial Filling	
			% KOH	% CO ₃
1-21	R.B. Ni(+)/R.B. CdO(-)	20	27.5	4.5
22-42	"	40	27.5	4.5
43-63	"	50	27.5	4.5
64-84	R.B. NiSp(+)/R.B. CdO(-)	20	26.1	5.3
85-105	"	40	26.1	5.3
106-126	"	50	26.1	5.3
127-129	(Blanks) Ag°w/NiCo Pl.(+)/Ni°(-)	20	34.4	0.6
130-132	"	40	34.4	0.6
133-135	"	60	34.4	0.6
136-138	"	50	34.4	0.6
139-159	R.B. C°(+)/Ni°(-)	20	33.8	1.2
160-180	"	40	33.8	1.2
181-201	"	60	33.8	1.2
202-222	R.B. C°Sp(+)/Ni°(-)	20	35.7	0.77
223-243	"	40	35.7	0.77
244-264	"	60	35.7	0.77
265-267	(Blanks) Ag°w/NiCo Pl.(+)/Ni°(-)	20	34.8	0.77
268-270	"	40	34.8	0.77
271-273	"	60	34.8	0.77
274-276	"	50	34.8	0.77
277-279	R.B. NiSp(+)/R.B. CdO(-)	50	25.7	3.5
280-282	R.B. NiSp(+)/R.B. CdO(-)/10% CO ₃	50	24.4	13.2
283-285	R.B. NiSp(+)/R.B. CdO(-)/15% CO ₃	50	24.3	18.0
286-288	R.B. NiSp(+)/R.B. CdO(-)/20% CO ₃	50	22.0	21.4

TABLE 2-8. SUMMARY OF CELL CONSTRUCTION & ELECTROLYTE ANALYSIS (Continued)

Cell Group Number	Construction	Temp °C	Electrolyte Analysis After Formation & Initial Filling	
289-291	Sin. Ni(+)/R.B. CdO(-)	50	26.4	6.8
292-294	Sin. Ni(+)/R.B. CdO(-)/10% CO ₃	50	25.2	13.7
295-297	Sin. Ni(+)/R.B. CdO(-)/15% CO ₃	50	23.4	17.0
298-300	Sin. Ni(+)/R.B. CdO(-)/20% CO ₃	50	24.0	20.0

LEGEND: - R.B. Ni(+)/R.B. CdO(-) Roll-bonded positive nickel electrode/Roll-bonded negative cadmium electrode
 - R.B. NiSp(+)/(-) Roll-bonded positive nickel electrode with cobalt spinel coated graphite
 Ag[°]w/NiCO PL(+)/Ni[°](-) Nickel, cobalt plated silver foil collector on positive/nickel foil on negative collector
 - R.B. C[°](+)/Ni[°](-) Roll-bonded graphite on positive/Nickel foil on negative collector
 Sin. Ni(+)/Sintered nickel positive electrode

TABLE 2-9. FLOAT CURRENTS

Temp. °C	Current Density mA/in ²	Current mA
20	.06	1.4
40	.25	5.6
50	.37	8.3
60	.37	8.3

LONG-TERM TESTING

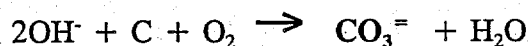
At the end of the first two-month test interval, three cells were removed from each of the various groups and one cell from each blank group. For the remaining test intervals up to 12 months, three cells of each group of graphite and cell groups and one from each blank group were removed for analysis.

At the two-month period, the cells under the simulated and effect of K₂CO₃ were removed and discharged at the 1C rate followed by a charge at C/5 and a second capacity test discharge at the 1C rate to a cutoff cell voltage of 0.80 V/cell. Upon completion of these test discharges, electrolyte samples from each cell were removed and analyzed for %KOH and %K₂CO₃.

The results are presented in Tables 2-10 and 2-11 respectively. Table 2-10 provides the initial formation capacities, the first and second (residual) capacities on float and the average cell voltages after formation and after two months. Also identified in the plate construction the cell group No. and temperature. From this table it can be seen that, of primary importance is the fact that none of the cells, even those containing high amounts of carbonate, show any loss of residual capacity after two months at up to 50°C.

Another point of importance is that nickel cells containing spinel coated graphite exhibited higher cell capacities, as a function of temperature. It can also be seen that the first discharge after storage shows a lesser capacity than the second (residual) capacity. This is because the float currents used were not quite sufficient to compensate for self-discharge especially at higher temperatures. Of importance is that no loss of capacity was observed between the formation and the capacity after two months on float.

Although the average cell voltages of the cells doped with carbonate are lower than the other cells, this difference is insignificant. Also of notice are slightly lower cell voltages for cells with sintered nickel as compared to the roll-bonded electrodes. Referring to Table 2-11 results of the electrolyte analysis, it can be seen an increase in carbonate content as it was expected with time and with increase in temperature. It is also observed that the percentage of KOH decreases in proportion to the amount of carbonate increase with temperature indicating that the reaction to form $\text{CO}_3^{=}$ proceeded as follows:



However, of interest is the small increase of KOH concentration at room temperature (20°C), accompanying the small increase of carbonate content. The increase in KOH concentration which is also found in the blanks at all temperatures can be attributed to a loss of total water content upon aging. Even though the level of electrolyte in the cells was kept constant, the porosity of the separator system decreases with time and temperature, water is forced out of the swollen materials and is not completely replaced within the pores and thus the concentration of KOH becomes slightly higher in percentage.

Following capacity determinations in the three cells of each variation removed from the test after two months, Soxhlet extractions of electrodes and separators were conducted. Drying, weighing and comparing the samples to the initial weights showed a weight loss which is assumed to be carbon. The blanks also showed small weight losses as a function of temperature, which is attributed to the plating oxidation of the collector.

These results are summarized in Table 2-12 which lists the average carbon weight loss of the various groups, net carbon weight loss and the carbon loss as calculated from the carbonate content of each cell group of three. Plots reflecting the results presented in Tables 2-10, 2-11 and 2-12 will be presented later as a family of curves as a function of temperature and time after the 12th month of analysis.

TABLE 2-10. SUMMARY OF CAPACITY DATA OF CORROSION CELLS AFTER 2 MONTHS

Comparison of Cell Capacity and Average Cell Voltages

Cell Group No.	Type (+) Plate	Temp. °C	Capacity After Form., Ah	Initial Discharge Cap. After 2 Mos., Ah	Residual Cap. After 2 Mos., Ah	Avg. Discharge Voltage After Form.	Avg. Discharge Voltage After 2 Mos.
1-21	R.B. Ni	20	2.39	2.63	3.07	1.166	1.129
22-42	R.B. Ni	40	2.39	2.23	2.75	1.123	1.055
43-63	R.B. Ni	50	2.39	2.52	2.94	1.133	1.103
64-84	R.B. NiSp	20	2.43	2.66	3.20	1.144	1.145
85-105	R.B. NiSp	40	2.43	2.56	3.05	1.140	1.123
106-126	R.B. NiSp	50	2.39	2.60	2.99	1.140	1.106
277-279	R.B. NiSp	50	2.53	2.52	2.89	1.154	1.132
280-282	R.B. NiSp w/10% CO ₃	50	2.53	2.64	3.04	1.127	1.100
283-285	R.B. NiSp w/15% CO ₃	50	2.47	2.53	2.70	1.100	1.066
286-288	R.B. NiSp w/20% CO ₃	50	2.43	2.20	2.40	1.090	1.028
289-291	Sin. Ni	50	3.29	3.05	3.35	1.153	1.073
292-294	Sin. Ni w/10% CO ₃	50	3.20	2.97	3.34	1.130	1.069
295-297	Sin. Ni w/15% CO ₃	50	2.97	2.64	3.23	1.112	1.023
298-300	Sin. Ni w/20% CO ₃	50	2.82	2.67	3.16	1.097	1.013

TABLE 2-11. SUMMARY OF CORROSION TEST CELL DATA AFTER 2 MONTHS
Comparison of Electrolyte Analysis

Cell Group Number	Construction	Temp °C	Electrolyte Analysis After Formation		Electrolyte Analysis After 2 Mos.	
			% KOH	% CO ₃	% KOH	% CO ₃
1-21	R.B. Ni(+)/R.B. CdO(-)	20	27.5	4.5	30.5	5.50
22-42	"	40	27.5	4.5	28.2	7.47
43-63	"	50	27.5	4.5	27.7	8.89
64-84	R.B. NiSp(+)/R.B. CdO(-)	20	26.1	5.3	28.6	6.14
85-105	"	40	26.1	5.3	25.7	8.77
106-126	"	50	26.1	5.3	25.2	9.46
127-129	(Blanks) Ag°w/NiCo Pl.(+)/Ni°(-)	20	34.4	0.6	34.7	1.18
130-132	"	40	34.4	0.6	36.0	2.46
133-135	"	60	34.4	0.6	36.0	2.17
136-138	"	50	34.4	0.6	35.5	1.21
139-159	R.B. C°(+)/Ni°(-)	20	33.8	1.2	35.0	2.57
160-180	"	40	33.8	1.2	29.4	8.4
181-201	"	60	33.8	1.2	22.0	14.89
202-222	R.B. C°Sp(+)/Ni°(-)	20	33.8	0.77	34.9	3.26
223-243	"	40	35.7	0.77	26.4	7.06
244-264	"	60	35.7	0.77	25.9	10.60
265-267	(Blanks) Ag°w/NiCo Pl.(+)/Ni°(-)	20	34.8	0.77		
268-270	"	40	34.8	0.77		
271-273	"	60	34.8	0.77		
274-276	"	50	34.8	0.77		
277-279	R.B. NiSp(+)/R.B. CdO(-)	50	25.7	3.5	26.7	9.5
280-282	R.B. NiSp(+)/R.B. CdO(-)/10% CO ₃	50	24.4	13.2	23.9	20.3
283-285	R.B. NiSp(+)/R.B. CdO(-)/15% CO ₃	50	24.3	18.0	21.3	25.1
286-288	R.B. NiSp(+)/R.B. CdO(-)/20% CO ₃	50	22.0	21.4	19.4	30.0
289-291	Sin. Ni(+)/R.B. CdO(-)	50	26.4	6.8	30.7	6.3
292-294	Sin. Ni(+)/R.B. CdO(-)/10% CO ₃	50	25.2	13.7	26.6	15.1
295-297	Sin. Ni(+)/R.B. CdO(-)/15% CO ₃	50	23.4	17.0	24.6	19.2
298-300	Sin. Ni(+)/R.B. CdO(-)/20% CO ₃	50	24.0	20.0	22.3	24.3

LEGEND:

- R.B.Ni(+)/R.B.(CdO(-) - Roll-bonded positive nickel electrode/Roll-bonded negative cadmium electrode
- R.B.NiSp(+) - Roll-bonded positive nickel electrode with cobalt spinel coated spinel coated graphite
- Ag°w/NiCo PL(+)/Ni°(-) - Nickel, cobalt plated silver foil collector on positive/Nickel foil on negative collector
- R.B.C°(+)/Ni°(-) - Roll-bonded graphite on positive/Nickel foil on negative collector
- Sin. Ni(+)/ - Sintered nickel positive electrode

TABLE 2-12. WEIGHT LOSS OF CELL COMPONENTS AFTER 2 MONTHS

Cell Group No.	Type (+) Plate	Temp. °C	Average Wt. Loss, gms	Net Wt. Loss, gms	C° Loss Calc. From Final $\text{CO}_3 =$ / gms
1-21	R.B. C°	20	2.81	2.81	0.586
22-42	R.B. C°	40	3.51	2.85	0.795
43-63	R.B. C°	50	3.93	3.30	0.947
64-84	R.B. C° Sp	20	3.42	3.42	0.654
85-105	R.B. C° Sp	40	3.56	2.90	0.934
106-126	R.B. C° Sp	50	3.31	2.68	1.01
139-159	R.B. Ni	20	1.68	1.68	0.30
160-180	R.B. Ni	40	2.25	1.59	0.983
181-201	R.B. Ni	60	2.60	1.87	1.74
202-222	R.B. Ni Sp	40	1.82	1.82	0.38
223-243	R.B. Ni Sp	60	2.08	1.42	0.826
244-264	R.B. Ni Sp	50	3.08	2.35	1.24
277-279	R.B. Ni Sp	50	3.51	2.88	1.01
280-282	R.B. Ni Sp w/10% CO_2	50	3.53	2.90	2.16
283-285	R.B. Ni Sp w/15% CO_2	50	3.63	3.00	2.67
286-288	R.B. Ni Sp w/20% CO_2	50	3.50	2.87	3.19
289-291	Sin. Ni	50	1.75	1.12	
292-294	Sin. Ni w/10% CO_2	50	1.76	1.13	
295-297	Sin. Ni w/15% CO_2	50	1.51	0.88	
298-300	Sin. Ni w/20% CO_2	50	1.81	1.81	
265	Blank	20	0		
268	Blank	40	0.66		
274	Blank	50	0.63		
271	Blank	60	0.73		

During the balance of this development work, cells were removed from each test temperature at every two-month test interval. Three cells of each group with nickel/nickel spinel, graphite/graphite spinel and one cell of the blank group were analyzed for capacity performance. KOH/K₂CO₃ content and electrode weight loss comparison were conducted. The following Tables 2-13, 2-14 and 2-15 summarizes the capacity data, electrolyte analysis and electrode weight.

From the capacity results, plots were developed showing cell capacities for nickel electrodes with and without spinel coating at 20°, 40° and 50°C as a function of time. These results are presented in Figures 2-4, 2-5 and 2-6. These figures which are the most important data obtained, show that after 12 months of float testing, all cells are still yielding capacities well above their 100 percent nominal capacities. As expected at the lower temperatures, the cells yielded higher capacities and at the same time it can also be seen that cells containing coated spinel graphite yielded capacities about 10 percent higher. Figure 2-7 shows the variation of carbonate content in the electrolyte as a function of temperature and time. It can be seen that cells containing nickel showed an increase of about 12 percent carbonate, where cells with only graphite showed an increase in carbonate of about 48 percent at the end of the 12-month period.

In addition to determining the affect of continuous float charge on the electrodes, after the 8th month, the resistivity and specific gravity of the KOH was recorded and compared to "clean" KOH. The summary of the data is presented in Table 2-16 and shows that the specific gravity of used KOH after 8, 10 and 12 months is lower than the fresh KOH. Although the resistivity of KOH didn't change with time it can be seen that it increased with temperature, in the electrolyte with nickel electrodes without spinel, but it is more stable in the electrolyte with spinel coated graphite.

From the nickel electrode weight loss results Figure 2-8 shows that after 12 months electrodes lost an average weight of 18 percent which is assumed to be carbon and collector oxidation. The graphite electrodes show a loss of about 82 percent. Since the graphite electrodes do not contain nickel, during charge the current is directly corroding 100 percent of the carbon, whereas in the nickel electrodes, the current is charging the active material and not totally corroding the graphite.

In order to determine the condition of the current collectors after 12 months on float, the collectors were stripped of the active materials and SEM micrographs were taken. Shown in Figures 2-9, 2-10 and 2-11 are collectors used in 20°, 40° and 50°C temperatures. For comparison a SEM of a "green" collector was also taken and is shown in Figure 2-12. Of importance is that the silver foil substrate does not show any evidence of oxidation even though the cobalt plating appears to be oxidized and lost at the 40° and 50°C temperatures.

TABLE 2-13. SUMMARY OF CAPACITY DATA OF CORROSION CELLS

Type(+)Plate	Temp.°C	Cap. After Form., Ah	Initial Discharge Capacity After, Ah			Residual Capacity After, Ah			Avg. D'Chge Voltage After Form.	Average Discharge Voltage, V		
			2 Mos.	4 Mos.	6 Mos.	2 Mos.	4 Mos.	6 Mos.		2 Mos.	4 Mos.	6 Mos.
R.B. Ni	20	2.39	2.63	2.38	2.43	3.07	2.76	2.92	1.166	1.129	1.144	1.155
R.B. Ni	40	2.39	2.23	2.11	2.33	2.75	2.42	2.61	1.123	1.055	.946	1.057
R.B. Ni	50	2.39	2.52	2.27	2.34	2.94	2.55	2.64	1.133	1.103	.934	.918
R.B. NiSp	20	2.43	2.66	2.51	2.75	3.20	3.05	3.18	1.144	1.145	1.164	1.158
R.B. NiSp	40	2.43	2.56	2.30	2.46	3.05	2.71	2.86	1.140	1.123	1.130	1.134
R.B. NiSp	50	2.39	2.60	2.31	2.43	2.99	2.70	2.70	1.140	1.106	.991	1.146

Type(+)Plate	Temp.°C	Cap. After Form., Ah	Initial Discharge Capacity After, Ah			Residual Capacity After, Ah			Avg. D'Chge Voltage After Form.	Average Discharge Voltage, V		
			8 Mos.	10 Mos.	12 Mos.	8 Mos.	10 Mos.	12 Mos.		8 Mos.	10 Mos.	12 Mos.
R.B. Ni	20	2.39	2.54	2.53	2.48	2.90	2.74	2.73	1.166	1.159	1.096	1.121
R.B. Ni	40	2.39	2.41	2.39	2.39	2.75	2.73	2.73	1.123	1.137	1.042	1.053
R.B. Ni	50	2.39	2.38	2.40	2.16	2.57	2.60	2.38	1.133	1.038	1.063	1.003
R.B. NiSp	20	2.43	2.60	2.90	2.51	3.03	3.27	2.97	1.144	1.167	1.157	1.121
R.B. NiSp	40	2.43	2.46	2.55	2.54	2.81	2.74	2.90	1.140	1.167	1.113	1.083
R.B. NiSp	50	2.39	2.31	2.34	2.27	2.54	2.57	2.56	1.140	1.047	1.109	1.051

TABLE 2-14. SUMMARY OF CORROSION TEST CELL DATA AFTER MONTHS 2, 4 & 6
Electrolyte Analysis

Cell Group #	Construction	Temp. °C	Electrolyte Analysis After Formation		After 2 Mos.		After 4 Mos.		After 6 Mos.	
			%KOH	%CO ₂	%KOH	%CO ₂	%KOH	%CO ₂	%KOH	%CO ₂
1-21	R.B. Ni(+)/R.B. CdO(-)	20	27.5	4.5	30.5	5.50	24.9	5.87	21.9	6.1
22-42	"	40	27.5	4.5	28.2	7.47	22.5	10.5	19.76	8.8
43-63	"	50	27.5	4.5	27.7	8.89	19.0	12.1	16.56	11.8
64-84	R.B. NiSp(+)/R.B. CdO(-)	20	26.1	5.3	28.6	6.14	24.3	6.66	22.8	6.7
85-105	"	40	26.1	5.3	25.7	8.77	21.5	10.6	20.0	8.77
106-126	"	50	26.1	5.3	25.2	9.46	19.2	11.9	17.76	10.5
127-129 265-267	(Blanks) Ag ⁺ /NiCo Pl.(+)/Ni ⁰ (-)	20	34.4	0.6	34.7	1.18	33.5	1.42	35.3	1.519
130-132 268-270	"	40	34.4	0.6	36.0	2.46	35.2	1.12	25.2	1.548
133-135 271-273	"	60	34.4	0.6	36.0	2.17	39.5	1.74	42.8	2.17
136-138 274-276	"	50	34.4	0.6	35.5	1.21	33.4	1.04	32.5	1.508
139-159	R.B. C ⁰ (+)/Ni ⁰ (-)	20	33.8	1.2	35.0	2.57	28.4	3.49	30.35	6.34
160-180	"	40	33.8	1.2	29.4	8.4	17.5	20.0	11.5	23.2
181-201	"	60	33.8	1.2	22.0	14.89	3.57	49.3	3.64	48.0
202-222	R.B. C ⁰ Sp(+)/Ni ⁰ (-)	20	33.8	0.77	34.9	3.26	29.9	2.65	28.2	5.24
223-243	"	40	35.7	0.77	26.4	7.06	18.6	19.6	17.6	20.2
244-264	"	60	35.7	0.77	25.9	10.60	8.32	36.2	1.96	42.0

TABLE 2-14. SUMMARY OF CORROSION TEST CELL DATA AFTER MONTHS 8, 10 & 12 (Continued)
Electrolyte Analysis

Cell Group #	Construction	Temp. °C	Electrolyte Analysis After Formation		After 8 Mos.		After 10 Mos.		After 12 Mos.	
			%KOH	%CO ₂	%KOH	%CO ₂	%KOH	%CO ₂	%KOH	%CO ₂
1-21	R.B. Ni(+)/R.B. CdO(-)	20	27.5	4.5	24.7	6.59	24.9	6.45	22.3	7.8
22-42	"	40	27.5	4.5	17.7	10.95	17.3	12.7	15.4	14.9
43-63	"	50	27.5	4.5	15.13	13.76	13.6	13.73	13.3	16.5
64-84	R.B. NiSp(+)/R.B. CdO(-)	20	26.1	5.3	23.9	7.42	23.8	8.15	22.5	7.3
85-105	"	40	26.1	5.3	18.17	11.3	16.9	13.69	15.9	14.8
106-126	"	50	26.1	5.3	15.9	11.8	14.37	13.88	12.6	14.4
127-129 265-267	(Blanks) Ag ⁺ /NiCo Pl.(+)/Ni ⁰ (-)	20	34.4	0.6	36.1	.493	34.6	1.01	34.7	1.27
130-132 268-270	"	40	34.4	0.6	28.9	1.87	26.0	1.90	25.5	1.27
133-135 271-273	"	60	34.4	0.6	25.1	2.52	30.18	2.35	32.6	4.75
136-138 274-276	"	50	34.4	0.6	26.8	1.92	24.3	1.61	27.7	1.61
139-159	R.B. C ⁺ /Ni ⁰ (-)	20	33.8	1.2	29.16	7.51	26.0	8.61	24.5	9.0
160-180	"	40	33.8	1.2	5.74	30.0	3.14	44.2	2.6	40.8
181-201	"	60	33.8	1.2	4.11	31.57	5.68	41.71	5.3	43.8
202-222	R.B. C ⁺ Sp(+)/Ni ⁰ (-)	20	33.8	0.77	23.4	6.46	25.87	7.37	25.3	9.0
223-243	"	40	35.7	0.77	7.65	28.55	6.6	31.83	4.0	40.7
244-264	"	60	35.7	0.77	.69	36.8	3.60	45.1	3.7	47.7

TABLE 2-15. WEIGHT LOSS OF CELL COMPONENTS FOR MONTHS 2, 4 & 6

Type (+) Plate	Temp. °C	Average Wt. Loss, gms			Net Wt. Loss, gms			C° Loss Calc. From Final K ₂ CO ₃ /gms		
		2 Mos.	4 Mos.	6 Mos.	2 Mos.	4 Mos.	6 Mos.	2 Mos.	4 Mos.	6 Mos.
R.B. C°	20	1.68	1.43	1.92	1.68	1.43	1.49	0.13	0.18	.32
R.B. C°	40	2.25	2.60	3.24	1.59	2.50	2.86	0.427	0.99	1.16
R.B. C°	60	2.60	3.50	4.55	1.87	3.11	4.21	0.756	2.31	2.4
R.B. C° Sp	20	1.82	1.04	1.57	1.82	1.04	1.14	0.165	0.13	.262
R.B. C° Sp	40	2.08	2.69	2.72	1.42	2.59	2.34	0.36	0.97	1.01
R.B. C° Sp	60	3.08	3.79	5.12	2.35	3.40	4.78	0.54	1.79	2.11
R.B. Ni	20	2.81	2.88	2.45	2.81	2.88	2.02	0.254	0.276	.28
R.B. Ni	40	3.51	2.47	2.43	2.85	2.37	2.05	0.346	0.491	.41
R.B. Ni	50	3.93	2.76	3.24	3.30	2.54	3.0	0.412	0.568	.55
R.B. Ni Sp	20	3.42	2.46	2.54	3.42	2.46	2.11	0.284	0.313	.315
R.B. Ni Sp	40	3.56	2.82	4.15	2.90	2.72	3.77	0.406	0.498	.41
R.B. Ni Sp	50	3.31	3.04	3.16	2.68	2.82	2.92	0.439	0.559	.491
Blank	20	0	0	0.43						
Blank	40	.66	.10	0.38						
Blank	50	.63	.22	0.24						
Blank	60	.73	.39	0.34						

TABLE 2-15. WEIGHT LOSS OF CELL COMPONENTS AFTER MONTHS 8, 10 & 12 (Continued)

Type (+) Plate	Temp. °C	Average Wt. Loss, gms			Net Wt. Loss, gms			C° Loss Calc. From Final K ₂ CO ₃ /gms		
		8 Mos.	10 Mos.	12 Mos.	8 Mos.	10 Mos.	12 Mos.	8 Mos.	10 Mos.	12 Mos.
R.B. C°	20	1.27	1.35	1.68	.98	1.00	1.36	.38	.45	.45
R.B. C°	40	3.28	3.81	3.28	2.58	2.96	2.71	1.50	2.21	2.04
R.B. C°	60	5.30	4.87	4.59	4.77	3.75	3.68	1.58	2.09	2.19
R.B. C° Sp	20	1.26	1.32	1.65	.97	.97	1.33	.32	.37	.45
R.B. C° Sp	40	3.37	3.51	3.76	2.67	2.66	3.19	1.43	1.59	2.04
R.B. C° Sp	60	4.78	5.32	5.06	4.25	4.20	4.15	1.81	2.26	2.39
R.B. Ni	20	2.09	1.99	2.03	1.80	1.64	1.71	.31	.30	.36
R.B. Ni	40	2.03	2.43	2.15	1.33	1.58	1.58	.51	.59	.69
R.B. Ni	50	2.50	2.83	2.62	1.52	1.78	2.02	.64	.64	.77
R.B. Ni Sp	20	1.87	1.61	2.45	1.58	1.26	2.13	.34	.38	.34
R.B. Ni Sp	40	2.54	2.77	2.86	1.84	1.92	2.29	.53	.64	.69
R.B. Ni Sp	50	2.68	3.07	3.19	1.70	2.02	2.54	.55	.65	.67
Blank	20	.29	.35	.32						
Blank	40	.70	.85	.57						
Blank	50	.98	1.05	.65						
Blank	60	.53	1.12	.91						

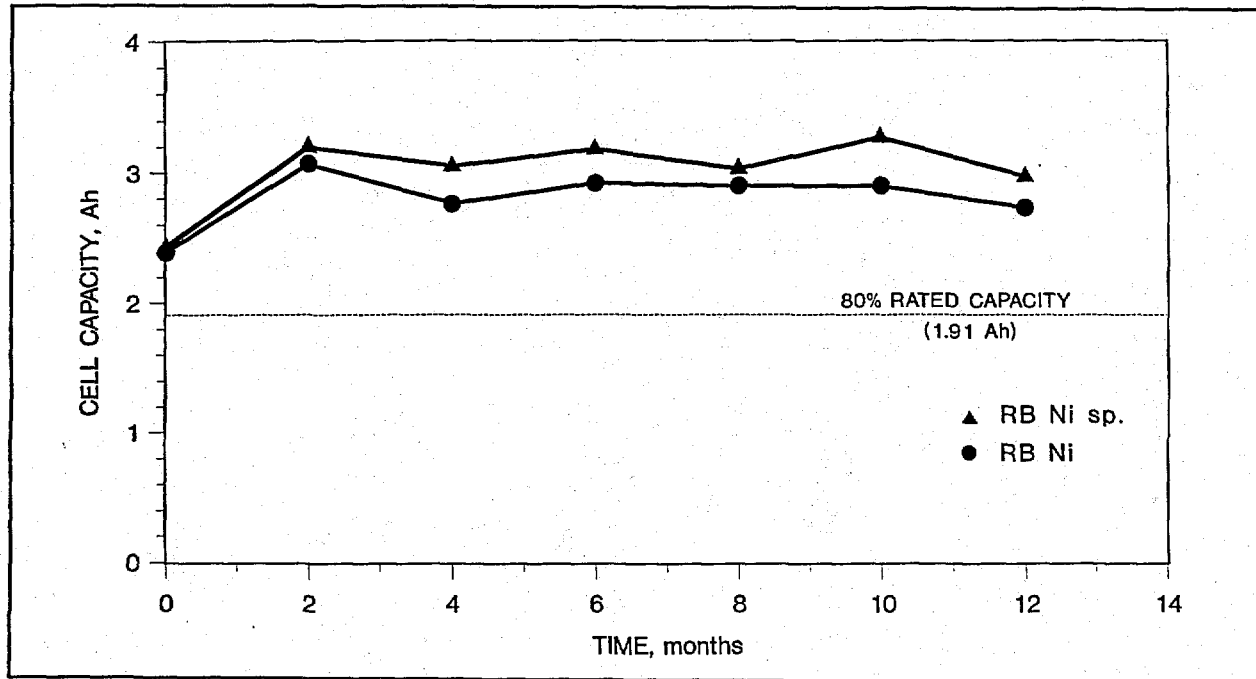


FIGURE 2-4. SUMMARY OF CORROSION CELL CAPACITIES
2nd Discharge @ 20°C

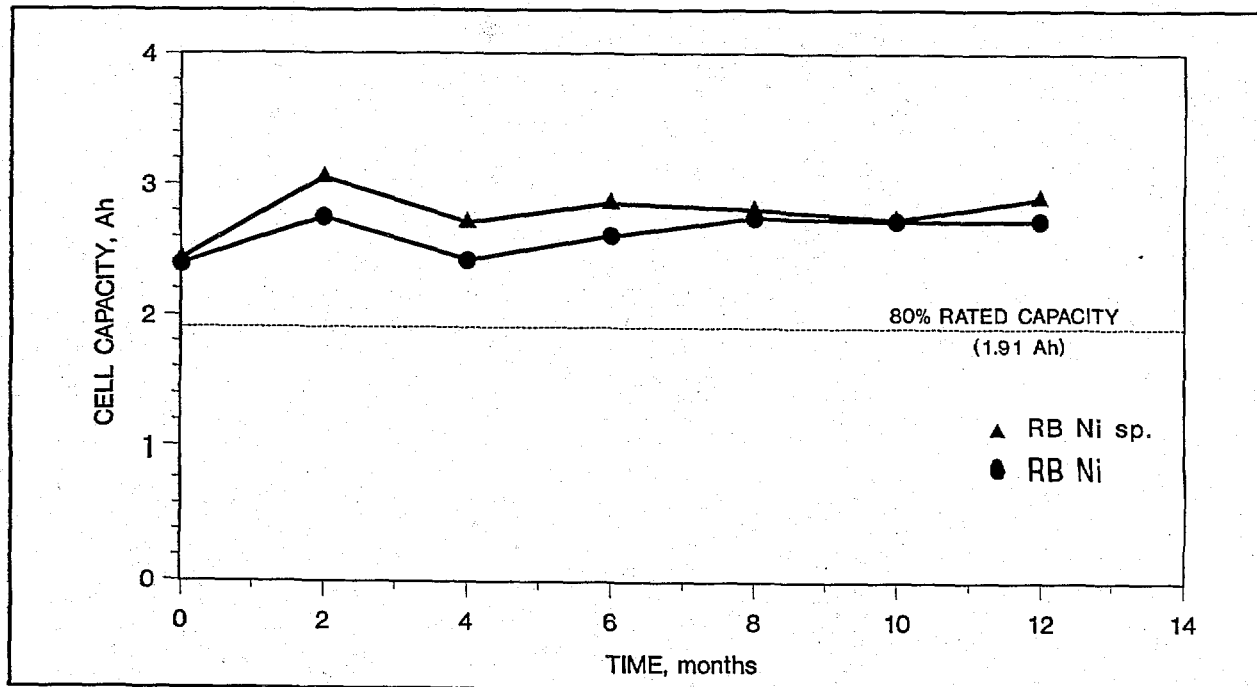


FIGURE 2-5. SUMMARY OF CORROSION CELL CAPACITIES
2nd Discharge @ 40°C

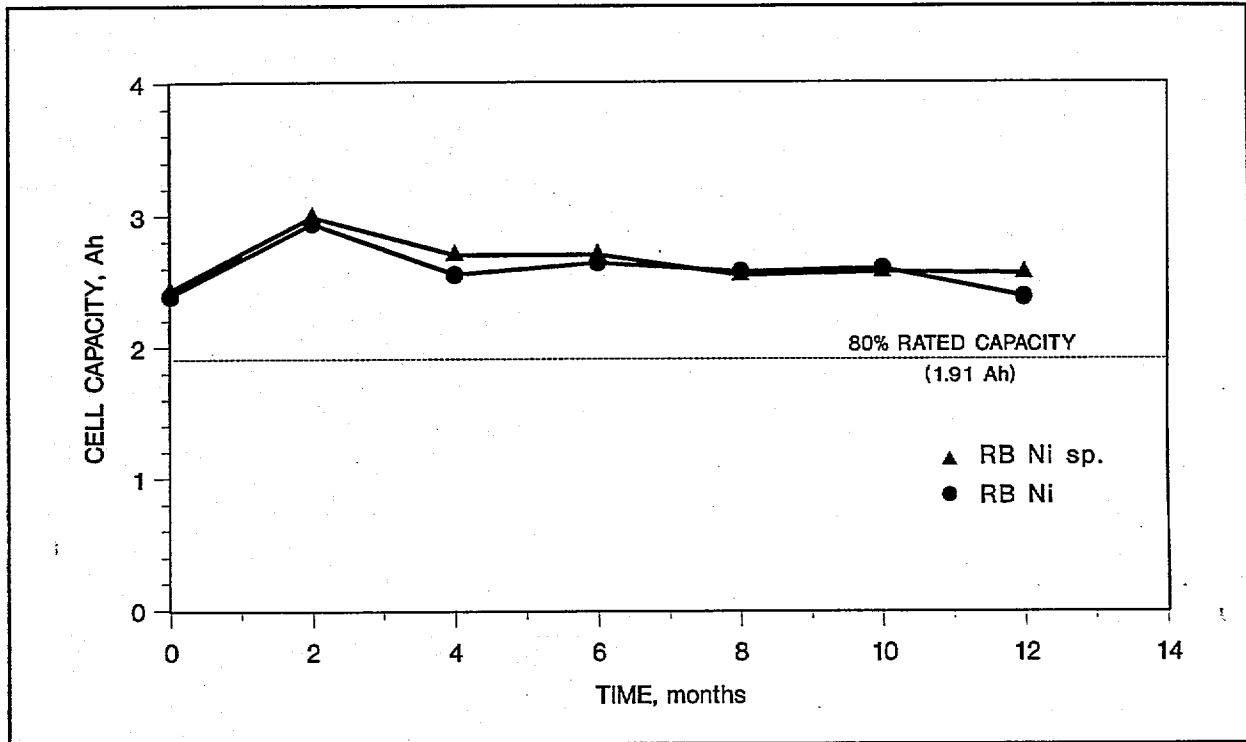


FIGURE 2-6. SUMMARY OF CORROSION CELL CAPACITIES
2nd Discharge @ 50°C

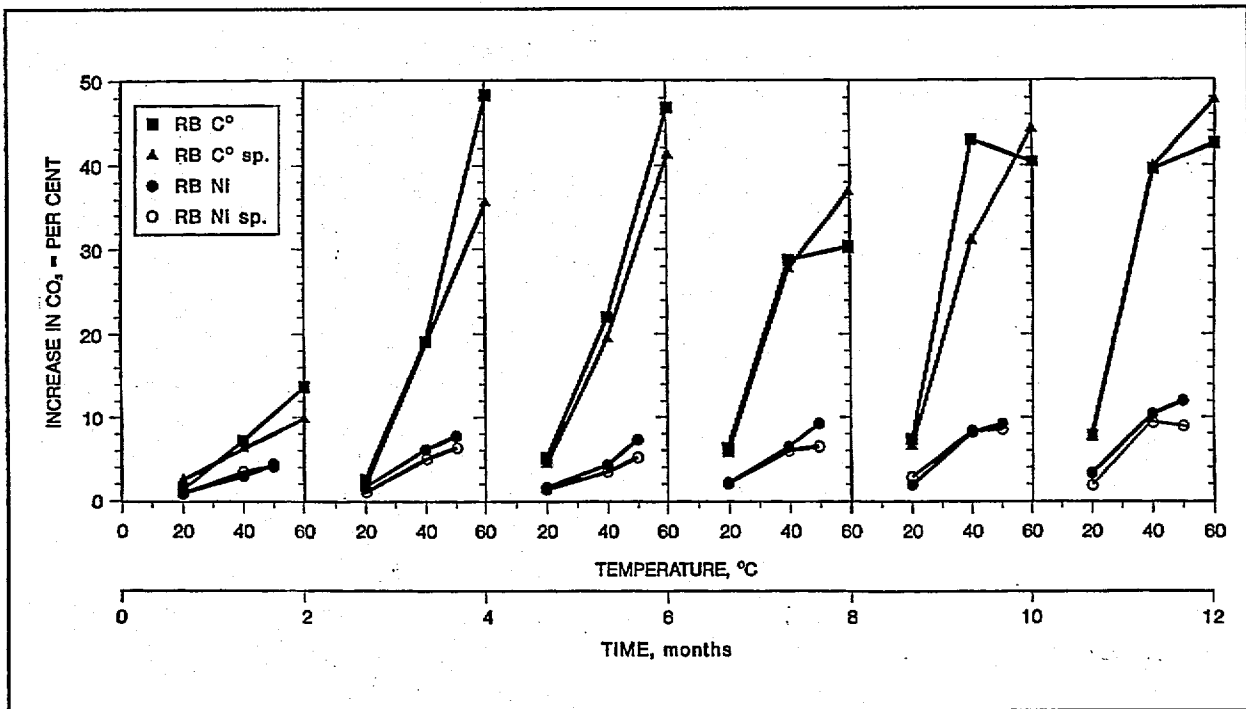


FIGURE 2-7. VARIATION OF CARBONATE CONTENT WITH TEMPERATURE
IN BONDED NICKEL ELECTRODE CELLS

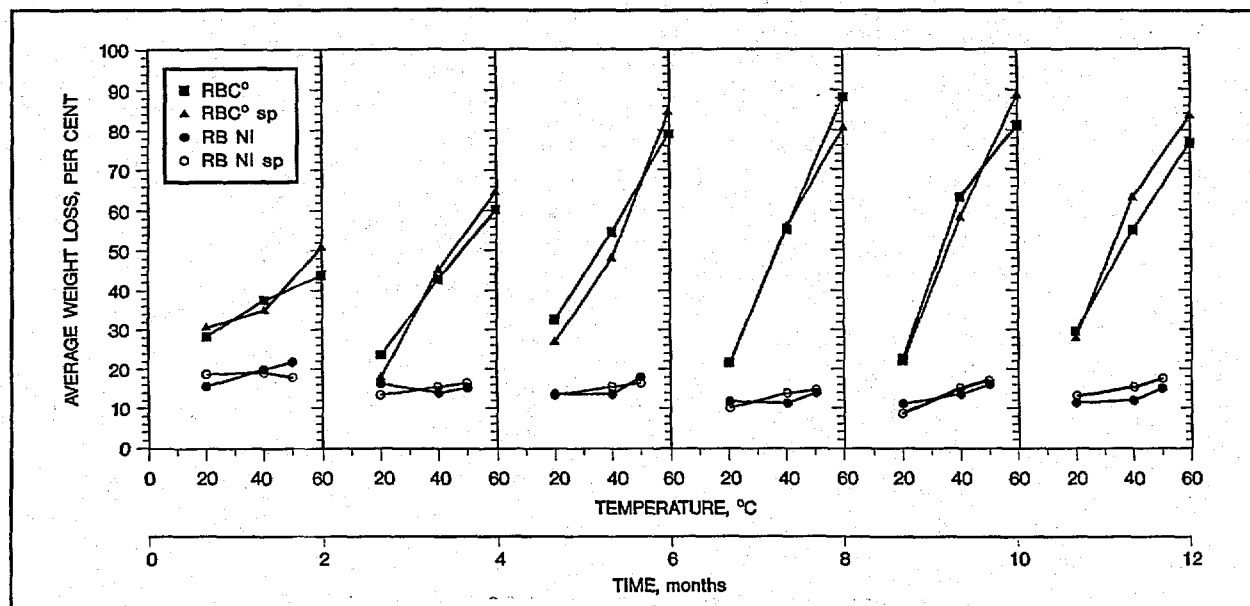


FIGURE 2-8. WEIGHT LOSS VS. TEMPERATURE ON FLOAT

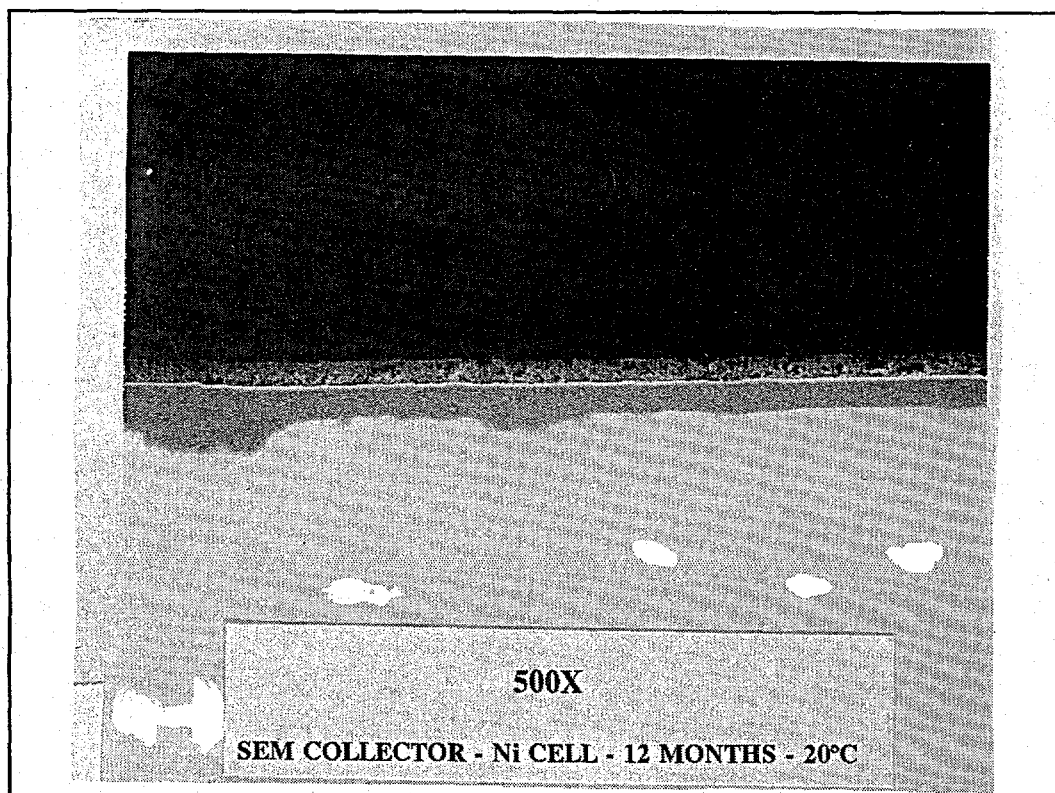


FIGURE 2-9. SEM MICROGRAPH @ 20°C

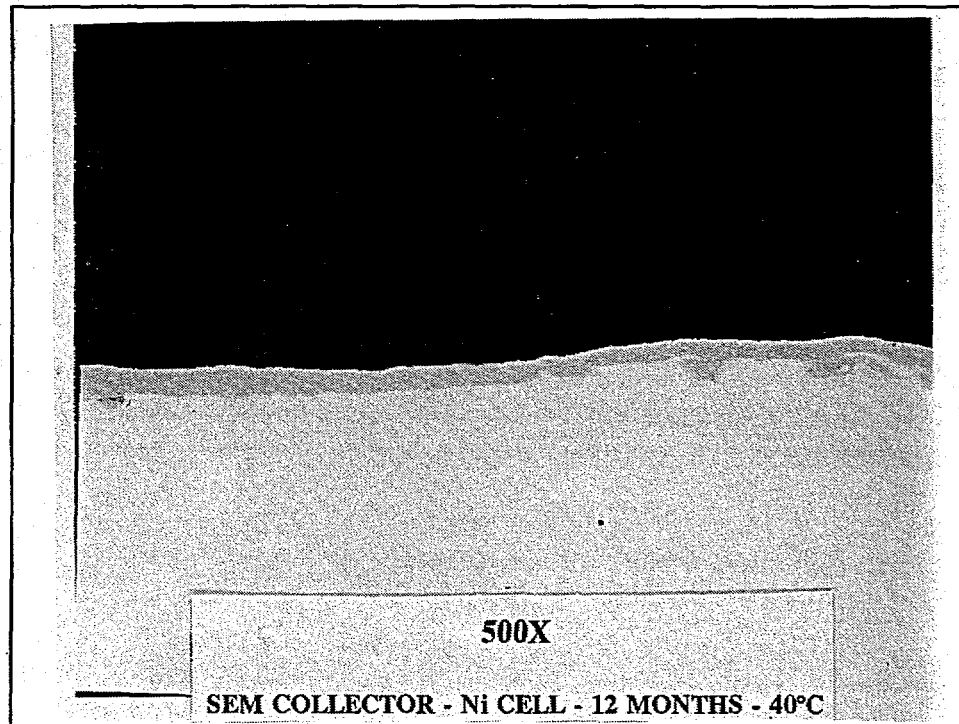


FIGURE 2-10. SEM MICROGRAPH @ 40°C

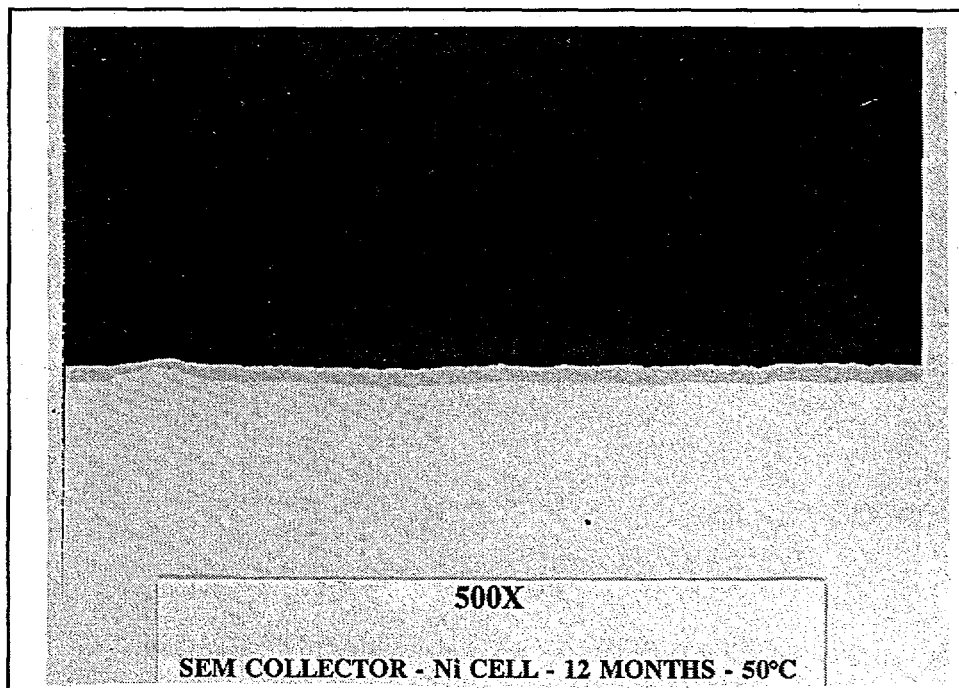


FIGURE 2-11. SEM MICROGRAPH @ 50°C

TABLE 2-16. SUMMARY OF CORROSION TEST CELL DATA
CONDUCTIVITIES OF ELECTROLYTE & SPECIFIC GRAVITIES

Cell No.			Cell Construction	Temperature °C	Resistivity of KOH (ohm-cms) Months 8-10-12	Specific Gravity (g/ml)		
						8 Mos.	10 Mos.	12 Mos.
10	13	16	R.B. Ni	"	1.016	1.30	1.33	1.29
11	14	17	"	"	1.333	1.30	1.30	1.34
12	15	18	"	"	1.016	1.33	1.33	1.30
73	76	79	R.B. NiSp	"	1.778	1.31	1.32	1.31
74	77	80	"	"	2.032	1.30	1.36	1.29
75	78	81	"	"	1.968	1.30	1.34	1.31
31	34	37	R.B. Ni	40	1.651	1.36	1.36	1.31
32	35	38	"	"	2.159	1.27	1.32	1.33
33	36	39	"	"	1.905	1.31	1.36	1.31
94	97	100	R.B. NiSp	"	2.286	1.30	1.32	1.29
95	98	101	"	"	1.968	1.28	1.32	1.31
96	99	102	"	"	1.714	1.28	1.32	1.30
53	55	58	R.B. Ni	50	4.127	1.30	1.33	1.32
54	56	59	"	"	3.492	1.27	1.29	1.32
55	57	60	"	"	2.222	1.28	1.30	1.32
115	118	121	R.B. NiSp	"	1.778	1.27	1.26	1.32
116	119	122	"	"	1.905	1.28	1.29	1.34
117	120	123	"	"	2.159	1.27	1.30	1.29
Fresh KOH				20 (RT)	.92	1.34	1.34	1.34

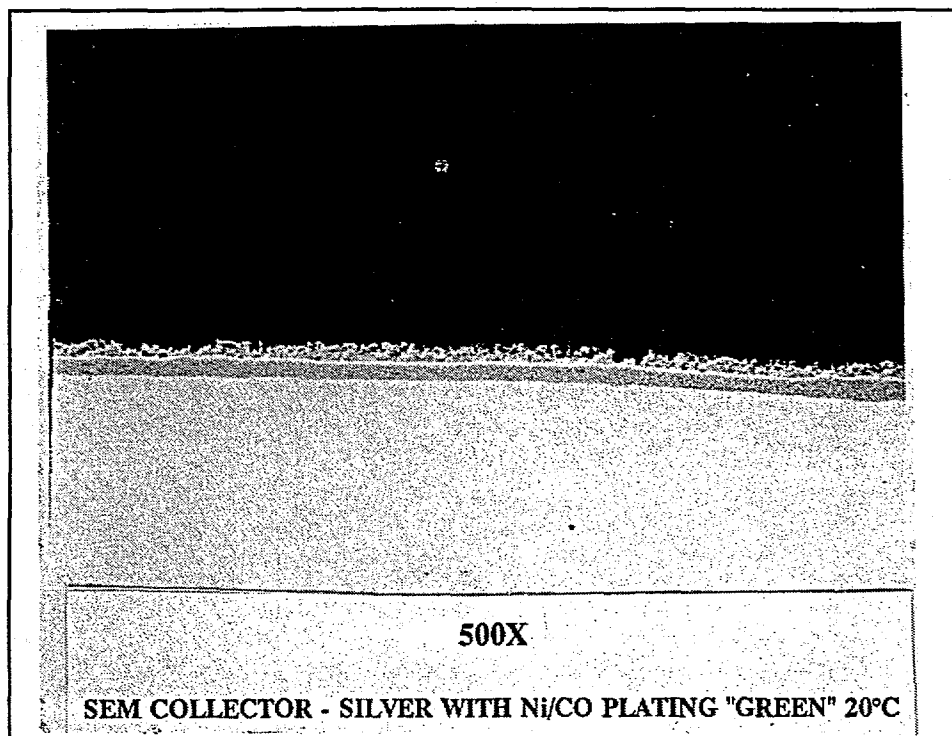


FIGURE 2-12. SEM MICROGRAPH "GREEN" ELECTRODE

Porosity measurements were also conducted on electrodes of preformation, 20°, 40° and 50°C tests, and compared to a "green" electrode. Table 2-17 presents the porosity results. Plots of each sample are presented in Figures 2-13, 2-14, 2-15, 2-16 and 2-17. From these results it can be seen that the porosity increases after the preformation period and a small decline from 33 percent to 28 percent occurred. This small reduction is due to a possible reaction of the active material with water which tends to swell the active material, with the formation of hydrates, hence reducing the porosity. The small net increase in porosity observed in these results could be the reason why the cells after 12 months are still performing above their normal capacity even though substantial oxidation of the carbon took place. The increased porosity allows extra electrolyte to penetrate the active material allowing better electrochemical utilization. This is true when a comparison is made of the cell porosities as a function of temperature, as less electrolyte penetrates the electrodes, a small reduction in capacity is observed.

TABLE 2-17. ELECTRODE POROSITY

Period of Performance	Temperature (°C)	Porosity %
"Green"	20	25
Preformation	20	33
12	20	30
12	40	32
12	50	28

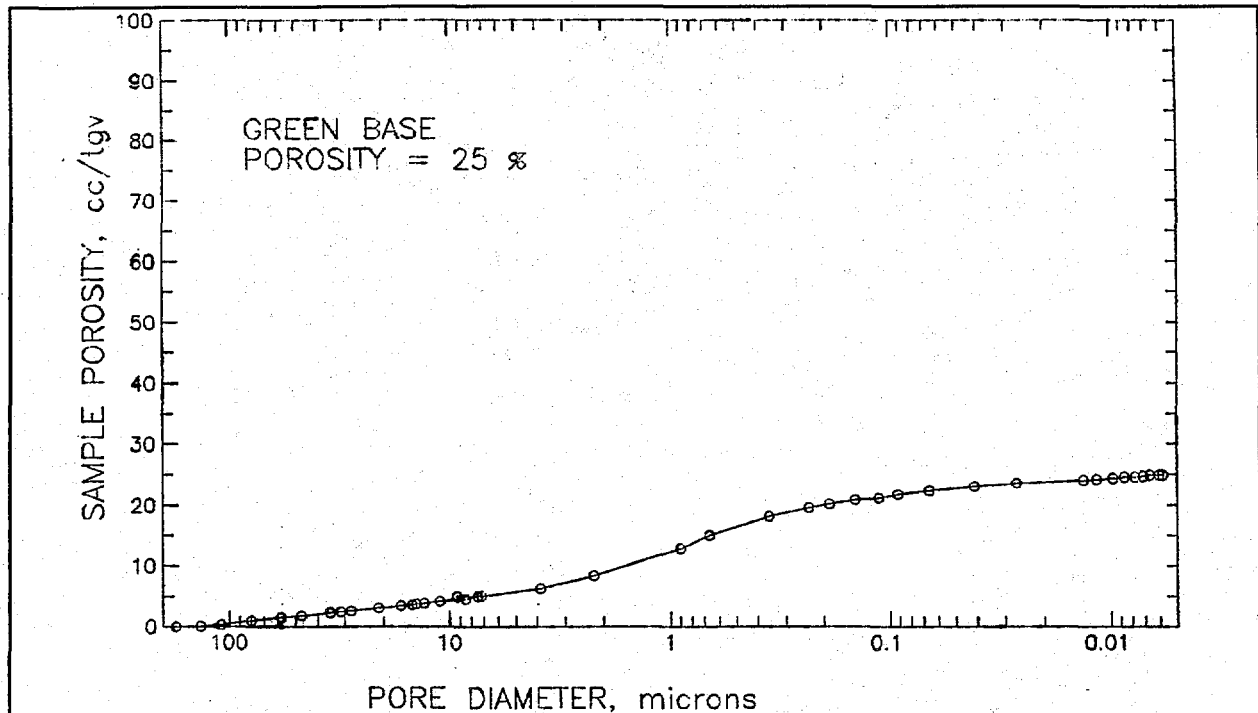


FIGURE 2-13. POROSITY "GREEN" ELECTRODE

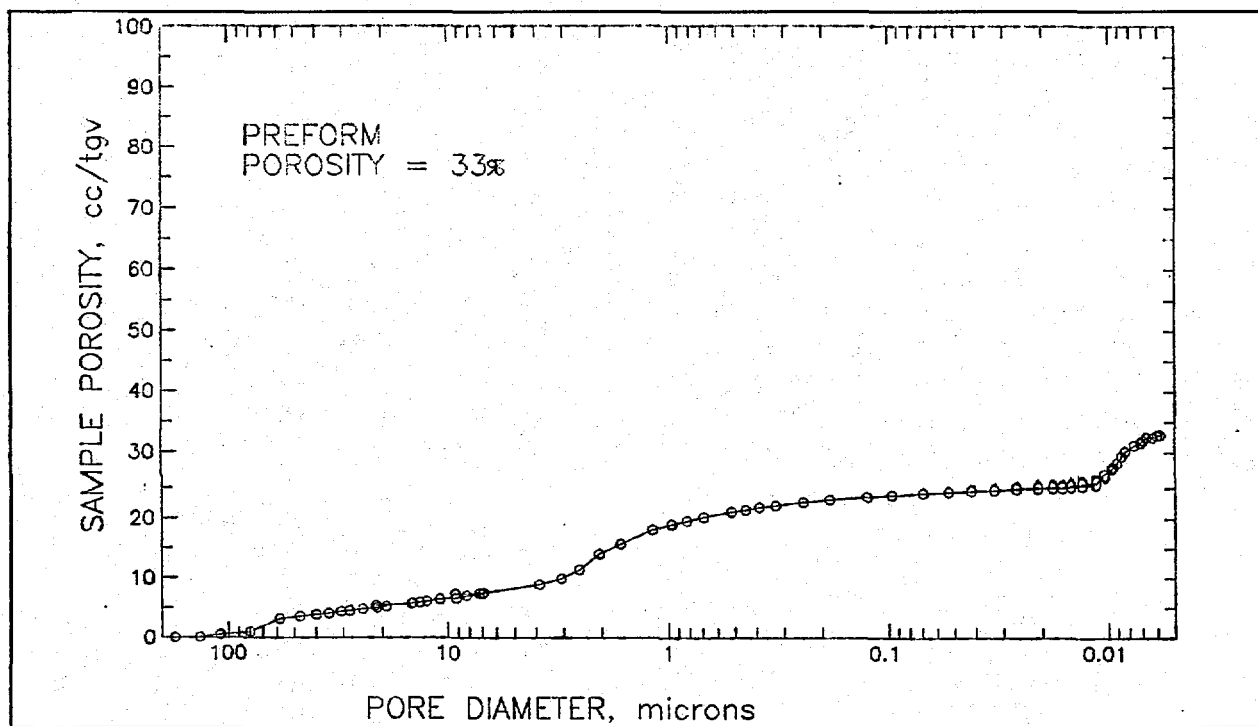


FIGURE 2-14. POROSITY PREFORM ELECTRODE

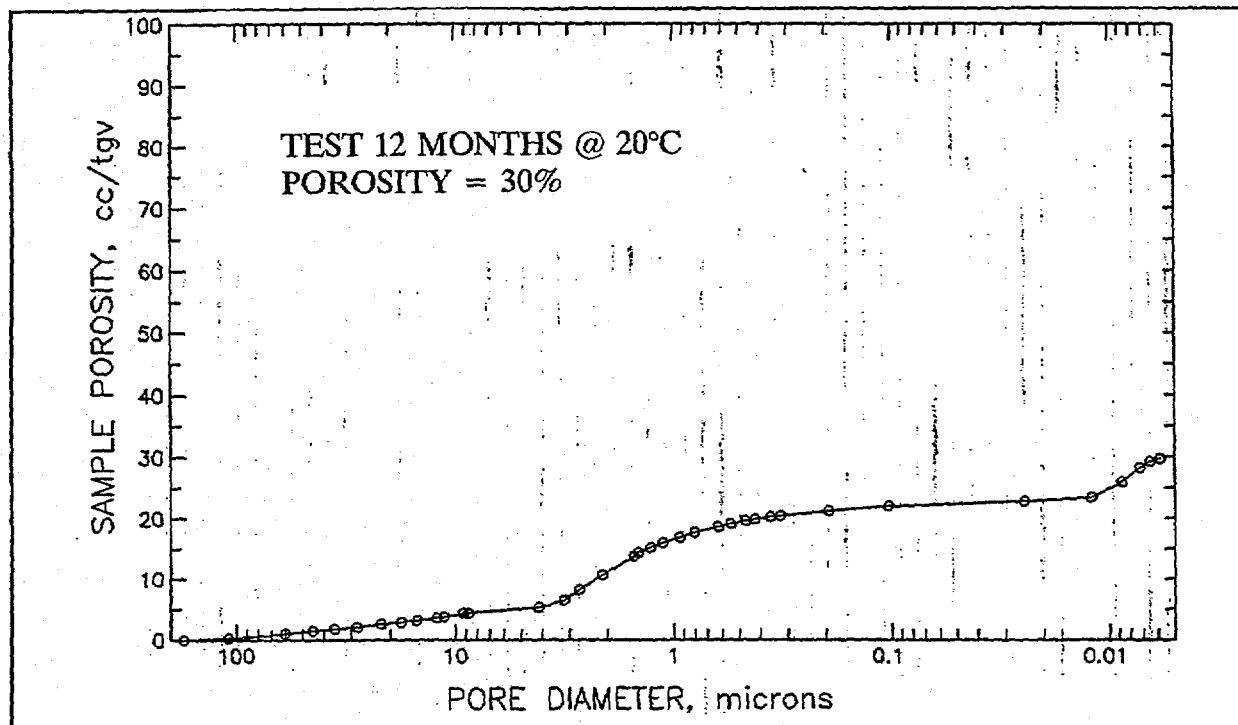


FIGURE 2-15. POROSITY 20°C ELECTRODE

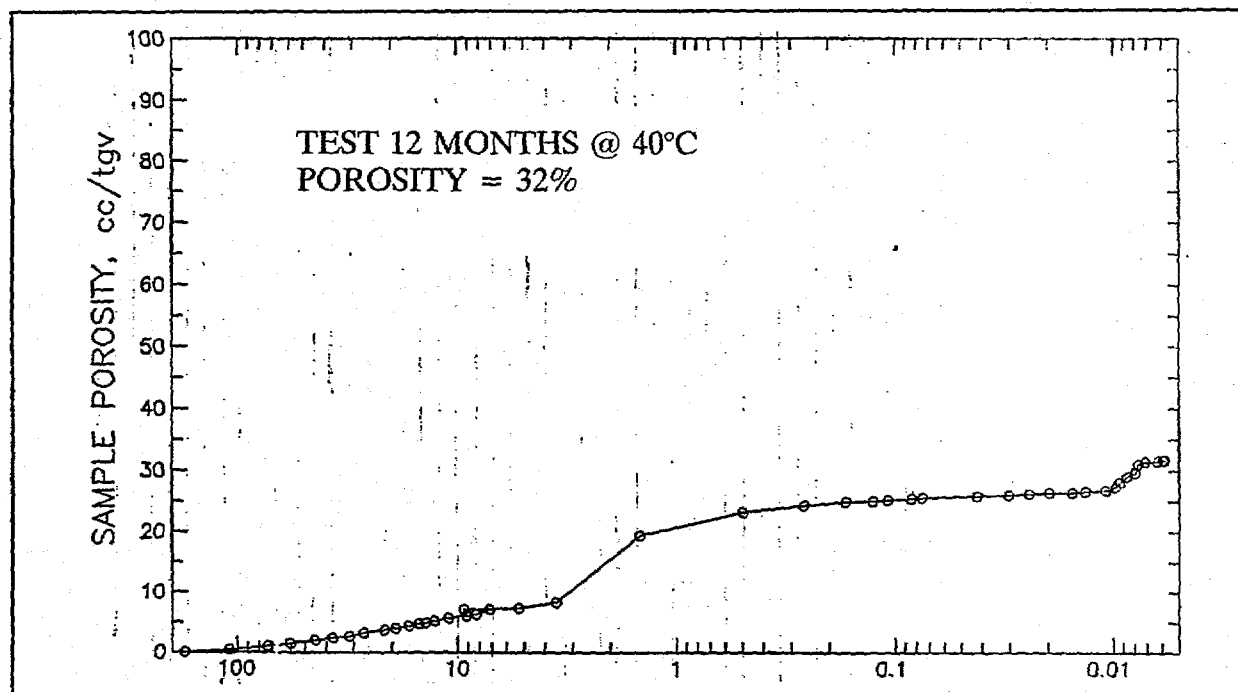


FIGURE 2-16. POROSITY 40°C ELECTRODE

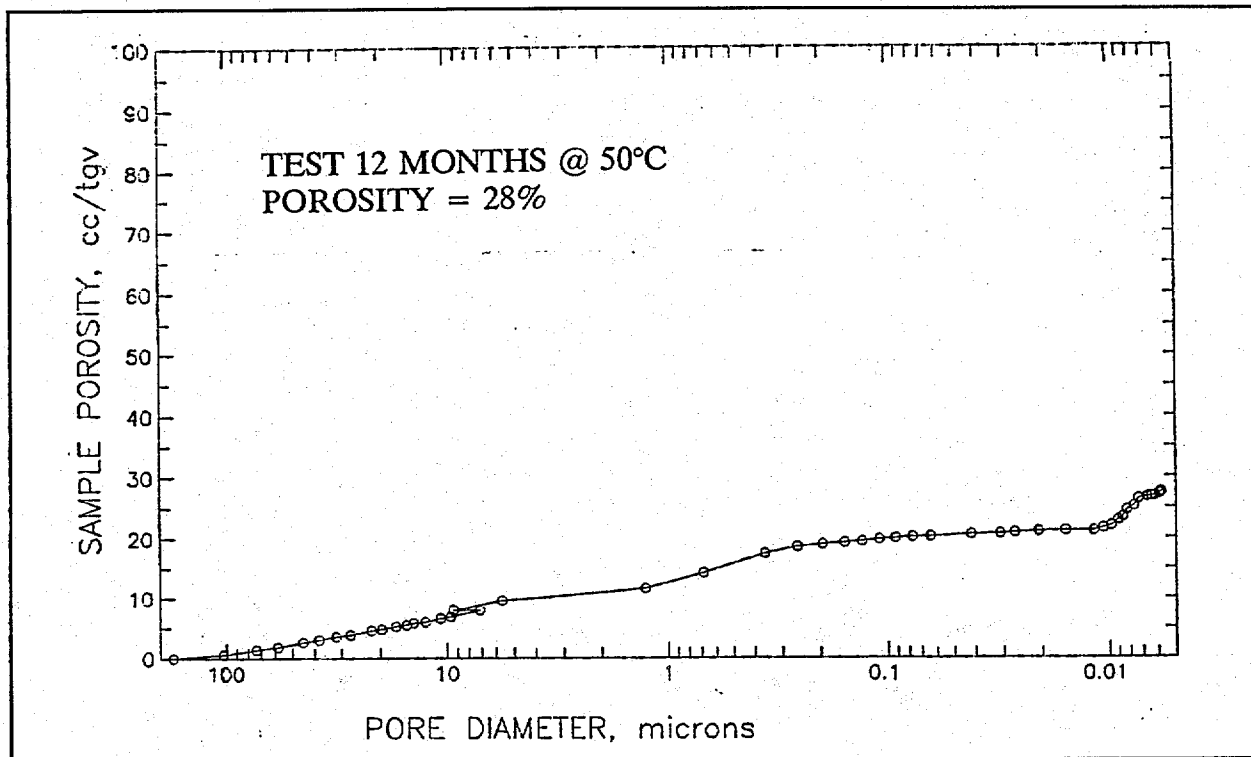


FIGURE 2-17. POROSITY 50°C ELECTRODE

The results obtained during these 12 months of carbon corrosion can be summarized and a long-term life prediction made.

An extrapolation of the carbon corrosion over 12 months can be made to predict the long-term life for this type of electrode. These results are presented in Figure 2-18, and show the average net carbon loss percent of total carbon as a function of months calculated as doubling/ 10°C increase in temperature. As indicated the nickel cells have accumulated 96 months of accelerated life (8 years) and still yielding above 100 percent of rated capacity. Although these extrapolated results indicate that a 10-year life is attainable, more corrosion tests would be necessary.

TASK 3 - FABRICATION OF SIX ADVANCED 2000-Ah NI-CD CELLS

During Phase I, ERC designed and built eight 2000-Ah cells to demonstrate 500 cycles. Two of these cells eventually developed mechanical shorts. After cell dissection, the analysis of cell components indicated that the internal shorts were caused by improper current collector design. A new current collector design was proposed which would demonstrate the cycling capability and component reproducibility of ERC's cell.

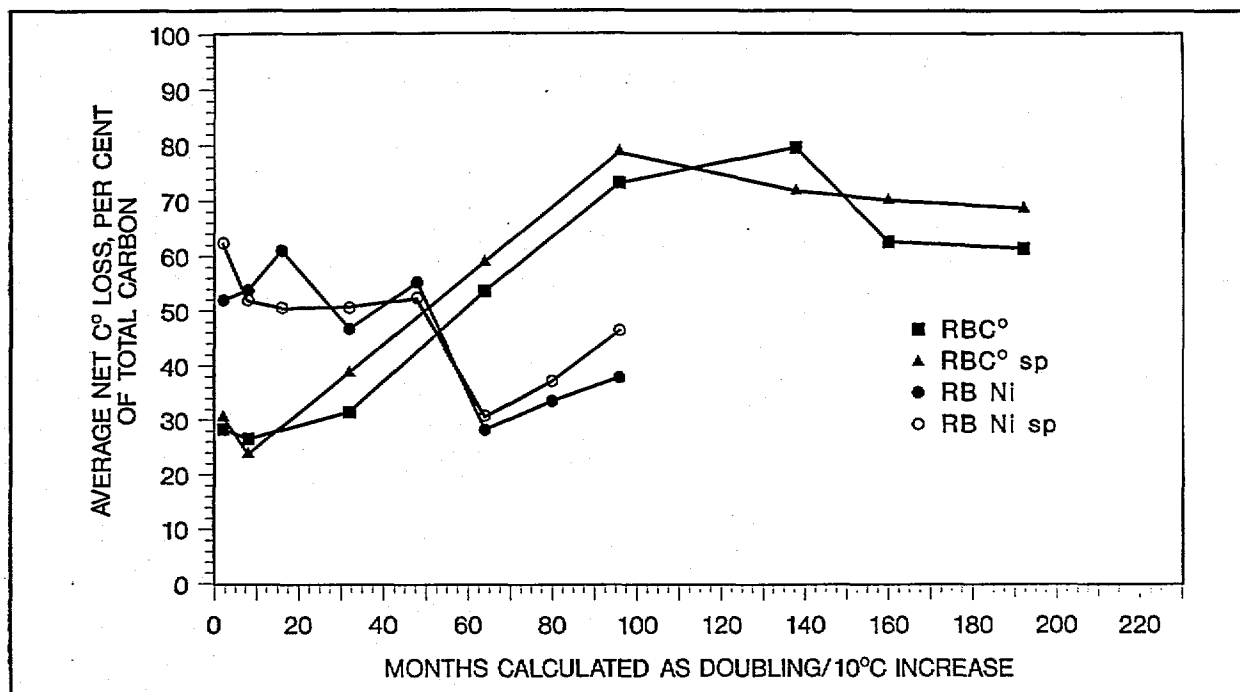


FIGURE 2-18. NET CARBON LOSS VS. ACCELERATED ESTIMATED LIFE FOR NICKEL AND GRAPHITE ELECTRODE

The sub-tasks presented below will show in detail the work that established ERC's cell performance of at least 500 cycles without the occurrence of mechanical shorts.

Subtask 3.1 Design and Assembly of the Piercing Machine

To improve the mechanical bond between the positive current collector silver foil and the active material $\text{Ni}(\text{OH})_2$, protrusions are made on both sides of the collector foil, (see Figure 2-19). This technique is accomplished by passing foil between two rollers containing pins which penetrate the foil from both sides (see Figure 2-20 - Piercing Machine).

During fabrication of the positive current collector material, under Phase I, the male and female discs in the existing piercing machine were consumed. A new set of male and female discs were designed, machined and assembled in the existing piercing machine. As it will be explained in detail in Subtask 3.2, these discs were designed not only to produce lower protrusions but also to produce a blank margin on each side of the collector as a design improvement to prevent mechanical shorts.

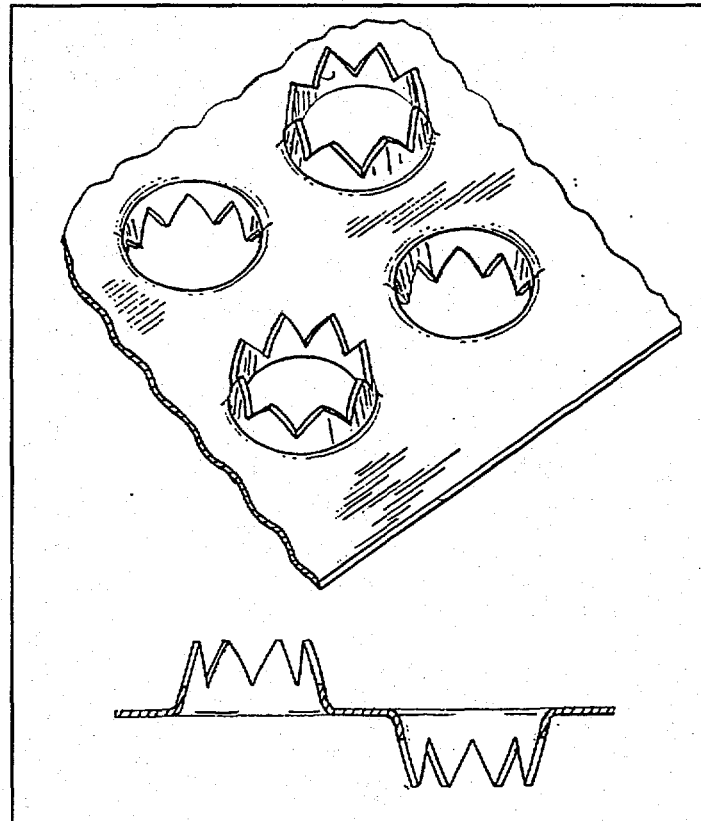


FIGURE 2-19. PIERCED FOIL

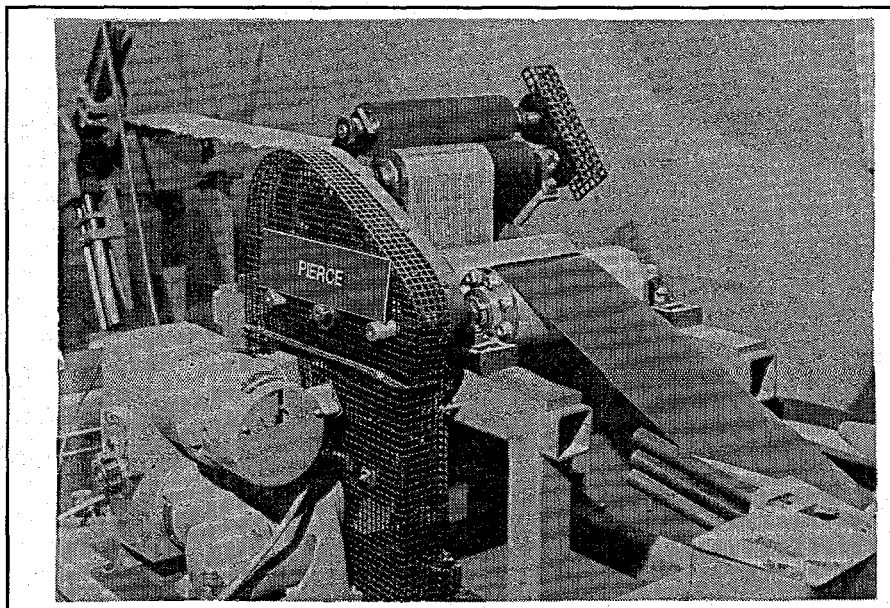


FIGURE 2-20. PIERCING MACHINE

All parts were ordered and the assembly of the discs was finalized. Upon completion of disc assembly, a preliminary test run was performed. After minor adjustments final run was performed. The piercing machine ran according to expectations and the entire lot of silver foil, positive current collector material was pierced.

Subtask 3.2 Design New Current Collector

In order to prevent the recurrence of mechanical shorts which were identified during examination of 2 shorted 2000-Ah cells from Phase I, a collector redesign task was initiated. The main focus under the task was to reduce the projection heights of the collector material and yet maintain an adequate mechanical bond between the collector and active material. A delamination test indicated that projections of .040-inch provided sufficient bonding between collector and active material. At the same time no penetration of the piercing through the active material was observed when pressing the electrode to the proper plate thickness. As to further prevent any mechanical shorts, incorporated into the collector design was a 1/4-inch wide flat selvage margin on all sides. Figure 2-21 shows the existing and proposed collector design.

All positive electrodes for the six 2000-Ah cells were manufactured using this new collector design.

Subtask 3.3 Assembly of Test Equipment - 2000-Ah Cell Cycle

To fulfill the cycling requirements set forth in Task 3.5 an automatic cycler was necessary. The existing 4000 Amp power supply together with the cycling equipment was disassembled at the conclusion of Phase I work. This equipment had to be reassembled to provide testing capabilities for the six 2000-Ah cells under test cycling as well as for the capacity test discharges for the cells on the float regime. The power supply/cycler equipment has the ability to automatic charge and discharge cells and monitor, charging/discharging currents, time, individual cell voltages and temperatures. A data recorder logs time and rate of charge/discharge, cell voltage, temperature and number of cycles accumulated. After several preliminary runs the test equipment was finalized and both types of cells were tested using this automatic cycler equipment.

Subtask 3.4 Manufacture of 6 Advanced 2000-Ah Ni-Cd Cells

Based on the performance obtained on each of the 2000-Ah cell designs under Phase I, it was determined that Design No. 2002 showed the best results. Presented below is the electrochemical design used to manufacture the 6 advanced 2000-Ah Ni-Cd cells.

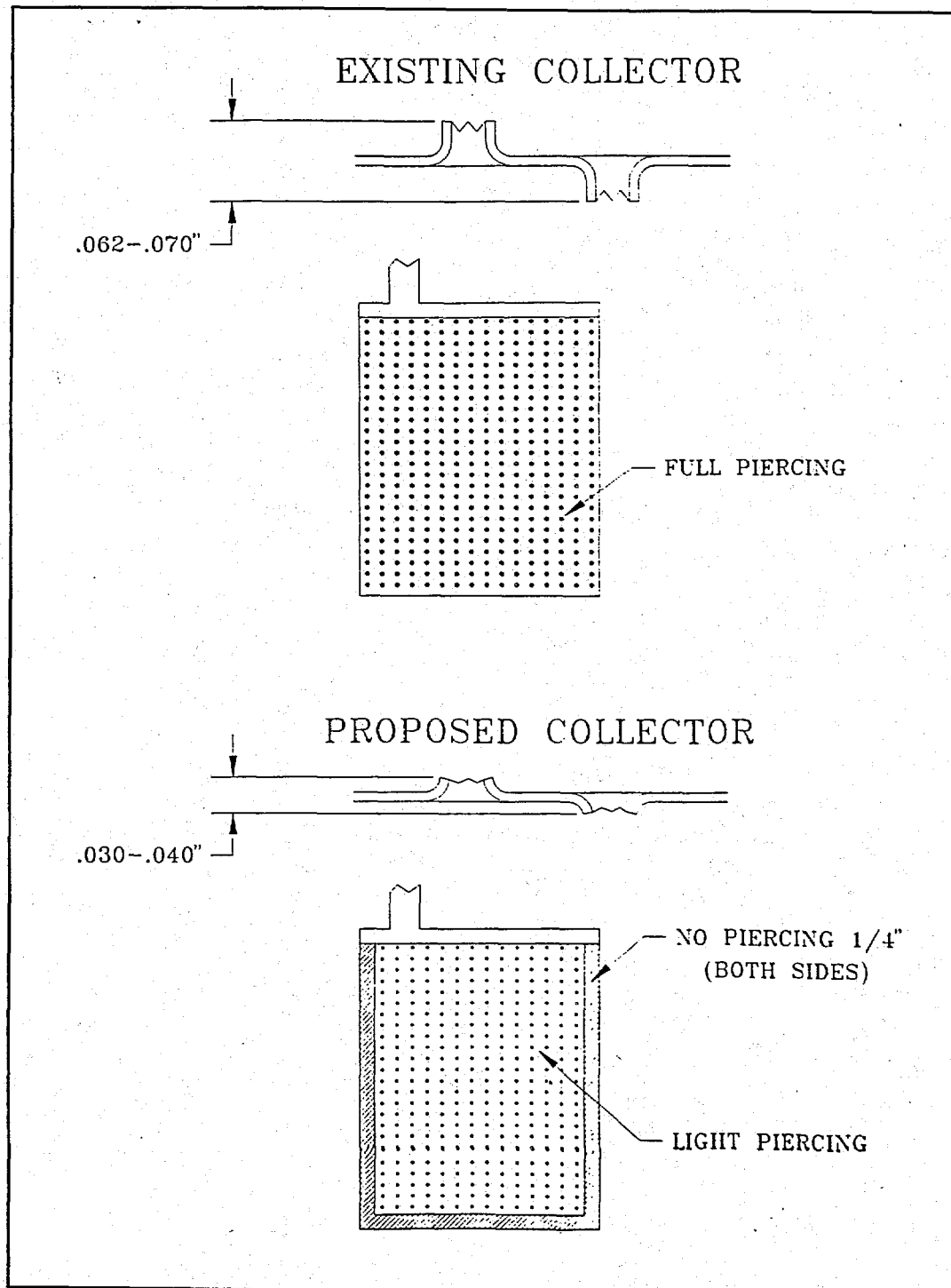


FIGURE 2-21. COMPARISON OF COLLECTOR DESIGN IMPROVEMENT

2000-Ah Cell Design

Positive Plates:	40
Electrode Dimensions:	20-inch H x 12-inch W x .058-inch T
Mix Formula:	67 percent Ni(OH) ₂ + 30 percent graphite* + 3 percent TFE
Collector:	.003-inch thick pierced silver foil to be nickel and cobalt plated
Nominal Capacity:	2000-Ah at 1-hour rate
Negative Electrodes:	44
Dimensions:	20-inch H x 12-inch W x .024-inch T
Mix Formula:	90 percent CdO + 8 percent Ni(OH) ₂ + 2 percent TFE
Collector:	.004-inch thick perforated copper foil nickel plated
Theoretical Capacity:	4400 Ah
Separator:	Positive - Celgard Negative - Two layers of Pellon .005-inch
Electrolyte:	35 percent KOH + 1 percent LiOH by weight

*Note: Graphite coated with 5 percent cobalt spinel

Figure 2-22 shows the 2000-Ah Ni-Cd cell pack assembly.

Upon completion of cell assembly, each cell was filled with approximately 13,000 cc of 35 percent KOH + 1 percent LiOH, followed by a soaking period of 96 hours. Following the soaking period each cell was given 6 formation cycles consisting of:

1st Charge at 250 Amps for 20 hrs
Discharge at 500 Amps to 1.00 V/cell

2nd Charge at 250 Amps for 16 hrs
Discharge at 500 Amps to 1.00 V/cell

3rd Charge at 250 Amps for 16 hrs
Discharge at 500 Amps to 1.00 V/cell

4th Charge at 500 Amps for 7 hrs
Discharge at 500 Amps to 1.00 V/cell

5th Charge at 500 Amps for 7 hrs
Discharge at 1000 Amps to 0.90 V/cell

6th Charge at 500 Amps for 7 hrs
Discharge at 2000 Amps to 0.80 V/cell

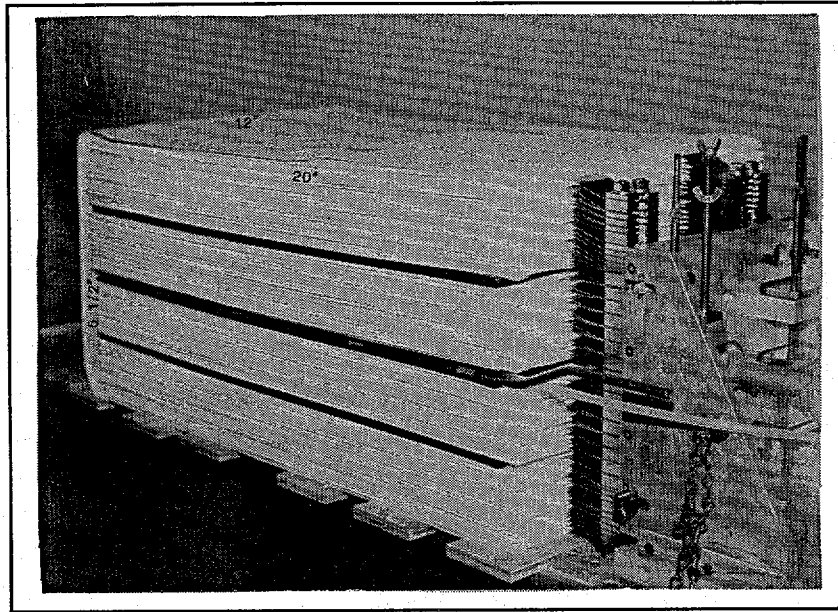


FIGURE 2-22. 2000-Ah NI-CD CELL PACK ASSEMBLY

During formation electrolyte levels were adjusted by removing approximately 1200 cc of KOH from each cell. Presented in Table 2-18 are the formation results. Presented in Figure 2-23 is the 6th formation discharge. The actual 500 Amp/7-hour charge curve is presented in Figure 2-24.

TABLE 2-18. INITIAL FORMATION

Discharge	Cell Output Capacity (Ah)					
	Cell No. 1	Cell No. 2	Cell No. 3	Cell No. 4	Cell No. 5	Cell No. 6
1	2000	2025	2025	2025	2025	2025
2	2385	2385	2385	2385	2385	2385
3	2785	2785	2785	2785	2785	2785
4	3075	3075	3075	3075	3075	3075
5	2970	2970	2970	2970	2970	2970
6	2800	2800	2800	2800	2800	2800

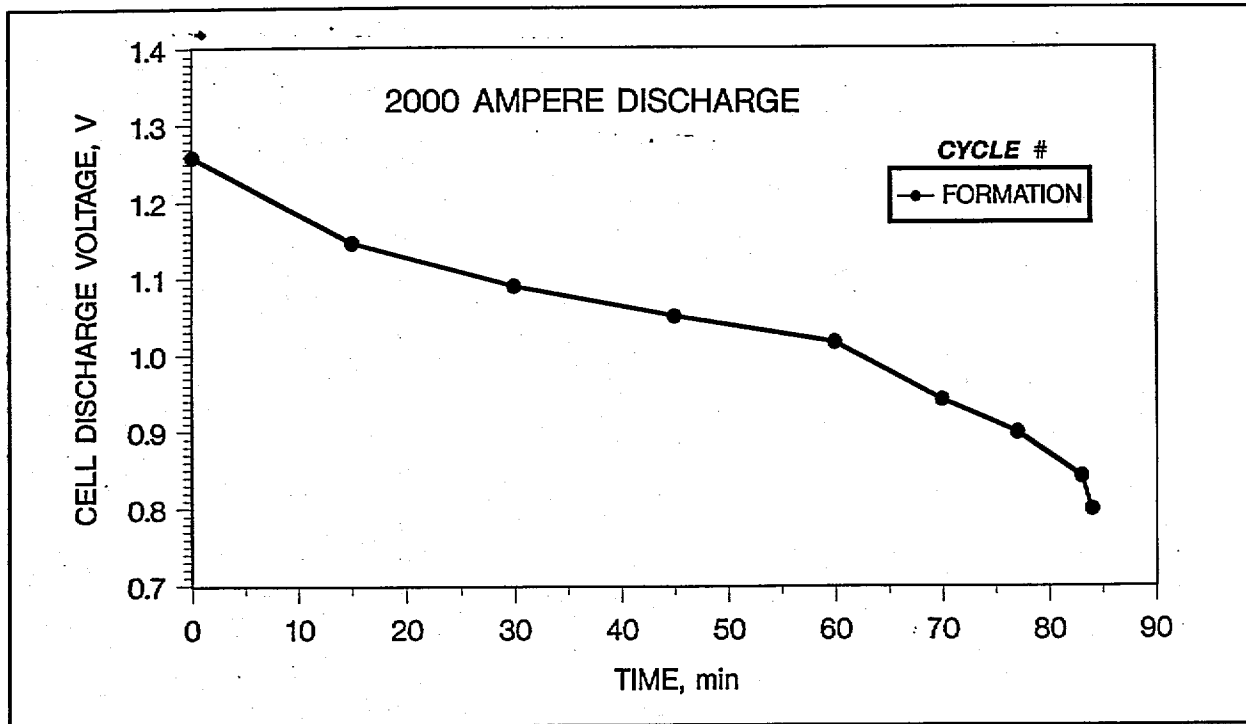


FIGURE 2-23. 2000-AH NI-CD CELL PERFORMANCE

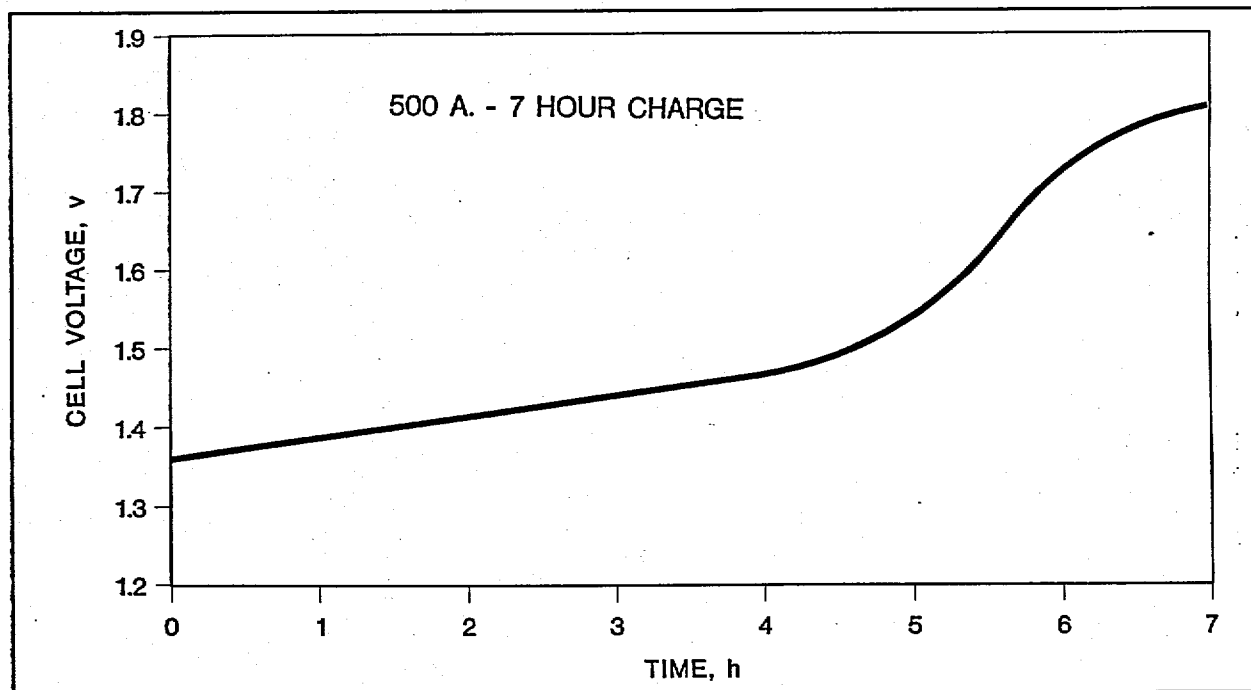


TABLE 2-24. 2000-AH NI-CD CELL

METHOD OF TEST

A continuous method of testing was used following the formation procedure as follows:

Charge 500 Amps for 2.5 hrs
Discharge 2000 Amps for 30 minutes

The cyler which was controlled by a computer designed by ERC, was programmed to perform 100 cycles as described above. The last charge was then secured and a capacity test discharge was performed at the 1-hour rate (2000 Amp) to 0.80 V. At the end of the discharge the cells were recharged at 500 Amp for 6 hours. A second capacity test discharge was again conducted at the 1-hour rate (2000 Amp) to a cell cutoff voltage of 0.80 V. These capacity test discharges were then performed at every 100th cycle.

A total of 3-4 cycles were performed in a 24-hour period because of the cell temperature rise during the 30 minutes, 2000 Amp discharge. Even though water was used as a cooling medium through the terminals to lower the cell temperature, a rest period of 2.5 to 3 hours was necessary following every discharge to allow the cell temperature to decrease to below 35°C. This temperature limit was set by the program before the next charge could take place to allow proper charge acceptance during the next cycle.

An arbitrary 80 percent of the nominal 2000-Ah capacity was set as the cutoff point for rejection and removal of the cells from the cyler.

TEST RESULTS

Upon completion of the formation procedures, each cell was connected in series and cycled using the 2000-Ah cyler. See Figure 2-25 for 2000-Ah test setup. The data presented in Table 2-19 represents the results obtained during every 99th and 100th cycle, for the cell capacity (Ah), average cell voltage (V) and cell temperature at the end of discharge (°C). Presented in Figure 2-26 is the cell discharge voltage performance vs. discharge time for the 6th formation cycle, 100th, 200th, 300th, 400th, 500th and 600th cycles. The cell capacity maintenance results are presented in Figure 2-27. During the shallow discharge cycling at the 1C rate for 30 minutes, the end cell voltages and temperatures were also recorded and are presented in Figure 2-28 vs. the number of cycles. During the 400th and 600th cycle samples of electrolyte were removed from each cell. Analysis for KOH and K₂CO₃ percent were performed and are presented in Table 2-20. These samples were removed from the top and bottom of the cells.

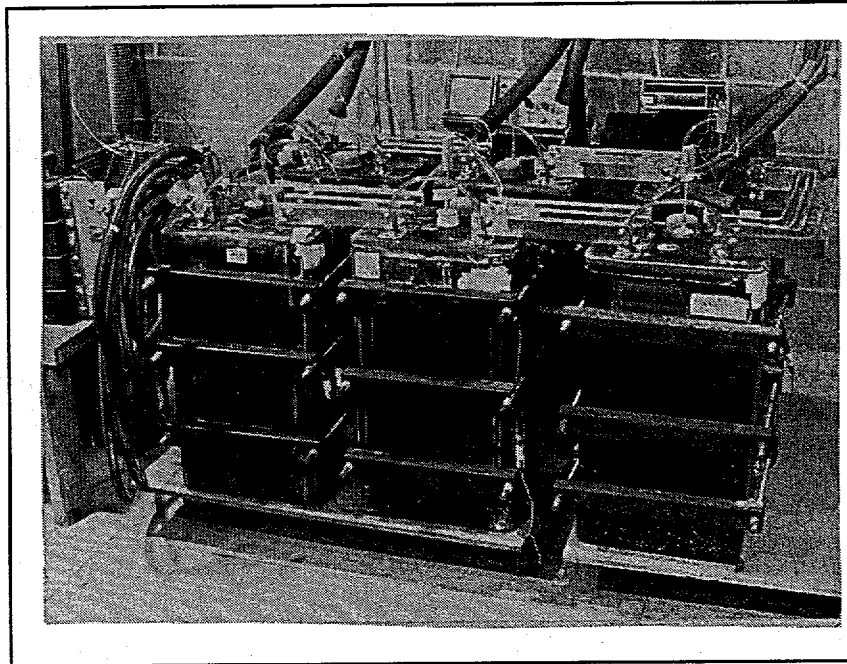


FIGURE 2-25. 2000-AH TEST SETUP

TABLE 2-19. 100% DOD TEST CAPACITY
2000 Amp Discharge To 0.80 V - 6-Cell Average

Cycle No.	Cell Capacity (Ah)	Average Cell Voltage (V)	Cell Temperature @ End of Discharge °C
Formation	2800	1.09	
99	2500	1.09	50
100	2600	1.09	
199	2150	1.09	55
200	2200	1.09	
299	2000	1.087	54
300	2100	1.088	
399	2150	1.084	50
400	2200	1.088	
499	2100	1.084	47
500	2166	1.085	
599	2050	1.080	45
600	2100	1.084	

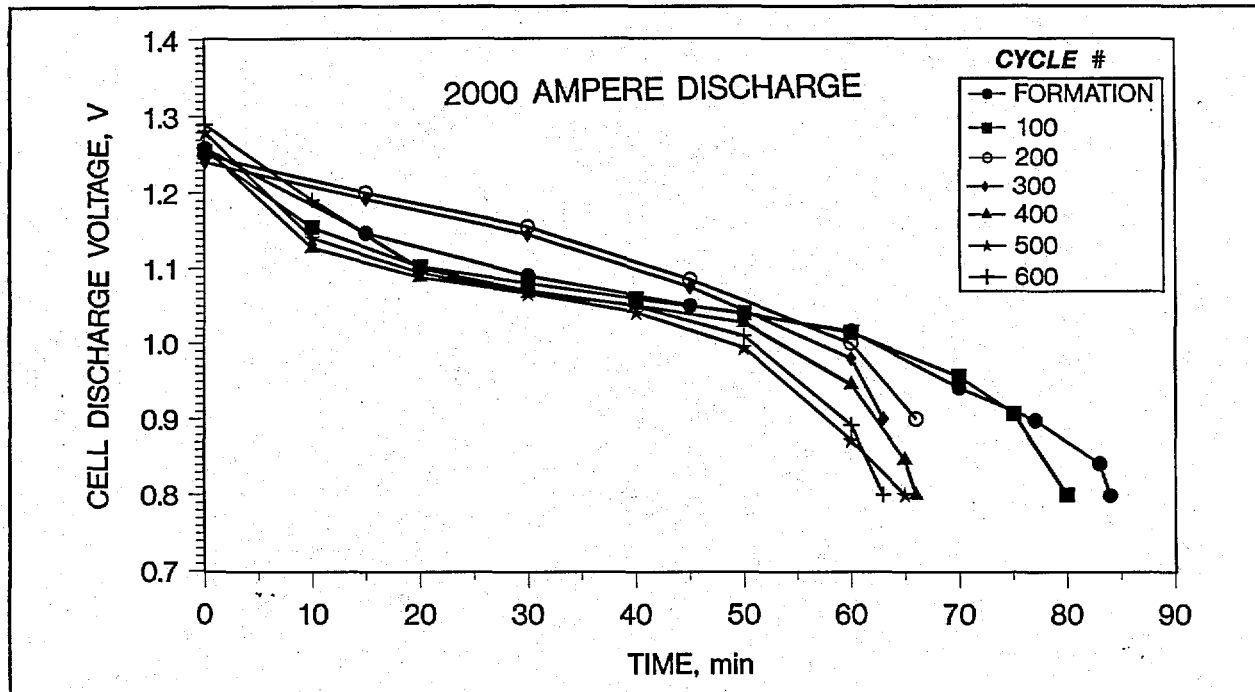


FIGURE 2-26. 2000-AH NI-CD CELL PERFORMANCE

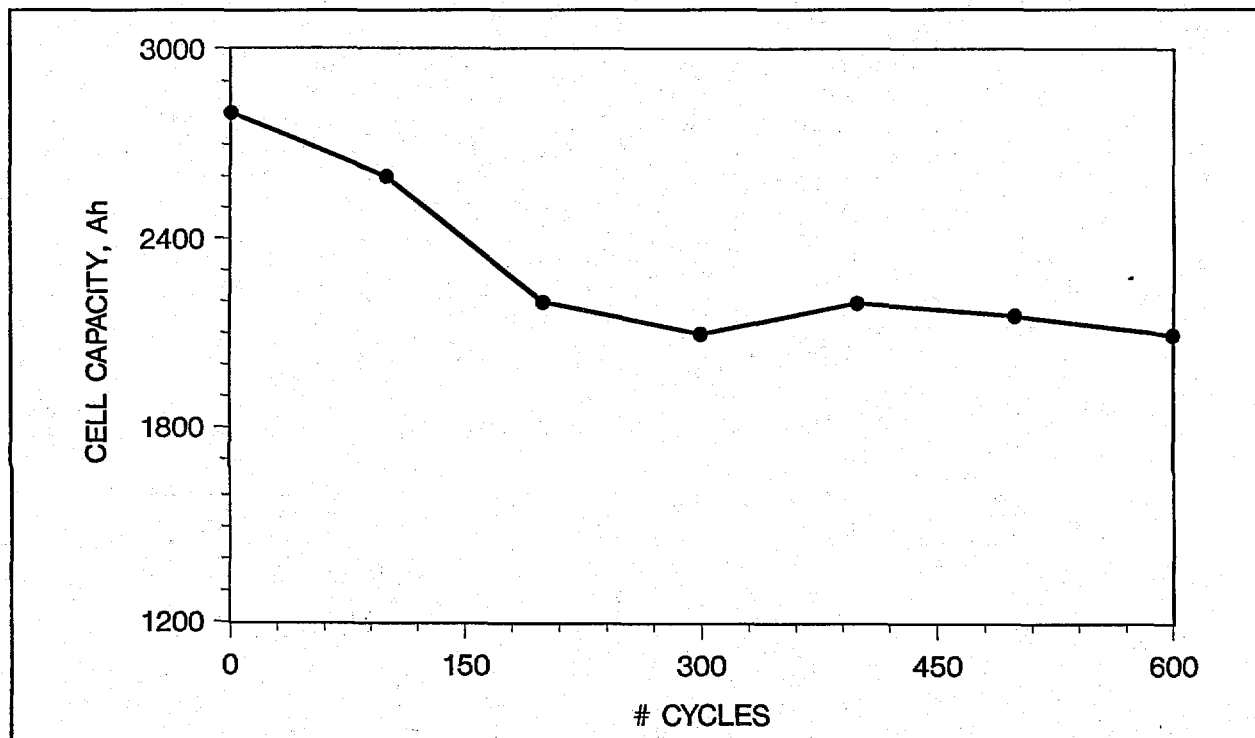
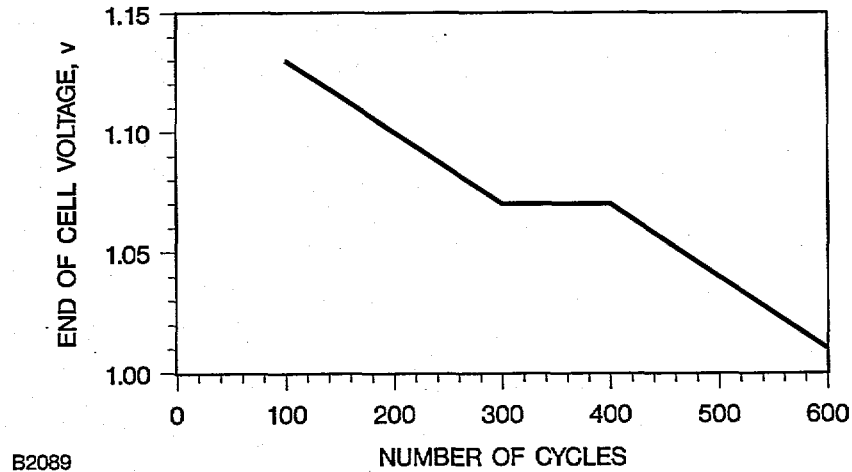


FIGURE 2-27. 2000-AH NI-CD CAPACITY PERFORMANCE

DISCHARGE ON SHALLOW CYCLES

DISCHARGE AT 2000 A. FOR 30 MINUTES
END CELL VOLTAGE vs. NUMBER OF CYCLES
(AVERAGE OF SIX CELLS)

**DISCHARGE ON SHALLOW CYCLES**

DISCHARGE AT 2000 A. FOR 30 MINUTES
CELL TEMPERATURE AT END OF DISCHARGE vs. NUMBER OF CYCLES
(AVERAGE OF SIX CELLS)

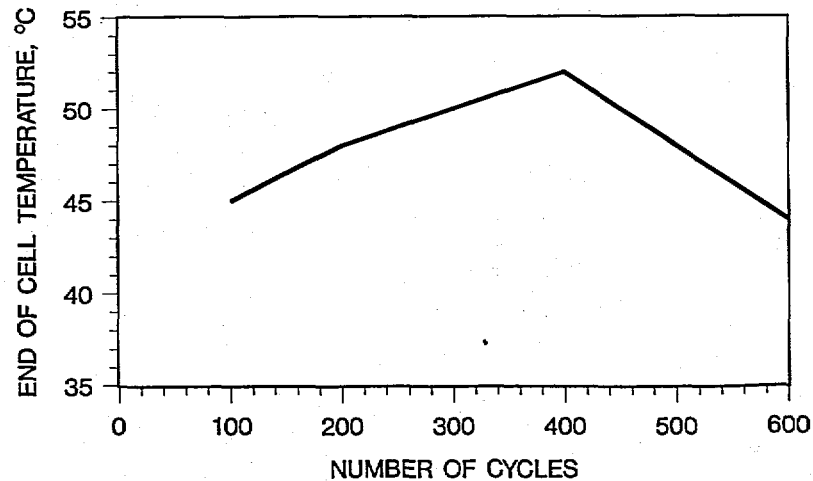


FIGURE 2-28. CELL VOLTAGE/TEMPERATURE DURING SHALLOW CYCLING

TABLE 2-20. ELECTROLYTE ANALYSES
2000-Ah NI-CD Cells

Cell Numbers													Number of Cycles
	1		2		3		4		5		6		
Extraction Point	KOH	CO ₃	KOH	CO ₃	KOH	CO ₃	KOH	CO ₃	KOH	CO ₃	KOH	CO ₃	
Top	25.19	10.6	23.52	10.67	25.37	9.65	26.21	10.09	25.7	9.9	25.19	10.34	400
Bottom	24.60	11.01	23.04	10.84	25.0	11.0	26.12	9.76	25.82	9.76	28.76	10.44	
Top	24.1	11.0	22.5	11.3	24.1	10.5	25.1	11.2	25.0	10.2	25.0	10.6	600
Bottom	23.9	11.1	22.8	11.4	24.4	11.1	26.0	10.1	25.7	10.1	26.8	11.0	

ANALYSIS AND DISCUSSION OF RESULTS

The most important data presented in Table 2-19, 2000 Amp Test Discharge, is the cycles accumulated without cell failure, the output capacity and average cell voltage. Although there was a drop of initial cell capacity from 2800 Ah to 2100 Ah after 600 cycles, the final cell capacity is still 105 percent above the rated cell capacity with an average cell voltage of 1.08 V. Furthermore, the 600 cycles accumulated during Phase II work were accomplished without the recurrence of mechanical shorts in any of these 2000-Ah cells. The gradual decline of cell capacity during the 2000 A discharges and the cell voltage during shallow cycling can be attributed to the rapid test cycling procedures which result in lower charge efficiency and trapped gas between the electrodes and separator system. Cell capacity loss can also be attributed to the aging of the nickel hydroxide active material through recrystallization.

It can be seen, from the data presented in Figure 2-28, that the cell temperatures did not rise above 52°C at the end of the 30 minutes, 2000 Amp discharge. Due to the continuous cycling regime used, cooling of the terminals was necessary to reduce cell temperature and minimize time between charge/discharge in order to accumulate at least 500 cycles during the testing period.

WEIGHT ANALYSIS FOR A 2000-Ah NI-CD CELL

From the actual weight analysis of each cell component, the weight breakdown of a 2000-Ah size cell is:

<u>Component</u>	<u>Weight/lbs</u>
Case	
Cover	20
Terminal/Hardware	
Cell Pack (positive/negative electrodes)	85
Pack Spacers	
Electrolyte (3.15 gals.)	<u>32</u>
TOTAL	137

Table 2-21 (Advanced 2000-Ah Ni-Cd Cell Specifications) was developed based on the results obtained and the weight analysis of the new 2000-Ah Ni-Cd cell.

TABLE 2-21. ADVANCED 2000-Ah NI-CD CELL SPECIFICATIONS

Cell Dimensions HxWxD (inches)	Cell Weight (lbs)	Cell Voltage (V)		Cell Capacity (Ah)		Specific Energy (Wh/lb)		Volumetric Energy Wh/in ³ 1-Hr Rate		Total Energy Storage (Wh)		Minimum Life	
		Initial	@ 600 Cycles	Initial	@ 600 Cycles	Initial	@ 600 Cycles	Initial	@ 600 Cycles	Initial	@ 600 Cycles	Years	Cycles
24 x 13 x 6 V = 1872 in ³	137	1.09	1.084	2800	2100	22.3	16.6	1.63	1.22	3052	2276	10	600

It can be seen from this table that several major accomplishments were attained.

- Six 2000-Ah cells accumulated 600 cycles
- No mechanical internal shorts
- Initial energy of 22.3 Wh/lb and 1.63 Wh/in³
- Energy Storage of 3052 Wh
- Extrapolation of test results showing a 10-year life.

CELL HARDWARE

Cell components were designed and purchased for the assembly of the 2000-Ah cells in accordance with the requirements of the contract. These components included: case, cover, liner, terminals, terminal rods and pressure pads, see Figure 2-29, 2-30, 2-31, 2-32, 2-33 and 2-34. In an effort to reduce costs the case and liner used here were acquired from the existing lead-acid Dolphin battery. For this reason during cell assembly 2" thick shims were used on each side of the cell pack to make up the proper thickness of the inside case dimensions of the existing cell case and liner. The case was fabricated of polyester/fiberglass compound, the liner from crosslinked polyethylene and cover was machined out of ABS plastic. The terminals and pressure pads were made of copper which were nickel plated. The terminal hardware made of stainless steel.

Figure 2-35 shows the 2000-Ah Ni-Cd cell as developed and tested by ERC.

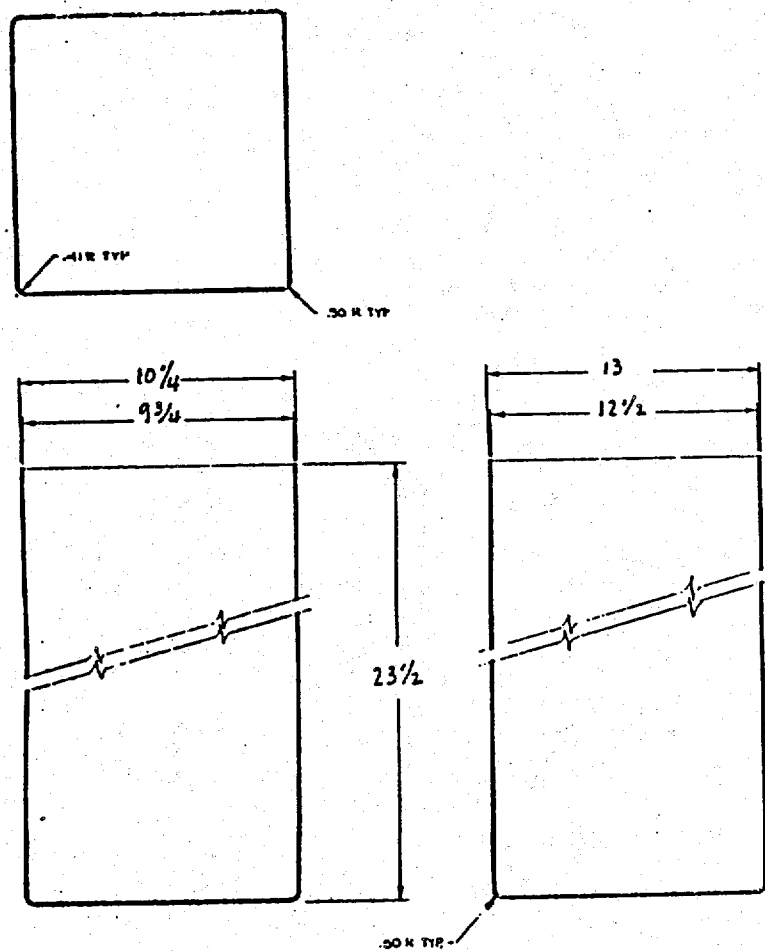


FIGURE 2-29. CELL CASE

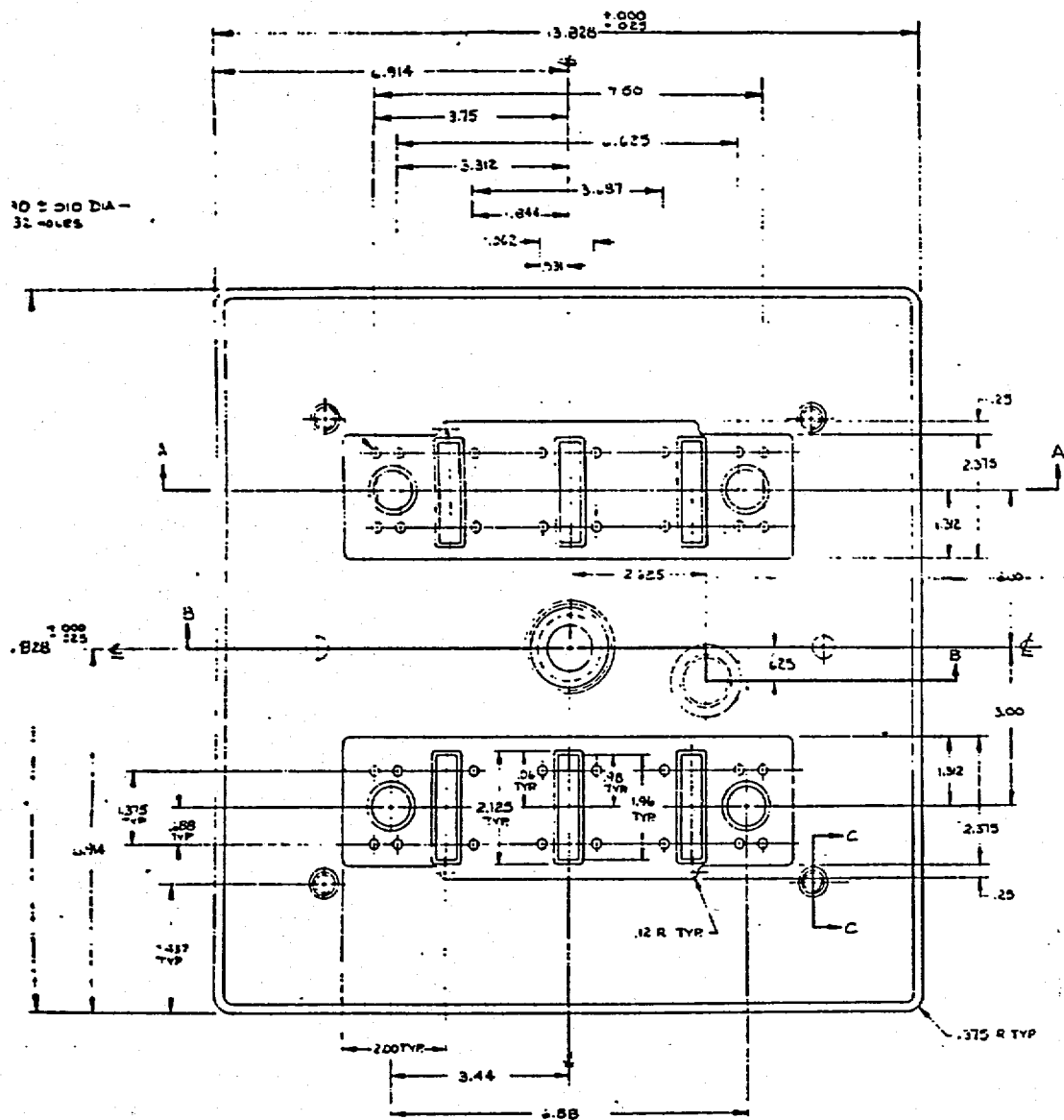


FIGURE 2-30. CELL COVER

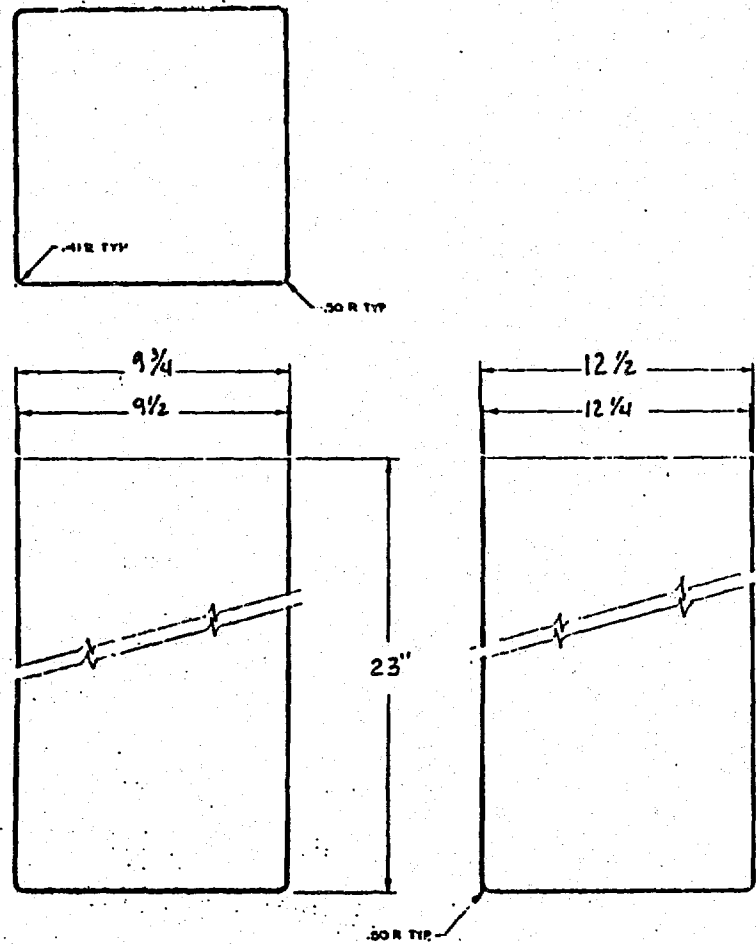


FIGURE 2-31. CELL LINER

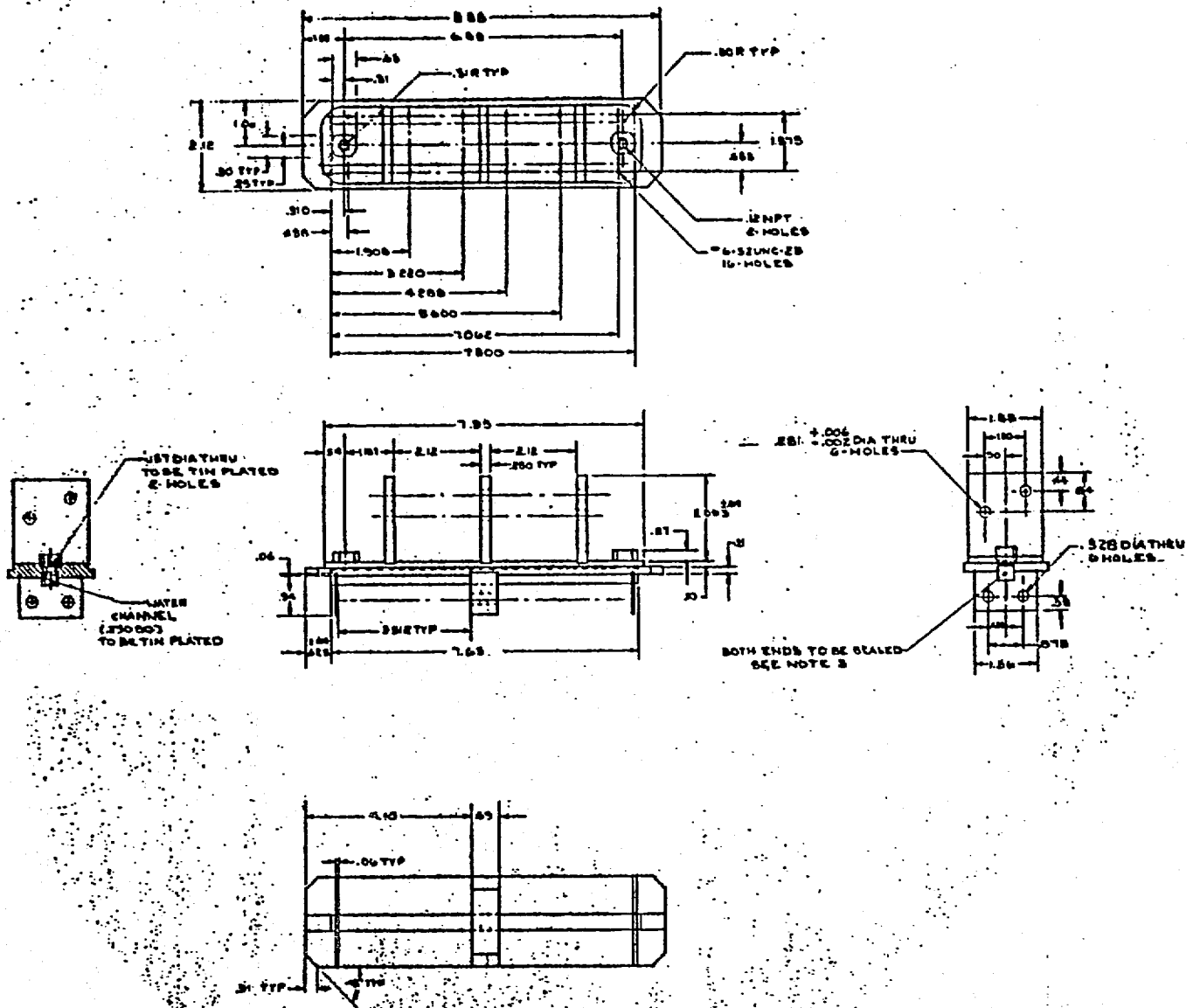


FIGURE 2-32. CELL TERMINAL

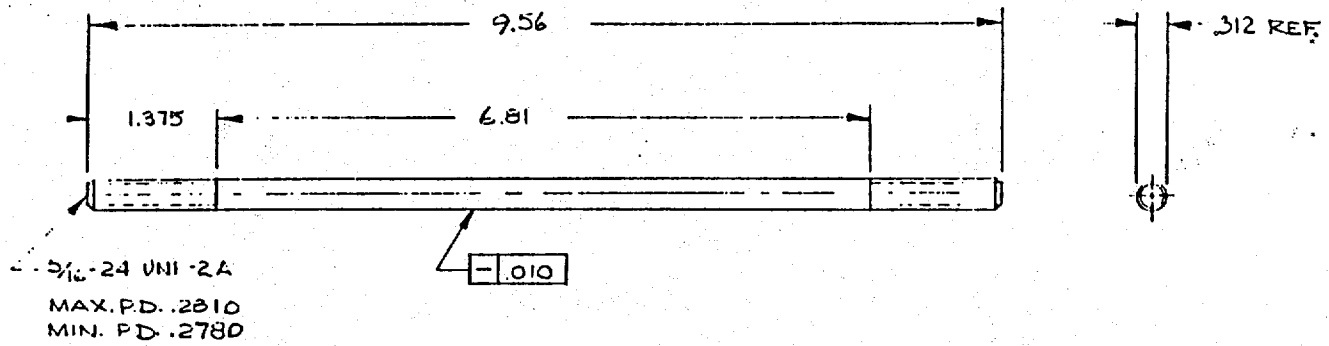
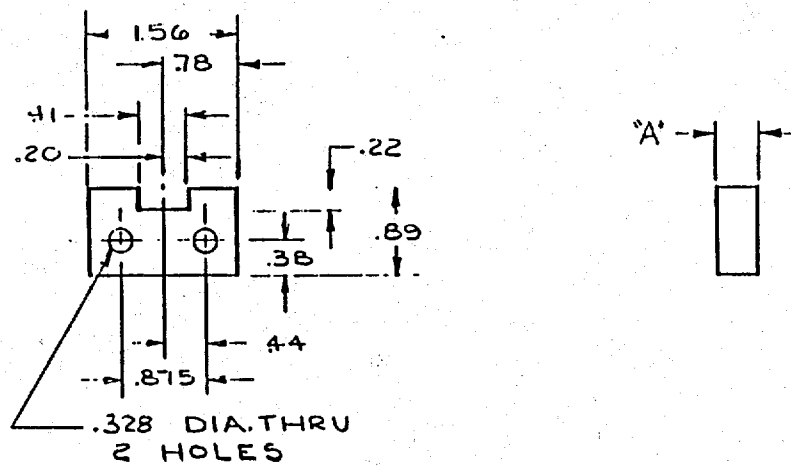


FIGURE 2-33. CELL TERMINAL ROD



PART NO.	DIM. A'
C000224-1	.438
C000224-2	.408

FIGURE 2-34. CELL PRESSURE PAD

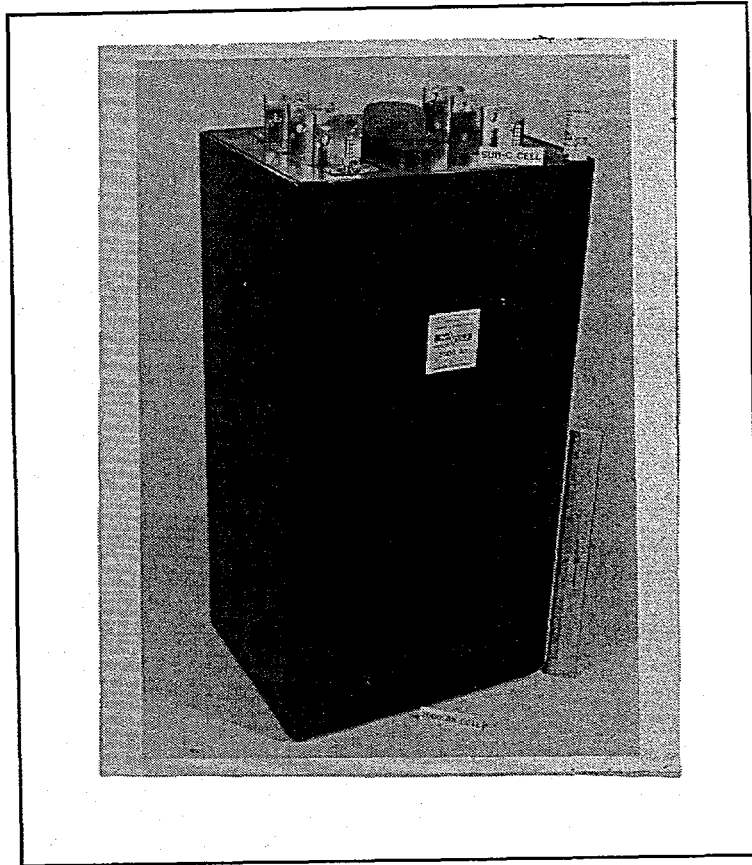


FIGURE 2-35. 2000-Ah NI-CD CELL

CONCLUSIONS AND RECOMMENDATIONS

The suitability of ERC's roll-bonded electrode technology has been demonstrated in meeting the Phase II goals of the program. Included below are the major conclusions and recommendations related to the program.

Major conclusions reached during the program:

- Through the continuation of the float regime it was demonstrated that ERC's Ni-Cd cells were capable of long-term float, yielding a capacity of 2200-Ah after 34 months.
- Six 2000-Ah Ni-Cd cells have demonstrated a cycling capability of at least 600 cycles at the 1C rate.
- Through the development of a new collector design the 2000-Ah cells were able to accumulate at least 600 cycles without any cell failure, due to mechanical shorting, therefore proving cell component reproducibility.
- The volumetric and gravimetric energy density goals were met and exceeded.
- Through the accelerated corrosion study, demonstration of at least eight years life, and by simple extrapolation it appears that greater than 10 years life can be obtained.
- Corrosion cells being tested at 20°C, 40°C and 50°C have demonstrated capacities of 2.97 Ah, 2.90 Ah and 2.56 Ah or 124 percent, 121 percent and 107 percent of nominal capacity after 12 months of continuous float.
- Cells containing coated spinel graphite yielded higher capacity at each temperature.
- Carbon losses of up to 18 percent of total carbon have little affect on reducing cell capacity.
- Carbonate contents up to 30 percent reduce cell voltage by 100 mV.
- The comparison of results based on final concentrations of KOH, CO₃ and percent of rated capacity correlates with the life extrapolation used.

RECOMMENDATIONS FOR FUTURE WORK

Although Phase II program was completed and had the goal of demonstrating the capability of ERC's Ni-Cd cell to accumulated at least 500 cycles and demonstrated a 10-year life, future work should address the following:

- Investigate the minimum percentage of graphite to permit a 10-year life.
- Investigate the amount of collector corrosion a cell can tolerate (loss of cobalt, nickel plating and substrate foil) before it affects cell voltage and capacity drops below 80 percent of rated capacity.
- Verify life extrapolation used in this program.
- Long-term verification of separator systems.
- Continuation of float testing to 48 months and test cycling to 1000/1500 cycles.

It is felt that these steps should verify the life extrapolation used in this program. The resulting product will be a large capacity, manufacturable cell with long calendar (greater than 10 years) and good cycle life suitable for diverse applications.

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13. ABSTRACT (Maximum 200 words) The roll-bonded fabrication of non-sintered nickel electrodes has been investigated by fabrication and testing of two 2000-Ah cell sets. The cells achieved at least 600 50-percent depth of discharge (DAD) 1C rate cycles. Sustained energy of 18-19 Wh/lb was delivered. A constant potential float of 34 months showed a modest decrease from initial capacity to 2200 Ah. A redesigned current collector in the second cell set eliminated all symptoms of internal shorting previously experienced. An Arrhenius type elevated temperature accelerated corrosion test was performed on small cells having similar electrode compositions as those of the full size cells. These tests indicated substantial conversion of the electrode graphite component to carbonate in the electrolyte. This oxidation results in a decrease in substrate conductivity and increase in electrolyte resistivity. In practice, however, relation of the data back to ambient temperature indicated at least a 10-year useful calendar cell life. While the cell technology developed here was intended for military use, it has good potential for transfer to other Government and commercial applications, such as in industrial systems, load leveling, uninterruptible power sources and electric vehicles.				
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