NASA Technical Memorandum 87774

Analysis of 12 AH Aerospace Nickel-Cadmium Cells From the Design Variable Program

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APRIL 1987

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**Scientific and Technical
Information Branch**

1987

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ANALYSIS OF 12 AH AEROSPACE NICKEL-CADMIUM CELLS FROM THE DESIGN VARIABLE PROGRAM

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INTRODUCTION

The National Aeronautics and Space Administration, Goddard Space Flight Center (NASA/GSFC) in conjunction with the General Electric Company (GE) started a Design Variable Program in early 1978. The objective of this program was to evaluate 9 of the most important nickel-cadmium aerospace cell designs selected from the designs that had been successfully used during the previous 15 years (Ref. 1 and 2). The need for a comprehensive evaluation was fully recognized since a review of the cell design history indicated that the cells that were in use bore only a slight resemblance to those used in the first satellite applications. A number of changes had been made in the cells with a view to achieve improved energy density, longer life, improved production yield, and enhanced cell performance while meeting the customer's requirements. Many of these changes had been tested and evaluated by various users but there was never a systematic approach to compare the performance and relative merits of each cell design. The objective of this report is to present the results of the physical examination, chemical and electrochemical analyses performed on the Design Variable Cells and to draw conclusions.

APPROACH

It was necessary to choose a test with a proven heritage and a physical design similar to that of other widely used aerospace nickel-cadmium cells. For these reasons, the GE 12 Ah cell was selected as the Design Variable test cell. It had been used in the past with much success and because its design is similar to that of the 6 Ah and 20 Ah cell designs used by the GSFC, the data collected could be adopted with confidence to those cells.

BASIC CELL DESIGN

The test cells had nominal capacity of 12 Ah and were manufactured by G. E. Figure 1 shows the basic cell design. The design consists of 11 positive plates and 12 negative plates with the following features:

1. Nickel braze, ceramic to metal seal at the positive and negative terminals,
2. Stainless steel cell case of 0.17 in (0.43 cm) nominal thickness.

Other design features which are unique to each test group are described in Section 1.3. Details of specification and manufacture of these cells are given in Ref. 3 and 4.

DESCRIPTION OF DESIGN VARIABLES

Information in this section and the sections on Background Information and Initial Evaluation Tests are from Ref. 10 and this provides the necessary background about the Design Variable Cells.

Eight of the most frequently used designs and an additional proposed design were selected as the design variables to be tested in this program. Thus, a Control group and eight design groups of 6 cells per group were manufactured:

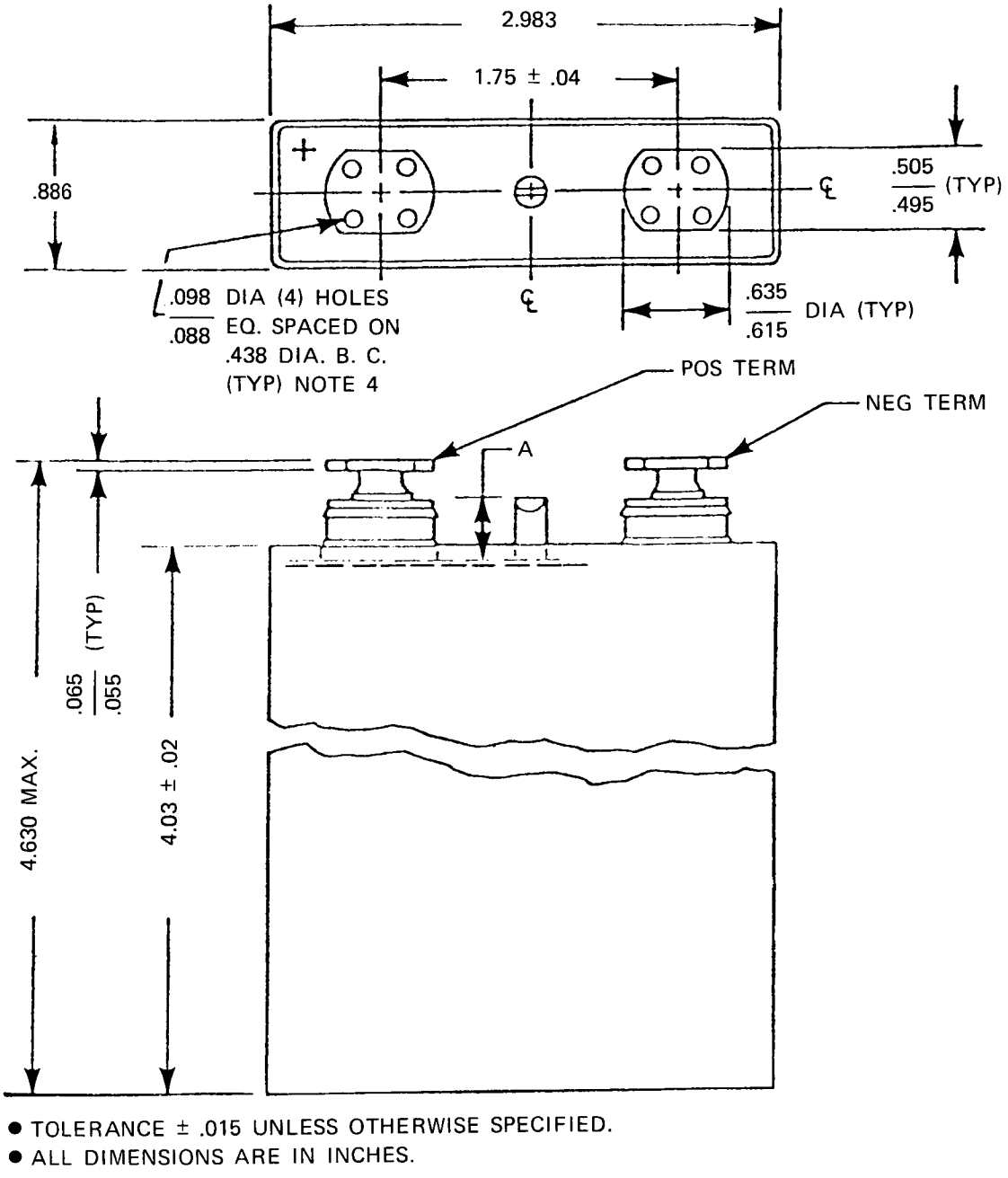


Figure 1. Basic Cell Design

1. Control: This group represents G.E.'s basic aerospace design and process as of 1978. The positives of these cells were subjected to cadmium treatment (PQ) as is indicative of G.E.'s process since 1970. The loading was somewhat lighter than normally used by G.E. during this time-frame. These lighter levels were chosen because the GSFC had recently procured 2 flight lots (IUE) with this design. The cells were manufactured with non-woven nylon separator (Pellon 2505) and all cells received decarbonation treatment.

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

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

4. Light Loading: The plates of this group have lighter loading (less active material) than those of the previous 3 groups. These plates are from the same impregnation post as the Control but are from different spirals. The purpose of this group was to evaluate a further reduction of plate loading with respect to initial and life benefits. Though no teflon or silver treatments were used, these cells contain 5cc more electrolyte than the Control cells.

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

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

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

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

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

Each Design Variable Group contained two cells with different signal electrodes. One signal electrode was the standard G.E. teflonated electrode that had been in use through 1983. The other electrode was of a new G.E. design and was designated the "Heart-Pacer Signal Electrode". The old G.E. standard electrode was discontinued in 1983 and the "Heart-Pacer Electrode" is now used across the board. Details concerning the design and performance of these two types of signal electrodes have been documented (Ref. 5).

TEST PROGRAM

The test program consisted of 2 segments (See Fig. 2). First an initial evaluation program was conducted. Initial evaluation tests were performed to characterize each cell, to compare initial behavior and to detect any manufacturing defects overlooked during acceptance testing. These tests were repeated on a 1 cell from each design after 1 year of cycling, and on all cells remaining in each group at the end-of-cycling. The repetitions were carried out in order to compare performance and degradation based on the same criteria at different points during the life of the cells.

The second segment of the Design Variable Program consisted of extended cycling in a LEO regime (Table 1). A higher dept of discharge (DOD) than is normally seen (40%) was used in this cycling regime in order to obtain observable results as quickly as possible without a truly accelerated test plan.

BACKGROUND INFORMATION

PHYSICAL MEASUREMENTS

A summary of the initial physical measurements of the plates of each design group is shown in Table 2.

ELECTROCHEMICAL CLEANING AND TESTING (ECT) DATA

ECT is a flooded test of temporary cells in which the capacities of the positive and negative plates are determined. Table 3 shows the average, maximum and minimum capacities obtained for each design group.

SEPARATOR ANALYSIS

The separator used in all the groups except the polypropylene group was Pellon 2505, Lot No. 29258, Roll No. 1. Details of specification for the separator has been documented in Ref. 6. The polypropylene separator used was from Lot No. 5382 and details of specification are available in Ref. 7. To meet the requirements, the separator was tested as per specifications documented in Ref. 8. A summary of the results of the separator test is shown in Table 4.

1. Initial Evaluation Tests*
   - Leak Tests
   - Capacity Tests
   - Internal Resistance and Short Test
   - Charge Retention Test
   - Overcharge Tests
   - Pressure Versus Capacity Tests

2. Low Earth Orbit Cycling

*Tests repeated after 1 year cycling and at end of program.

Figure 2. Design Variable Test Program Outline.

Table 1. Leo Cycling Test Parameters

Temperature	20 C
Depth-of Discharge	40 Percent
Orbit Period	90 Minutes
Charge Current	9.6 AMPS
Voltage Limit/Cell	1.453
Discharge Current	9.6 AMPS

Table 2. Electrode Physical Measurements

Group	Parameter	Positive	Negative
Common	Length (Cm)	7.615 to 7.623	7.618 to 7.625
Common	Width (Cm)	6.998 to 7.005	6.995 to 7.005
Control	Thickness (Cm)	0.069	0.079
Teflon	Thicknesses	0.069	0.079
Silver	Thicknesses	0.069	0.079
Light Loading	Thicknesses	0.069	0.079
No PQ	Thicknesses	0.069	0.079
Polypropylene	Thicknesses	0.069	0.079
A.K. Old	Thicknesses	0.081	0.066
A.K. Present	Thicknesses	0.081	0.066
Electrochem	Thicknesses	0.074	0.079

Table 3. ECT Plate Capacity Results

GROUP	POSITIVE CAPACITY (Ah) AVG.	MAX.	MIN.	NEGATIVE CAPACITY (Ah) AVG.	MAX.	MIN.	AVERAGE NEG. TO POS. RATIO
Control	16.04	16.20	15.80	28.02	28.50	27.30	1.75: 1
Teflon	16.04	16.20	15.80	28.02	28.50	27.30	1.75: 1
Silver	16.04	16.20	15.80	28.02	28.50	27.30	1.75: 1
Light Loading	13.83	14.10	13.68	24.95	25.40	24.63	1.80: 1
No PQ	15.63	15.76	15.58	27.88	28.51	27.34	1.78: 1
Polypropylene	16.04	16.20	15.80	28.02	28.50	27.30	1.75: 1
A.K.-Old	19.78	19.96	19.67	—[1]	—[1]	—[1]	1.25: 1
A.K.-Present	19.55	19.82	19.33	24.37	26.24	23.31	1.25: 1
Electrochemical	13.87	15.07	13.12	28.53	30.44	26.59	2.06: 1

1. Old Plate Processing: Negatives Discharged for 4 Hours Only.

Table 4. Separator Test Results

TEST	SEPARATOR TEST REULTS (Ref. 8) PELLON 2505	POLYPROPYLENE
Air Permeability	272.4 $Ft^3/Min/ft^2$	174.9 $ft^3/Min/ft^2$
Thickness (Dry)	0.0147 in.	0.0117 in.
Thickness (Wet)	0.0139 in.	0.0117 in.
Electrolyte Retention	95.2%	89.9%
Electrolyte Porosity	49.3%	36.2%
Wettability	5 Min.	0.5 Min.
Tensile Strength at Break Dry	182.52 $Kg/in.^2$	101.60 $Kg/in.^2$
After 24 Hr. Soak in 34% KOH	147.38 $Kg/in.^2$	122.10 $Kg/in.^2$
% Organic	0.63%	0.44%
% Inorganic	1.02%	0

KOH QUANTITY

The final KOH quantity varied from group to group because of different performance properties caused by each variable and loading level. The criteria for determining the amount of KOH was to obtain the maximum KOH allowable in each group consistent with reasonable overcharge pressures. The overcharge pressure design goal was 30 to 75 psia. The final KOH quantities and plate loading levels for different designs are shown in Table 5.

PRECHARGE

Precharge was set by the oxygen incremental venting technique. The cell procurement specifications required the precharge to be set to 40 ± 5 percent of the excess negative. The final precharge adjusted data shown in Table 5.

Table 5. KOH Quantity, Loading, and Neg. Precharge in Design Variable Cells

GROUP	KOH QUANTITY, cc/cell NON 3rd/3rd	LOADING g/dm^3 POS.	NEG.	PRECHARGE ADJUST Ah	% EXC. NEG.
Control	40/40	2095	2180	4.6	38.4
Teflon	48/49	2095	2180	4.6	38.4
Silver	43/44	2095	2180	4.6	38.4
Light Loading	45/46	1840	1833	4.6	41.4
No PQ	40/41	2113	2180	4.6	37.6
Polypropylene	39/40	2095	2180	4.6	38.4
A.K.-Old Process	38/39	2130	2542	–	–
A.K.-Present Process	39/40	2130	2542	1.8	37.3
Electrochemical	48/–	1276[2]	2280	5.8	39.6

1. Based on 228cc O_2/Ah.
2. By Hydrate Pickup, Not Hydrate Reduction.

INITIAL EVALUATION TESTS

The Design Variable Cell Initial Evaluation Program was performed at the Naval Weapons Support Center in Crane, Indiana under NASA Purchase Order S-57075A. The purpose of this evaluation test program was to ensure that all cells put into the life cycle program were of high quality by screening out those cells found to have electrolyte leakage, internal shorts, low capacity or the inability to recover an open-circuit voltage of 1.15 Volts during the internal short test. The re-evaluations after 1 year and at the end-of-cycling were done in order to compare to the initial data.

All evaluation tests were performed at room ambient (RA) pressure and temperature (25 +2 C) with discharges at the 2-hour rate unless otherwise specified. It consisted of:

a. phenolphthalein leak tests (2),
b. three capacity tests, the third at 20 C; with internal measurements during the second,
c. signal electrode characterization test,
d. charge retention test at 20 C,
e. internal short test,
f. charge efficiency test at 20 C,
g. overcharge tests at 0 C and 35 C,
h. pressure versus capacity test,
i. phenolphthalein leak test.

EVALUATION TEST RESULTS

Results of the evaluation and test procedures have been documented elsewhere (Ref. 9). Summary of the data for the initial evaluation tests for all the groups at the beginning and end-of-life as well as discussions on the results of 25 C capacity test, 25 C overcharge test and the 0 C overcharge test are available (Ref. 10).

TEAR DOWN ANALYSIS OF DESIGN VARIABLE CELLS

The preliminary results of the tear-down analysis of the uncycled cells and the cells that were taken out after 1 year of LEO cycling were presented at the 1981 NASA/GSFC Battery Workshop (Ref. 11). This report contains an update

of that analysis, including those which were cycled for 3 to 4 years under the Design Variable Program. Tear-down analysis was carried out according to the procedures given in the NASA document (Ref. 12).

EXPERIMENTAL APPROACH

The experimental techniques that have been followed in this investigation are:
Visual Inspection
Surface Examination
Physical Measurements
Chemical Analysis
Flooded Cell Capacity Test

Visual Inspection

When the cells were opened cell packs were found to be moist with electrolyte, the extent varying from one cell to another. With the exception of polypropylene group, the separators deteriorated to a great extent and invariably adhered to the surface of the negative electrode. The separator bags could not be taken out in one single piece as was in the case of an uncycled cell. The separator part that came off the electrodes had dark to light gray patches due to the different extents of cadmium migration. The cell with polypropylene separator showed heavy cadmium migration although the separators came off in one piece (Fig. 3F). The observation that strong adherence of a thin film of separator material on the negative electrode common to most of the other groups is illustrated in Figure 3. The positive electrode could easily be taken out of the separator bag.

Surface Examination

After the electrolyte extraction and subsequent drying in a nitrogen atmosphere, cell materials were photographed in groups of positives, negatives and separators of each cell. In addition, close-up views of selected positive plates, negative plates and the separator materials were taken. A comparison of pictures of materials of an uncycled cell (Fig. 4) and a cycled cell (Fig. 3) shows the deterioration of the separator material with different extents of cadmium migration and strong adherence of the separator material to the negative plate surface. In almost all the groups, the positive plate surface appeared clean except in the case of a shorted cell from Teflon group. The circular areas in the positive and negative plates in Figure 3 represent the discs cut for chemical analysis, SEM and EDAX.

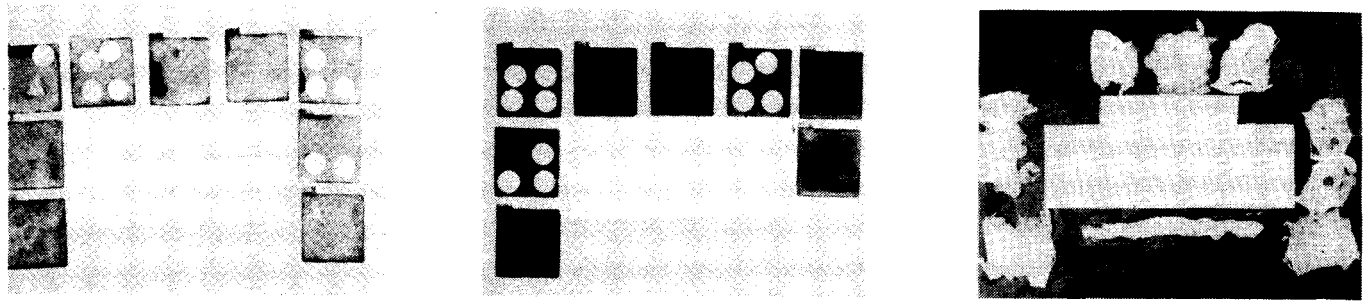
One of the cells in Group 2 was found to have a short. The short extends to a couple of plates on either side in the stack (see Fig. 5). The SEM of the short on the positive plate in Figure 6 shows the presence of large crystals of cadmium hydroxide which have migrated from the neighboring negative plates. The separator material was pierced, resulting in a short. The holes seen in some of the separators in Figure 5 are from piercing and shorting. The shorted region of the negative plate is shown in Figure 7. The SEM of this region shows cadmium hydroxide crystals.

Pictures of the positives, negatives and the separators of all groups are shown in Figure 3 and the SEMs of representative positive and negative plates are presented in Figure 8. A common feature that can be observed in the SEM of the negative plates of cycled cell is the presence of large crystals of cadmium hydroxide throughout the surface. On the other hand, the negatives of an uncycled cell do not have such large concentration of the crystals on their surface. Examination of the positive plate surface through SEM do not show such crystal growth however. This indicates that continuous cycling of these cells promotes crystal growth only on the negative. A combination of crystal growth and/or dendrite formation of cadmium hydroxide on the negative plate, swelling of the positive plate in the stack and weakening of the separator material create conducive conditions for a short to occur. It has been observed that in flooded cells, a continuous overcharging of the negatives leads to reduction of the size of the crystals (Ref. 13 and 14). However, in the case of sealed cells, a possible remedy is to recondition (deep discharge) the cells after a reasonable length of cycling.

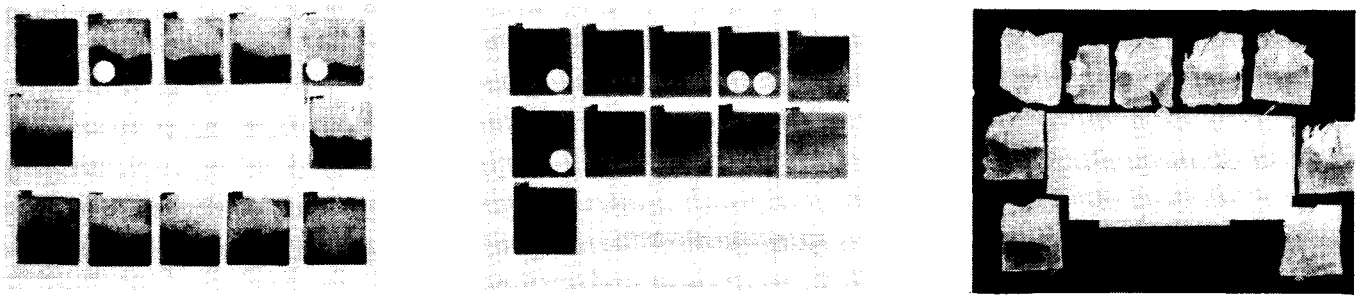
A brief analysis of surface examination is given for each group. SEMs of samples from each group can be seen in Figure 8.

Control: SEM of the negative from the cell that had 23,468 cycles shows heavy crystal growth of cadmium hydroxide throughout its suface. The SEM of the positive shows crystals only in some areas. No such crystals were found on the positives of the cell from the No PQ group which was cycled to the same extent, i.e., 23,282 cycles. This is due to the fewer number of nucleation sites provided by the No PQ positives compared to the PQ treated positives of the Control group. Under cycling conditions, it will take longer time for the migrating cadmium/cadmium hydroxide to build up large crystals on the No PQ positive plate. This will help in preventing the shorting, thereby extending cell life.

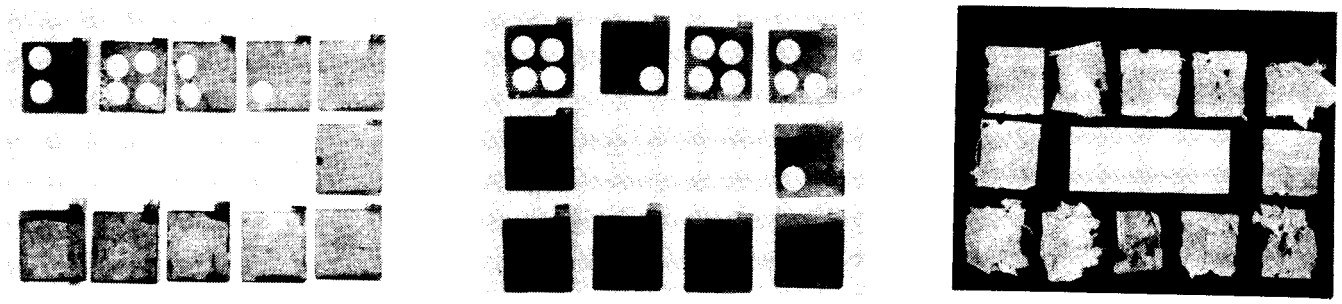
NEGATIVE POSITIVE SEPARATOR



A. S/N 006, Control, 23,468 Cycles



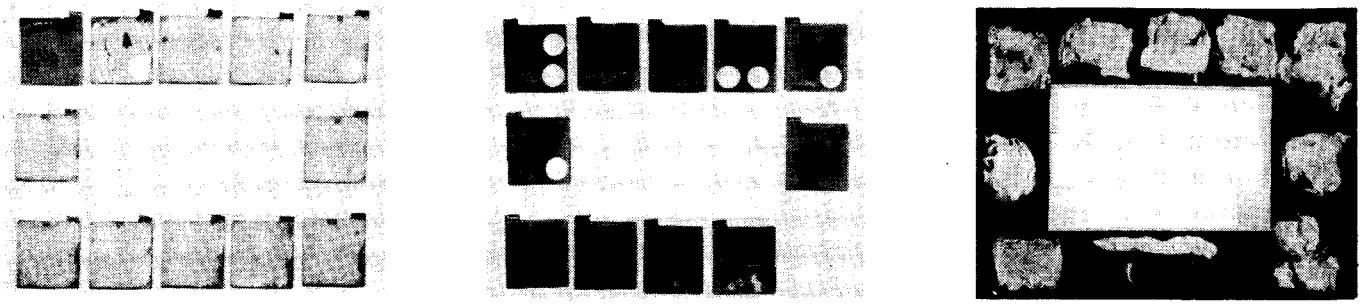
B. S/N 006, Teflon, 17,760 Cycles



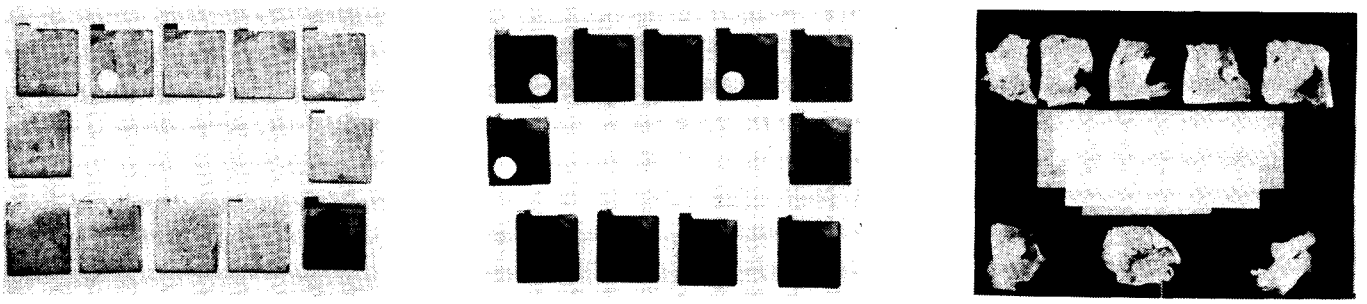
C. S/N 003, Silver, 17,781 Cycles

Figure 3. Pictures of Cell Materials from Design Variable Groups.

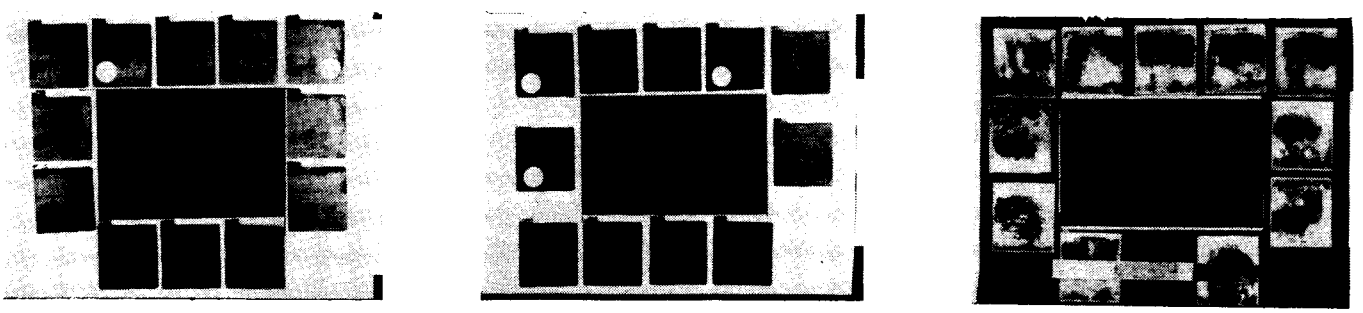
NEGATIVE POSITIVE SEPARATOR



D. S/N 005, Light Loading, 17,855 Cycles



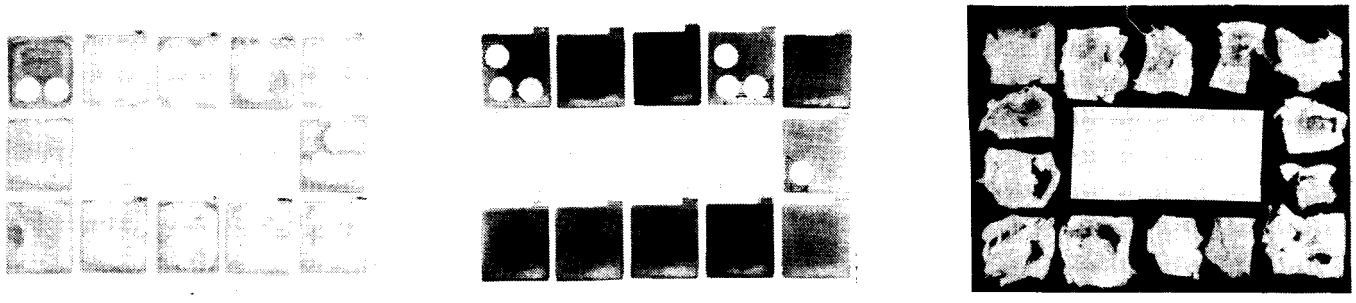
E. S/N 003, No PQ, 23,282 Cycles



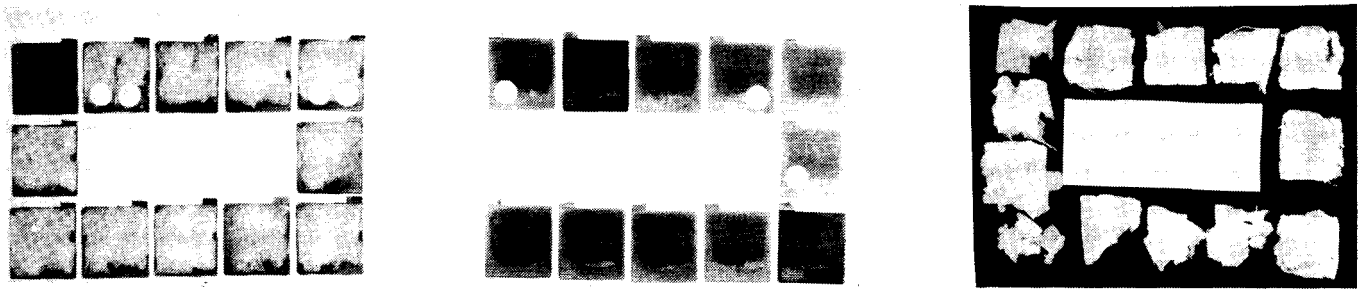
F. S/N 005, Polypropylene, 17,632 Cycles

Figure 3. Continued.

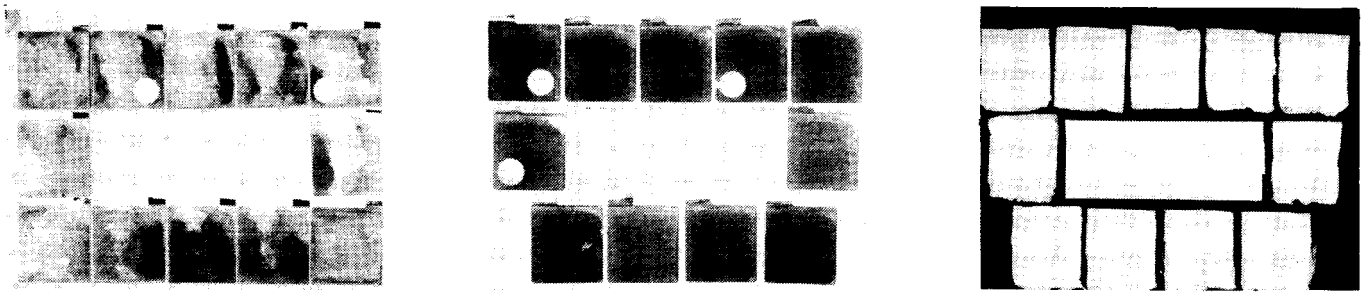
NEGATIVE POSITIVE SEPARATOR



G. S/N 001, A.K.-Old Process, 23,335 Cycles

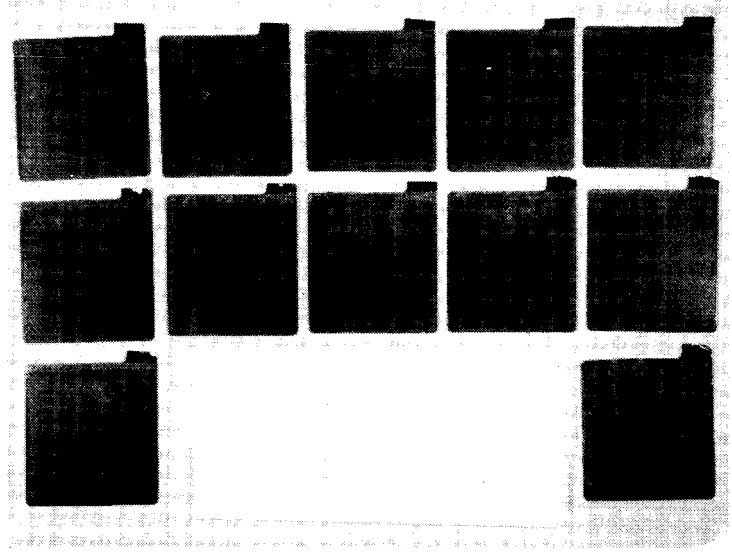


H. S/N 003, A.K.-Present Process, 17,300 Cycles

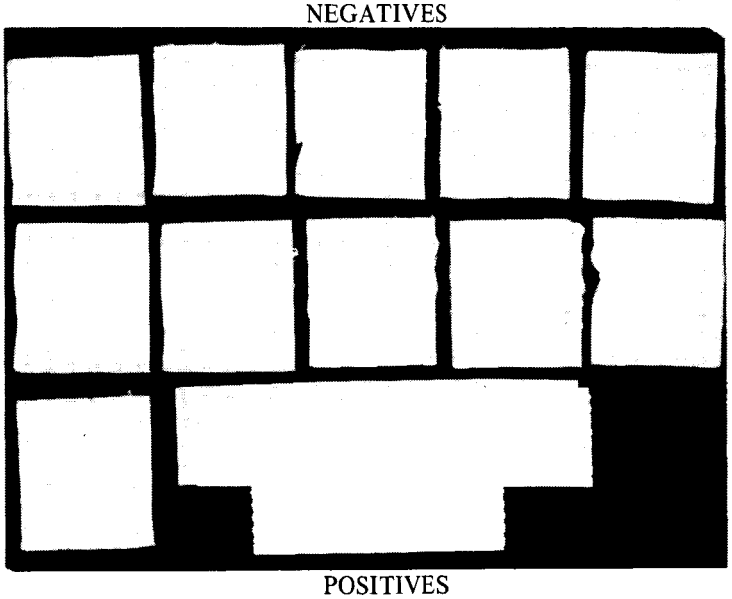


I. S/N 003, Electrochemical, 5818 Cycles

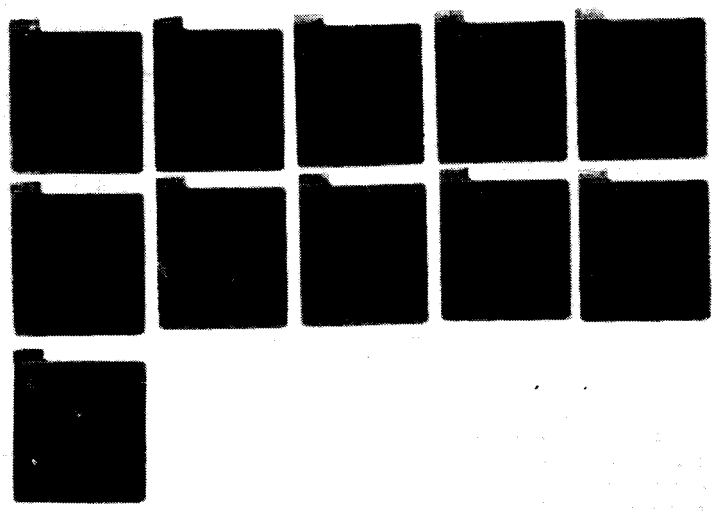
Figure 3. Concluded.



NEGATIVES



POSITIVES



SEPARATORS

Figure 4. Pictures and SEM of Cell Materials of Uncycled cell of Group 2.

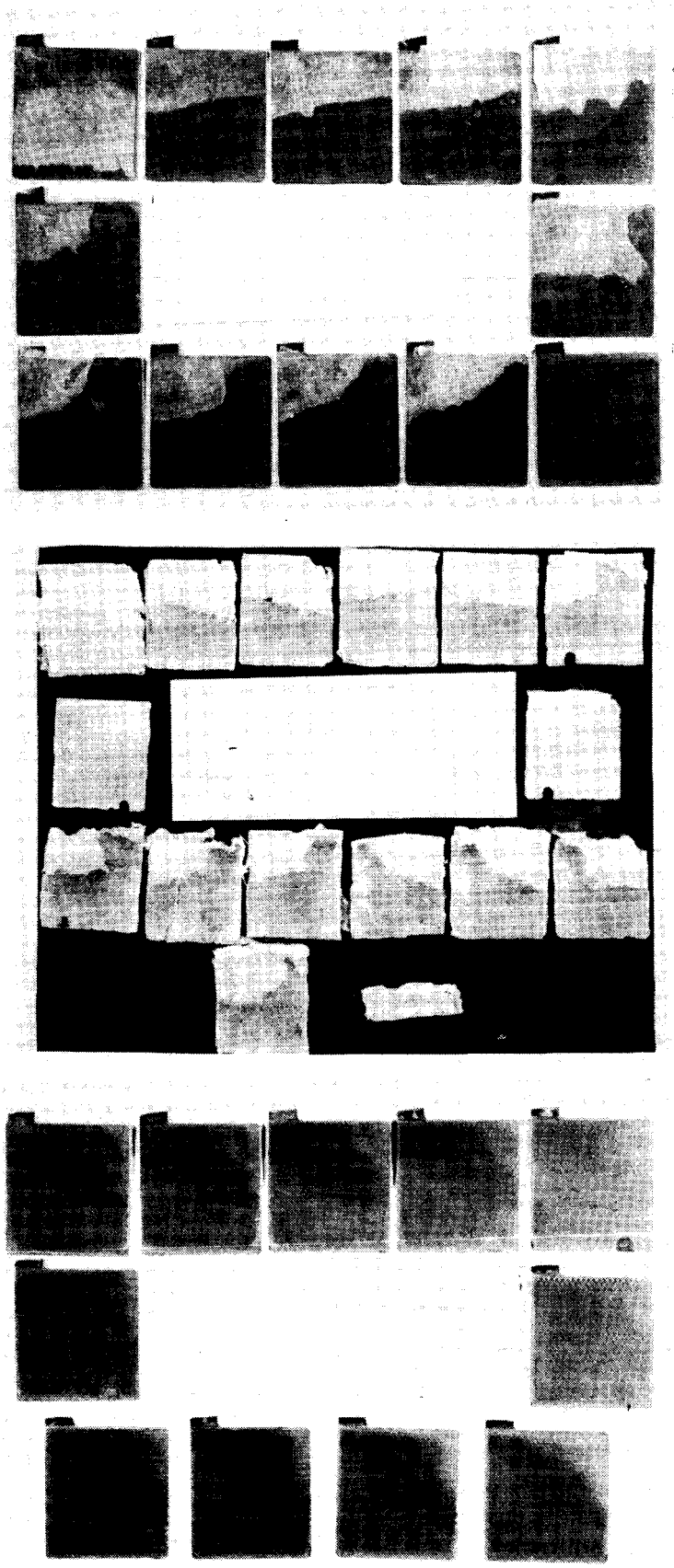
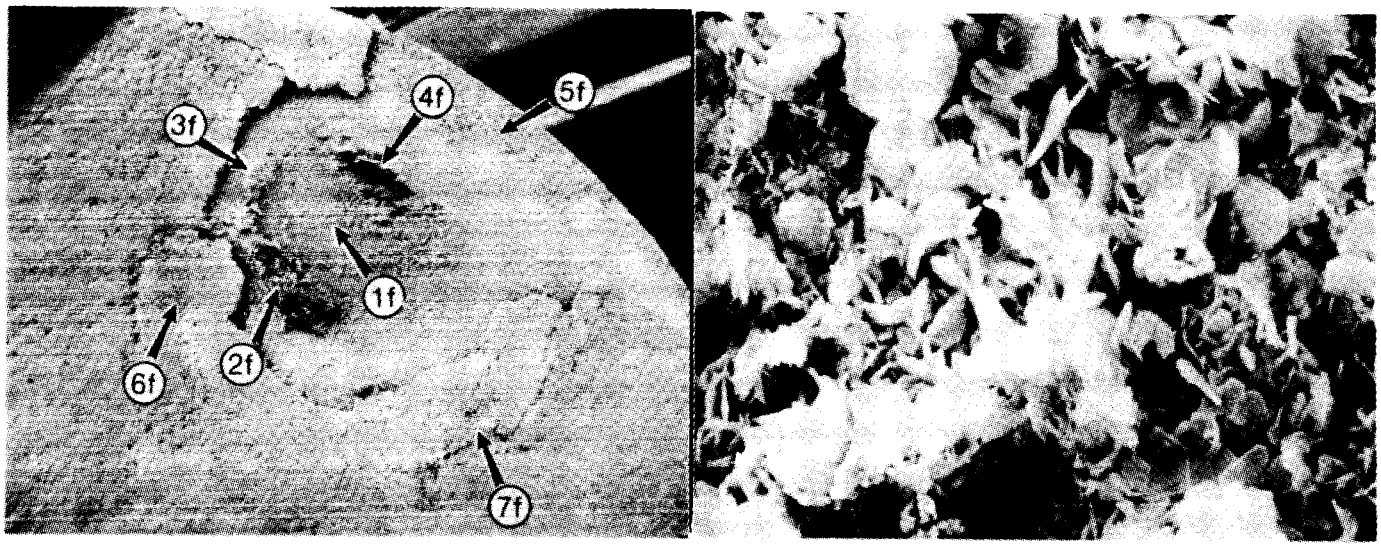


Figure 5. Pictures of Cell Materials from a Shorted Cell of Group 2.

Close-up View of Short on Negative.

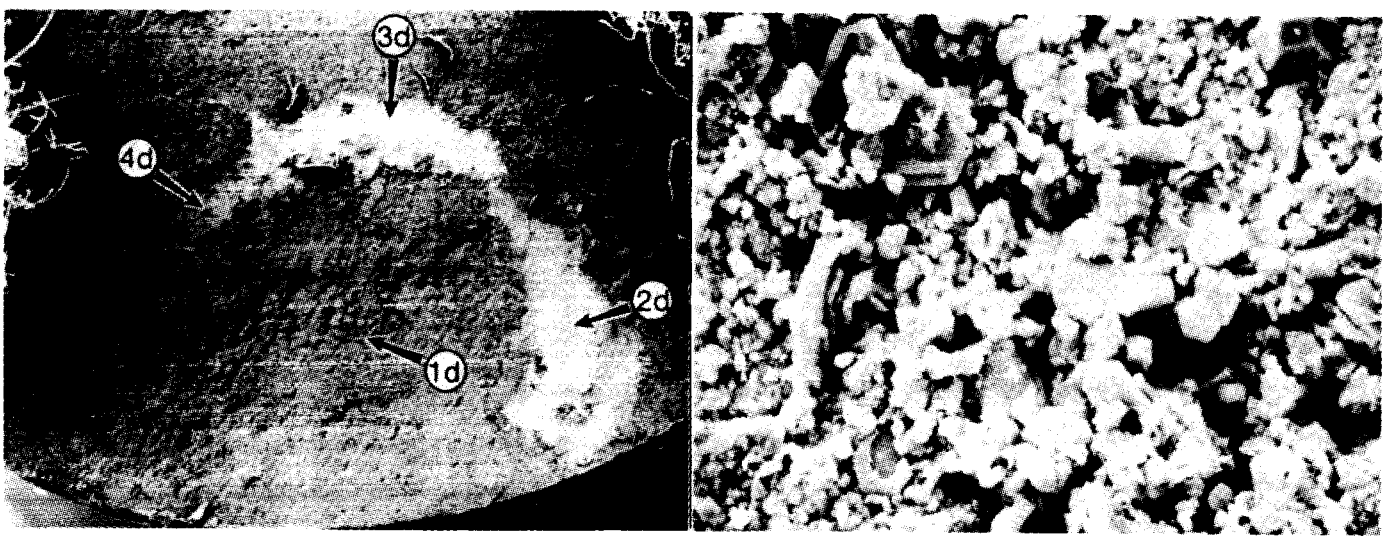
Close-up View of Short on Positive.



Shorted Region. 10 X

Crystals of $Cd(OH)_2$ Around the Short

Figure 6. SEMs of POS # 10, S/N 005 Group 2, 16,150 Cycles.



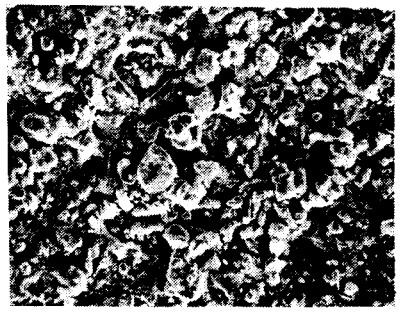
Shorted Region. 10 X

$Cd(OH)_2$ Crystals Around the Short 1250 X

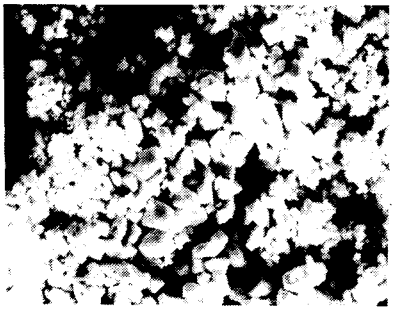
Figure 7. SEMs of NEG # 11, S/N 005 Group 2, 16,150 Cycles.

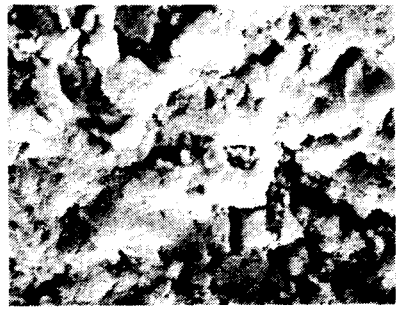
NEGATIVE

POSITIVE

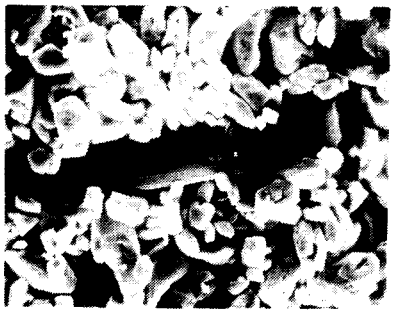


A. S/N 006, Control, 23,468 Cycles.





B. S/N 003, Teflon, 17,760 Cycles.

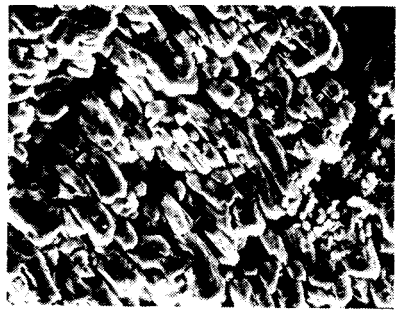


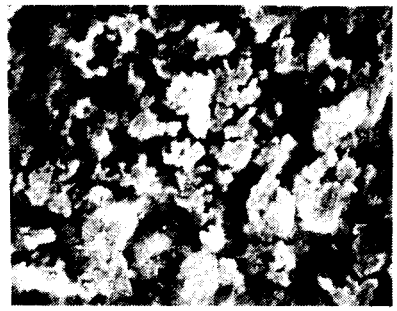
C. S/N 003, Silver, 17,781 Cycles.

Figure 8. SEMs of NEG and of Design Variable Cells.

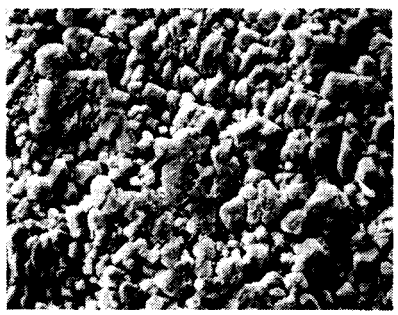
NEGATIVE

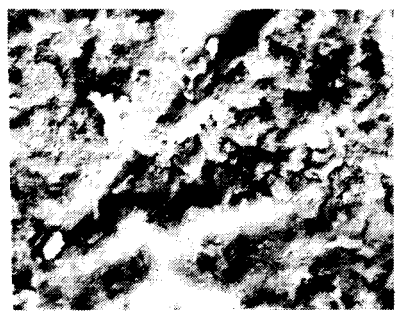
POSITIVE





D. S/N 005, Light Loading, 17,855 Cycles.





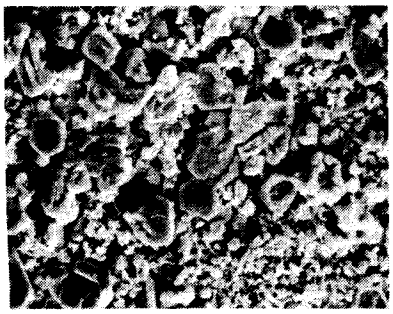
E. S/N 003, No PQ, 23,282 Cycles.

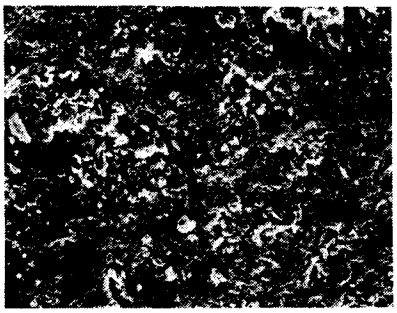
F. S/N 005, Polypropylene, 17,632 Cycles.

Figure 8. Continued.

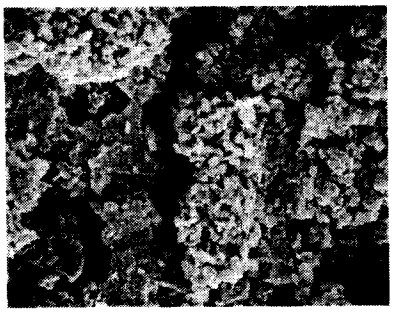
NEGATIVE

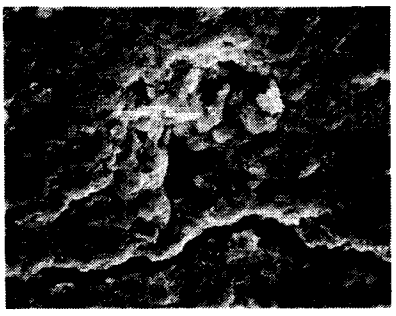
POSITIVE



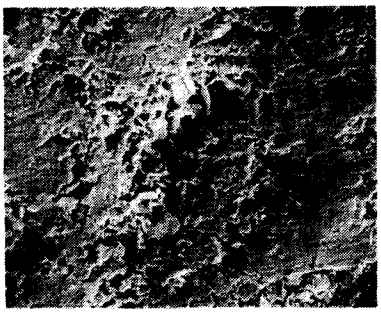


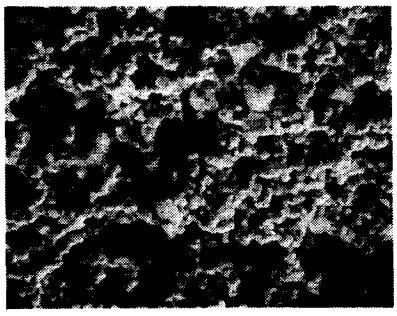
G. S/N 001, A.K.-Old Process, 23,335 Cycles.





H. S/N 003, A.K.-Present Process, 17,300 Cycles.





I. S/N 003, Electrochemical, 5818 Cycles.

Figure 8. Concluded.

Teflon: The cell with teflonated negatives underwent 17,760 cycles. The large number of crystals seen in the SEM of the negative indicate tht teflonation does not prevent or control cadmium migration and crystal growth. In fact as described earlier, one of the teflonated cells with only 16,150 cycles failed due to a severe short (Fig. 5). Pictures of cell materials in Figure 3B show how the separator is adhering strongly to some areas of the negative plates. The SEM of the positives do not show any crystals on their surface.

Silver: SEM of the negatives show large crystal growth and the separators adhering to the surface. The EDAX of negative and positive presented in Figures 9 and 10 do not show any silver present on the electrode surface. However, the Atomic Absorption analysis of the active material from the negative showed a very small content of silver. The performance of the electrodes in terms of capacity and utilization is not superior to those of the Control group. It appears that the addition of silver to the negative plate has not contributed in improving the performance of the cell of this group.

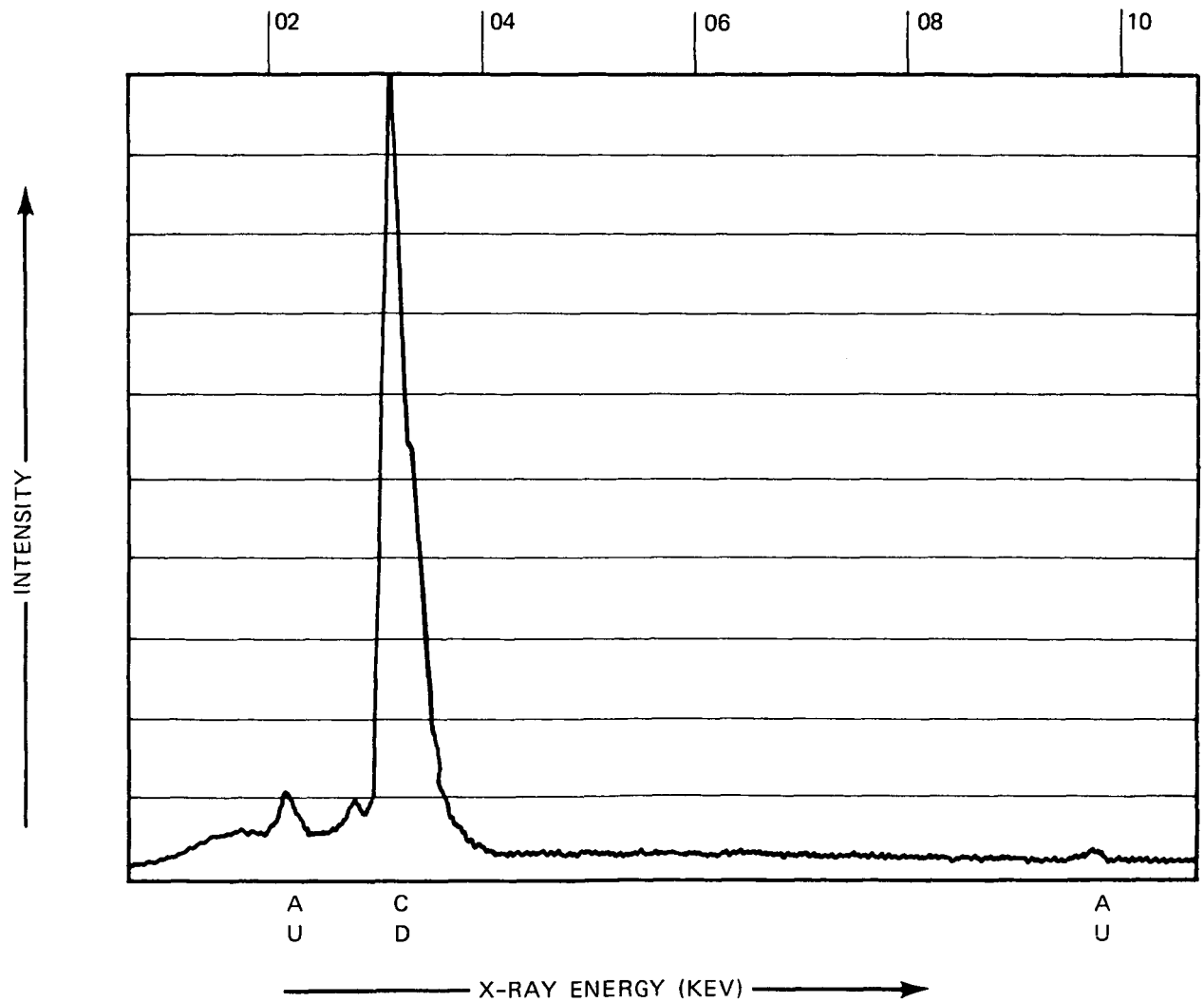


Figure 9. EDAX spectrum of NEG from Group 3.

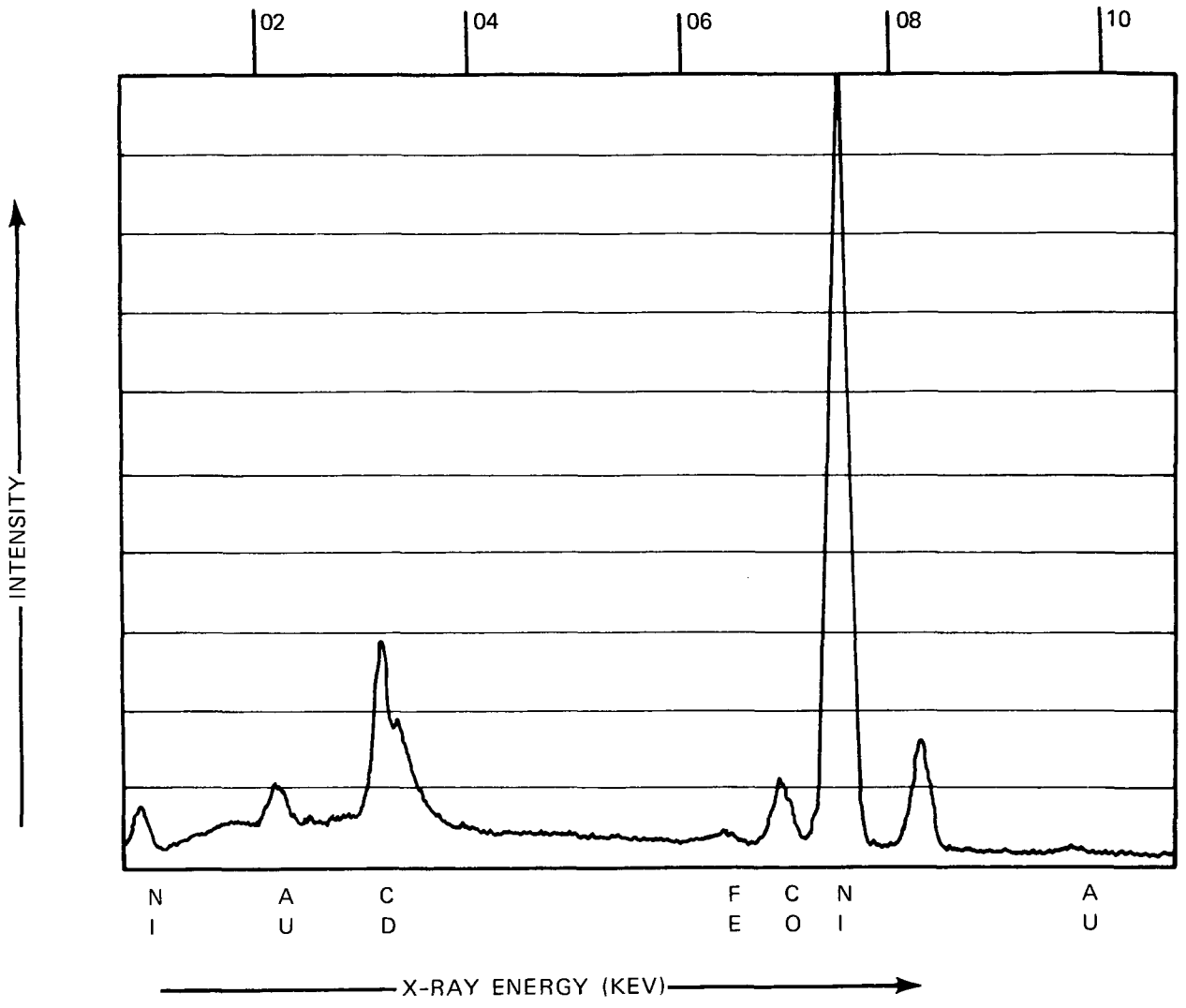


Figure 10. EDAX spectrum of POS from Group 3.

Light Loading: Pictures of the cell materials after 17,855 cycles are shown in Figure 3D. The negative plates have a thin layer of the separator material strongly adhering to the surface. The separators of this group show substantial deterioration. The SEM of negative plate of this cell in Figure 8D shows as usual, heavy crystal growth throughout the surface while the positives show uniform porous texture without any trace of crystal growth. The capacity and utilization are comparable to those of the cell from No PQ group which had 23,282 cycles, and lower than the values for the cell from the Control group with 23,468 cycles.

No PQ: Pictures of cell materials of this group (Fig. 3E) which had 23,282 cycles are similar to those from the Control group with 23,468 cycles, and from group 7 with 23,335 cycles (Fig. 3A and 3G). Discussion on the SEMs of No PQ group and Control group cell has already been made under Group 1.

Polypropylene: Pictures of the separators show that dark gray patches are due to cadmium migration, and that negatives do not have the separator material adhering to their surface (Fig. 3F) unlike in most of the other groups. The SEM of the negative shows heavy crystal growth, while that of the positive shows porous texture and crystals of

cadmium hydroxide in some areas. Capacity and utilization of the electrodes of this group are the lowest among all the groups. This should be ascribed to poor wetability of polypropylene. The cells of this group contained some quantity of electrolyte as the Control.

A.K. Old Process: Pictures of the cell materials from this group with 23,335 cycles in Figure 3G are similar to those of the Control group and No PQ group in Figures 3A and 3E, both of which have been cycled almost to the same extent. The SEMs, like all the other negatives show large crystals. Some of the positives also show crystals in some areas on their surface. A similar observation was made in the case of the positives of the control group cell. But the positives of No PQ group did not show any crystals. However, the overall performance of the electrodes of this group is better than those for the No PQ group and lower than those for the Control group (See Table 4).

A.K. Present Process: Pictures of the cell materials of this group in Figure 3H are similar to those from the Control group in Figure 3A except that the separators had slightly lesser degree of deterioration. The SEM of the negative plate shows crystals of small size while that of the positive shows a crystal free surface. (See Figure 8H) The utilization of the positive and negative is lower than the corresponding values from Control and No PQ groups.

Electrochemical: Pictures of the cell materials which had only 5818 cycles are shown in Figure 3I. The separators at this stage appear clean, with no signs of deterioration. The negative plate surface is mostly free from separator adhesion. The SEM of the negative plate in Figure 8I show crystals in very small areas. The positive plate surface is completely free from crystals and appear porous and uniform than the positives of other groups. SEMs taken after the cell has undergone 14,827 cycles have similar characteristics except that the crystal size on the negative has become slightly larger.

Energy Dispersive X-ray Spectra (EDAX)

The interaction of the electron beam with a specimen in the Scanning Electron Microscope (SEM) produces many signals, including X-rays. Some of the X-rays produced in this manner have energies and wave lengths that are characteristic of the elements in that specimen. To analyze the energies of these characteristic X-rays, an energy dispersive spectrometer is used and the information that comes out in the form of a spectrum is utilized. For example, Figure 9 shows the spectrum of S/N 003, Group 3, Negative #1 which has the peaks due to cadmium and gold indicating that these elements are present in the sample. The spectrum accumulated from S/N 003, Group 3, Positive #6 in Figure 10 shows cadmium, nickel, cobalt, iron and gold peaks. It should be noted that both specimen were coated with gold to provide a conducting path for the SEM electrons. If the specimen are not grounded in this manner there will be a charge build-up on the surface of the specimen which will in turn cause unwanted deflections of the SEM beam. This gold coating accounts for the gold peaks in these spectra. The intensity or the height of the peaks reflects the abundance of various elements in the specimen. For example, the spectra of Negative #1 from S/N 003, Group 3 cell (Fig. 9) shows the presence of essentially 100 weight per cent of cadmium, and that of Positive #6 from the same cell (Fig. 10) shows primarily nickel with trace amounts of cadmium, cobalt and iron. Presence of oxygen, hydrogen or carbon cannot be determined by this technique because the energy dispersive spectrometer accumulates information for element with atomic number 11 and higher only.

To identify traces of silver, the samples of negative and positive from Group 3 cell were examined by this technique. The detectability of the energy dispersive spectrometer is 1000 ppm (0.1 weight %) for most elements. The absence of silver peaks indicate that silver may be present on the surface in amounts less than 0.1 weight per cent.

The Energy Dispersive Spectra of positive plate samples of Group 1 and Group 5 are shown in Figures 11 and 12, respectively. It is evident from these spectra that both specimen consist of same elements: nickel, cadmium, cobalt and iron. The results of semi-quantitative analyses of these two spectra given in Table 6 and 7 indicate that the amounts of elements present in Groups 1 and 5 vary slightly. For example, Group 1 positive contains approximately 2 weight per cent of cobalt while Group 5 positive contains about 3 weight per cent. The first step in obtaining a semi-quantitative analysis from an energy dispersive spectrum is the measurement of peak intensity. The ratios of the measured peak intensities are then converted to elemental composition. The results can be improved by applying ZAF corrections for: i) Z-atomic number effects, ii) A-absorption effects and iii) F-flourescence effects. ZAF corrections are determined by computer reduction of data because of the complexity of the interactions. Application of ZAF corrections attempts to compensate for the three effects mentioned earlier. However, it should be noted that the results are semi-quantitative at best.

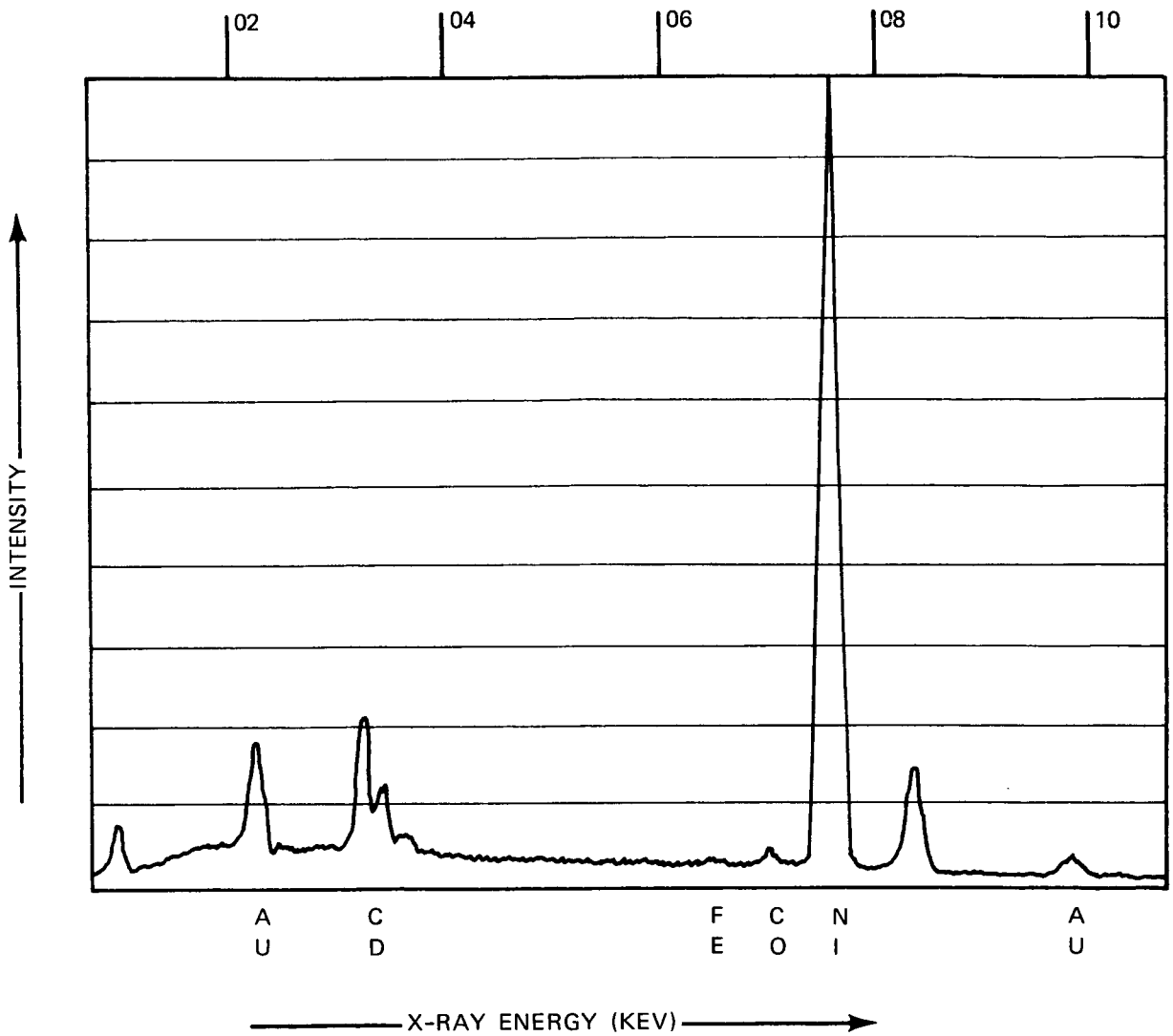


Figure 11. EDAX spectrum of POS from Group 1.

Table 6. EDAX Analysis for POS, S/N 004, Group 1.

ELEMENT	WEIGHT % (ZAF CORRECTED)
Cadmium	15.97
Iron	0.58
Cobalt	1.96
Nickel	81.49

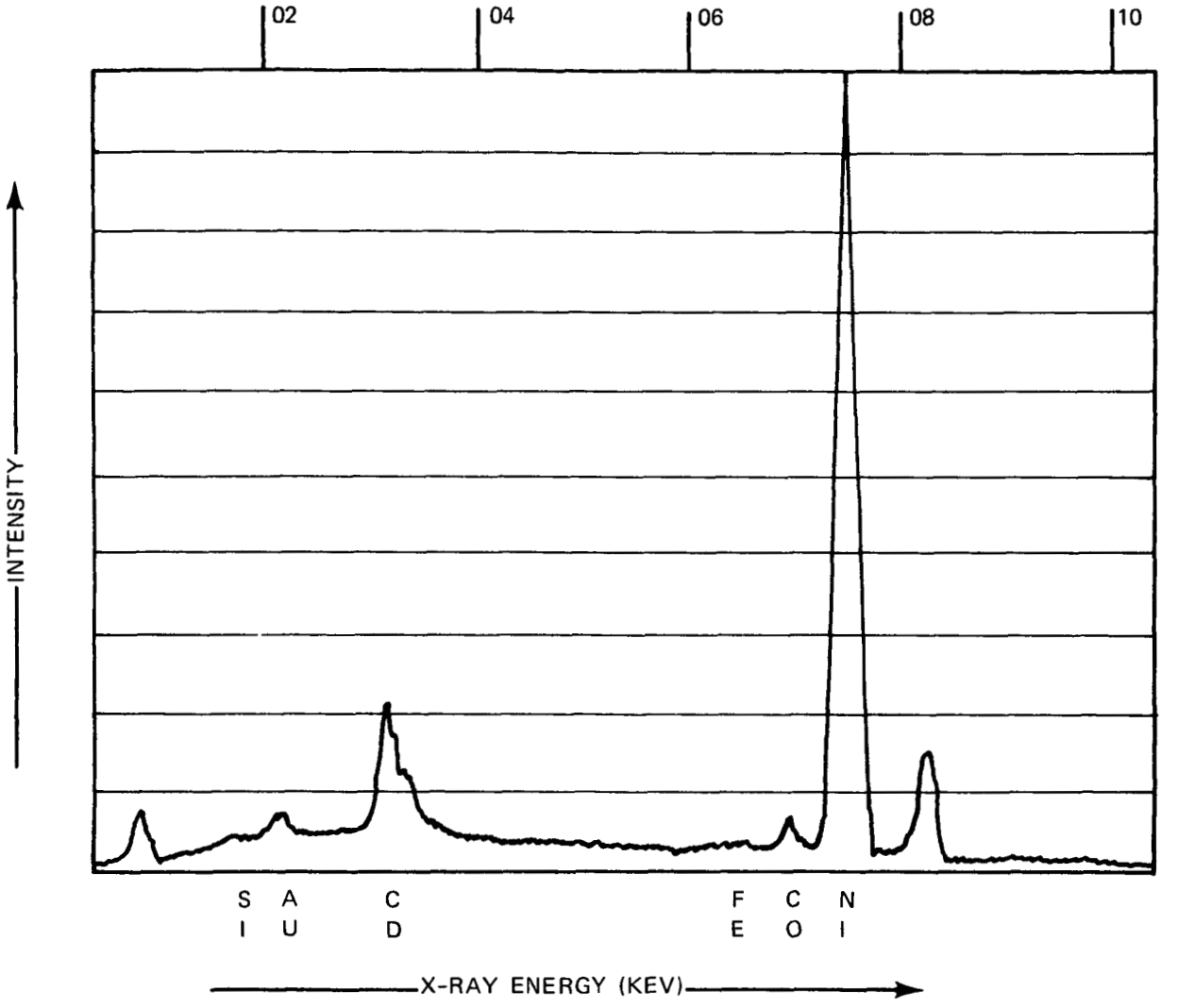
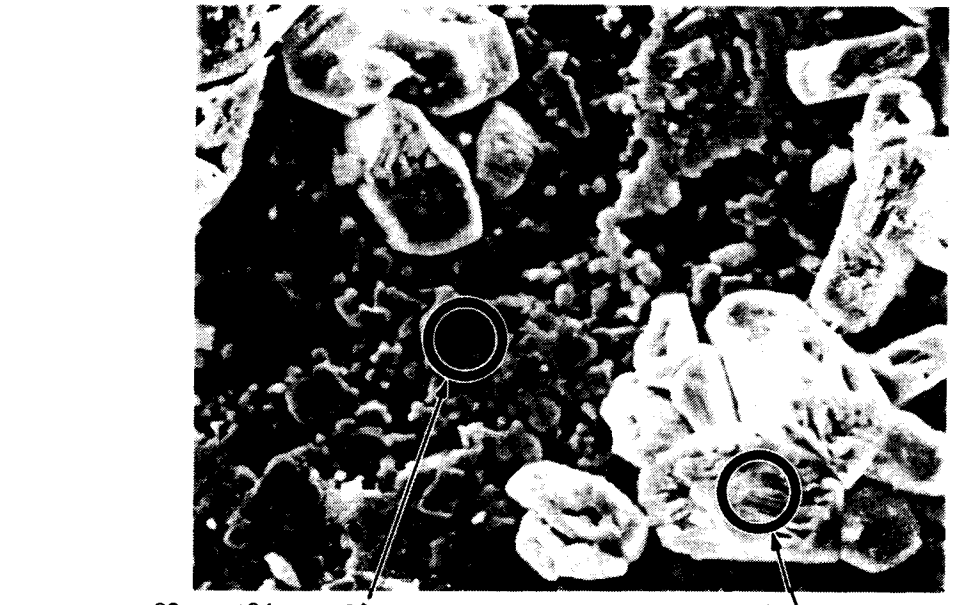


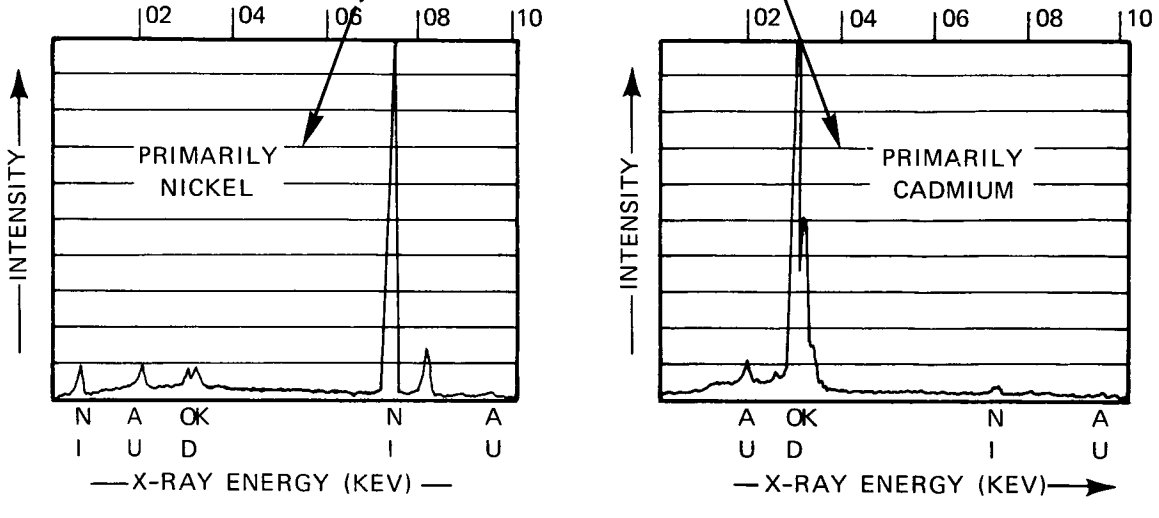
Figure 12. EDAX spectrum of POS from Group 5.

Table 7. EDAX Analysis for POS, S/N 003, Group 5.

ELEMENT	WEIGHT % (ZAF CORRECTED)
Cadmium	17.04
Iron	0.56
Cobalt	3.34
Nickel	74.82

The SEM of the negative plate from S/N 006 Group 1 cell and energy dispersive spectra taken at different areas are shown in Figure 13. The spectra indicates that cadmium and nickel are the primary constituents of the negative plate.





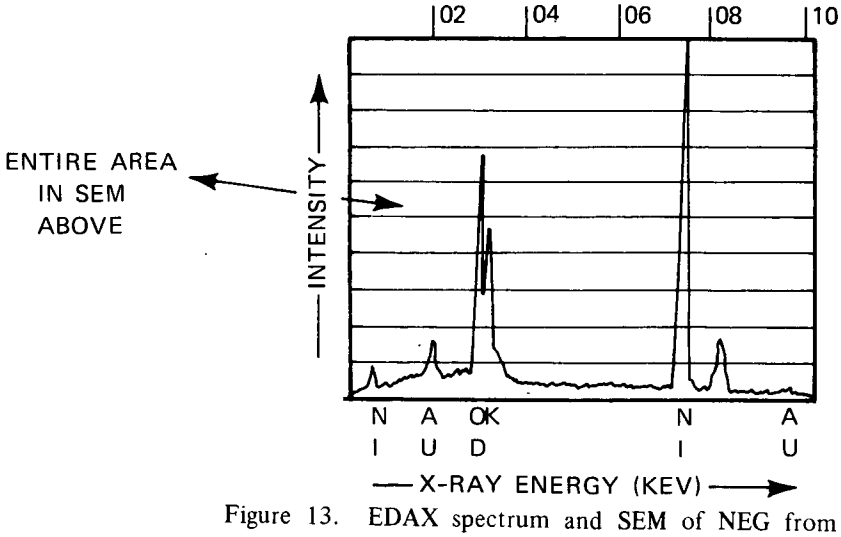


Figure 13. EDAX spectrum and SEM of NEG from Group 1.

Semi-quantitative analysis shows approximately 50 weight per cent of nickel and cadmium. Since the nature of analysis is confined to the top 1um of the surface of the specimen, the results depend on the area analyzed. Hence all spectra are accumulated on large areas. Ideal specimen for EDAX analysis should be smooth and flat. Because the battery plates being porous are not ideal specimen, they may introduce further approximation in the semi-quantitative results.

Physical Measurements

Each Design Variable 12 Ah Cell has 11 positive and 12 negative plates. The positive plates were housed in a bag of separator material. Physical measurements which involve the recording of the weight and thickness of each plate are given in Table 8. The thickness is measured in three separate places (top, middle, bottom) and then averaged. These measurements were done after the extraction of the electrolyte and subsequent drying of the cell materials in an oven at 45 C overnight in a nitrogen atmosphere.

Table 8. Physical Characteristics of Design Variable Cells.

GROUP #	S.N. OF CELL	NO. OF CYCLES	PLATE THICKNESS (cm) POSITIVE	NEGATIVE	PLATE WEIGHT WITH TAB (Gms) POSITIVE	NEGATIVE
1	04	UNCYCL	0.072	0.079	13.69	15.46
	01	5833	0.074	0.080	13.97	14.83
	06	23,468	0.079	0.083	13.79	15.82
2	04	UNCYCL	0.072	0.080	13.85	15.87
	01	5841	0.074	0.079	14.00	14.87
	03	17,760	0.077	0.081	13.97	14.96
3	01	5844	0.074	0.083	14.03	14.82
	03	17,781	0.077	0.083	13.97	15.46
4	01	UNCYCL	0.068	0.079	13.02	14.71
	02	5844	0.072	0.079	13.31	13.83
	05	17,855	0.074	0.080	13.11	14.41
5	01	UNCYCL	0.074	0.079	13.32	15.43
	02	5840	0.077	0.080	13.65	14.92
	03	23,282	0.082	0.083	13.87	15.15
6	02	UNCYCL	0.072	0.079	13.65	15.59
	01	5833	0.074	0.083	13.88	15.38
	05	17,632	0.076	0.082	13.97	13.68
7	05	UNCYCL	0.091	0.074	15.34	14.13
	06	5834	0.094	0.073	15.68	13.68
	01	23,335	0.097	0.079	15.95	13.88
8	02	UNCYCL	0.090	0.071	15.35	14.02
	06	2008	0.093	0.072	15.56	13.66
	05	2459	0.094	0.073	15.57	13.62
	03	17,300	0.102	0.079	16.01	13.74
9	03	5818	0.076	0.078	12.35	15.98
	02	14,827	0.079	0.083	13.10	15.42

The thickness of the positives is plotted as a function of number of cycles in Figure 14. The general behavior in these curves is that the positive swelling increases linearly during the first 6000 cycles, reaching a limiting value. In the case of the positives of Groups 2, 3, 4 and 6, thickness reached a limiting value after about 18,000 cycles. As the cell ages, swelling of the positive plate leads to the squeezing of the deteriorated separator and electrolyte loss between the plates. Dryness of the plates may result in cell failure.

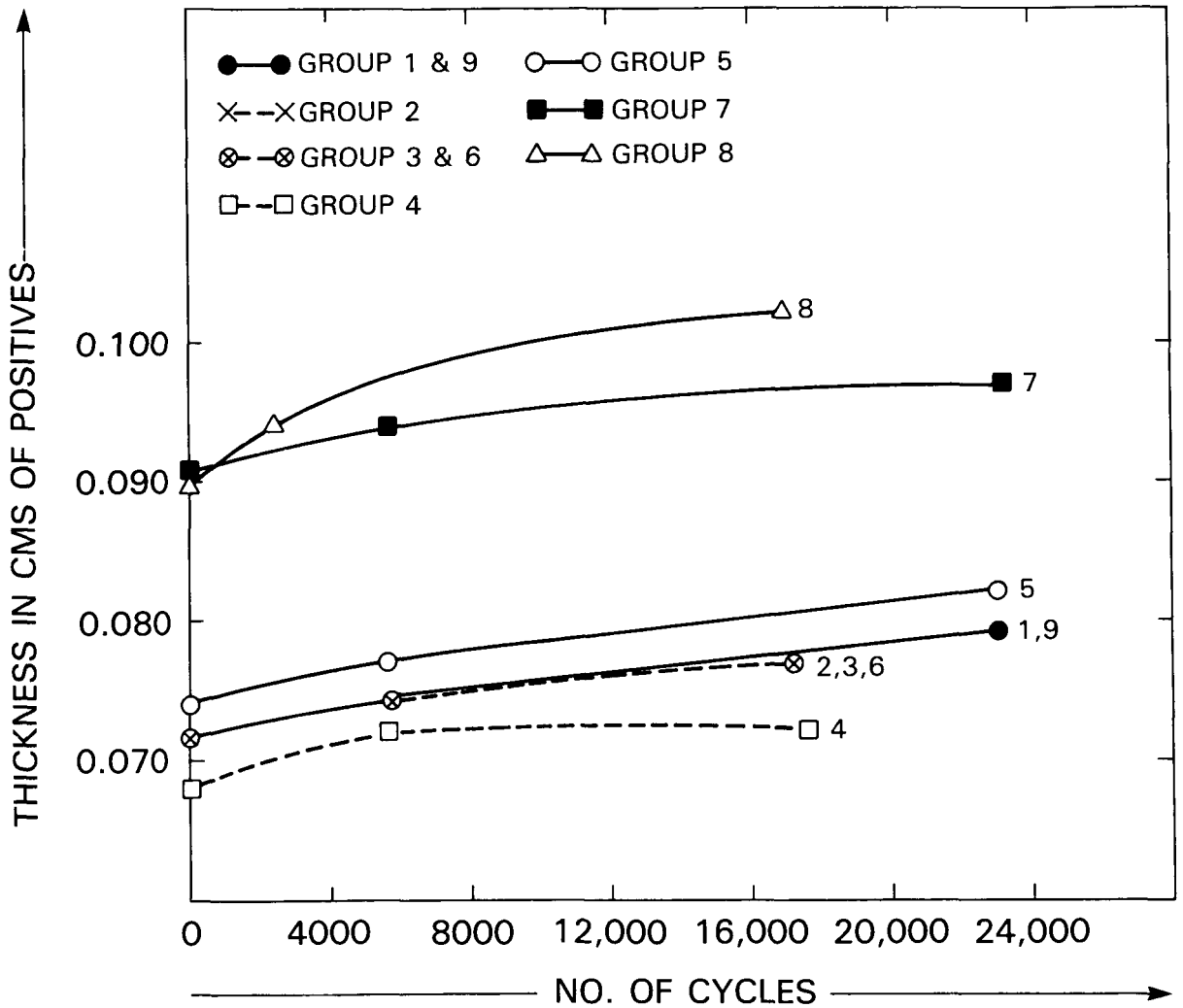


Figure 14. Plot of Positive thickness versus Number of Cycles.

The electrode physical measurements (see Table 8) are in agreement with McDermott and Sommerfeldt (Ref. 15) who reported in the analysis of data from the Accelerated Test Program on 6 Ah Nickel-Cadmium Cells, that there was a strong correlation between interelectrode separation and number of cycles. They also have shown that as the separation of distance decreases, so does the amount of electrolyte in the separators. Moreover, Lim (Ref. 16) has reported that the nickel electrode expands during discharge and that there is a linear relationship between the bending rate (expansion) and depth-of-discharge. The results of nearly 4 years of cycling of the Design Variable Cells show that at a fixed rate of DOD (40%), positive swelling is linear during the first few thousand cycles (6000) and is likely to reach a limiting value later on.

Electrolyte Analysis

Results of electrolyte analysis are given in Table 9. Within a group, carbonate content generally increased as a function of number of cycles. This is expected since the pellon separator material is a polyamide of the formula (-NH-

Table 9. Results of Electrolyte analysis of Design Variable Cells.

GROUP #	NO. OF CYCLES	Gms Electrolyte NEG	POS	SEP	TOTAL	% KOH	% K_2CO_3	ML KOH FOUND	ADDED
1	–	22.55	15.69	13.56	51.80	21.64	9.21	39.85	40/40
	5833	29.32	16.14	9.09	54.55	23.94	6.76	41.42	
	23,468	30.48	20.60	3.06	54.14	22.86	11.83	41.65	
2	–	20.91	15.99	24.63	61.53	26.82	6.49	47.33	48/49
	5841	26.68	16.16	22.42	65.26	25.26	6.91	50.20	
	17,760	29.34	19.40	14.87	63.61	21.03	9.88	48.93	
3	5844	31.03	15.86	9.95	56.84	25.69	6.87	43.72	43/44
	17,781	31.18	19.67	4.77	55.62	19.94	8.36	42.79	
4	–	24.14	16.49	18.17	58.80	25.25	6.45	45.23	45/46
	5844	31.51	16.36	14.70	62.57	19.65	4.71	48.13	
	17,855	37.28	19.51	6.80	63.59	18.40	12.54	48.91	
5	–	23.38	17.77	9.84	50.99	25.40	8.97	39.22	40/41
	5840	28.15	18.12	4.64	50.91	23.53	10.45	39.16	
	23,282	30.61	20.19	0.0	50.80	25.00	11.73	39.08	
6	–	21.80	5.41	8.16	45.37	29.41	7.36	34.90	39/40
	5833	29.84	16.73	3.42	49.99	26.20	9.63	37.45	
	17,632	32.06	18.14	3.64	53.84	17.82	13.71	41.41	
7	–	22.78	20.11	7.63	50.52	22.01	13.35	37.87	38/39
	5834	25.54	21.47	3.70	50.71	20.47	16.08	37.82	
	23,335	24.72	22.38	1.87	48.97	15.72	17.02	37.67	
8	–	21.42	20.10	9.25	50.77	22.50	14.94	37.95	39/40
	2008	27.92	15.47	6.46	49.85	23.43	15.47	37.22	
	2459	22.69	20.58	7.40	50.67	22.15	16.08	37.79	
	17,300	24.60	21.75	1.21	47.56	22.14	13.60	36.59	
9	5818	26.06	25.05	12.10	63.21	14.85	4.53	47.53	48
	14,827	29.49	24.37	5.74	59.60	21.41	11.73	45.85	

(CH2)5-CO)n. The amide groups (-CONH-) that link the hydrocarbon react slowly with the hydroxyl ions of the electrolyte increasing the wetability and ultimately leading to the decomposition of the separator and increasing the carbonate level. This further leads to the degradation of the properties of the separator. The electrolyte distribution follows the same order in all the groups and appears to be independent of the number of cycles. The observed distribution order for the electrolyte is: NEG>POS>SEP.

Capacity and Utilization

Results of capacities and ultization obtained from flooded cell tests are presented in Table 10. The content of additives in positive and negative plates as found by analysis in Table 11. For purpose of comparison, it may be necessary to put the groups into three categories: 1) Groups 2, 3, 4, 6, and 8 that had approximately 17,300 cycles, 2) Groups 1, 5 and 7 that underwent approximately 23,000 cycles, and 3) Group 9 which had 14,827 cycles.

Table 10. Capacities for Design Variable Cells.

NAME	GROUP #	S.N. OF CELL	NO. OF CYCLES	CAPACITY ON CELL BASIS (AH) CHEMICAL POS	CHEMICAL NEG	BASELINE POS	BASELINE NEG	% UTILIZATION POS	% UTILIZATION NEG
CONTROL	1	04	–	22.64	34.02	15.54	25.60	68.87	75.25
		01	5833	21.22	30.30	14.63	18.52	58.92	61.30
		06	23,468	16.74	25.25	11.49	20.16	68.64	79.84
TEFLON	2	04	–	21.74	36.28	16.39	25.56	75.39	70.45
		01	5841	22.90	30.77	15.99	18.67	69.82	60.69
		03	17,760	25.08	26.75	12.70	18.94	50.66	70.80
SILVER	3	01	5844	20.86	32.80	15.55	20.14	74.54	61.06
		03	17,781	23.03	31.84	12.89	19.86	55.97	62.37
LIGHT LOADING	4	01	–	20.02	30.48	14.43	23.83	72.07	78.17
		02	5844	21.44	26.17	13.98	14.47	65.21	55.30
		05	17,855	21.52	28.09	11.33	19.44	52.65	69.21
NO PQ	5	01	–	22.69	34.65	16.91	28.11	74.55	81.11
		02	5840	22.44	32.11	17.02	23.54	75.85	73.31
		03	23,282	22.83	28.82	12.08	20.01	52.91	69.43
POLYPROPYLENE	6	02	–	22.36	36.62	15.89	28.14	71.06	76.83
		01	5833	23.20	31.35	16.66	19.07	71.81	60.83
		03	17,632	25.10	27.83	11.86	14.73	47.25	52.92
A.K.-PLATE OLD PROCESS	7	05	–	25.23	32.54	19.61	24.99	77.70	76.81
		06	5834	26.85	28.83	18.85	23.00	70.20	79.78
		01	23,335	29.46	27.53	16.20	19.51	54.99	70.87
A.K.-PLATE NEW PROCESS	8	02	–	25.63	32.93	16.52	24.86	64.46	75.52
		06	2008	26.97	31.69	19.02	23.47	70.50	74.06
		05	2459	27.90	30.92	18.78	22.96	67.30	74.26
		03	17,300	28.68	27.08	14.85	18.51	51.78	68.35
ELECTROCHEMICAL	9	03	5818	20.82	36.15	13.64	20.88	65.51	57.76
		02	14,827	21.19	30.31	11.10	19.88	52.37	65.59

Table 11. Additives in Design Variable Cells.

NAME	GROUP	S.N. OF CELL	NO. OF CYCLES	% $Cd(OH)_2$ IN POSITIVE	% $Co(OH)_2$ PLATE	AH CHARGED Cd IN NEG	% $Ni(OH)_2$ IN NEG
CONTROL	1	04	UNCYCL	10.74	2.81	0.59	4.04
		01	5833	12.17	2.78	0.75	5.39
		06	23,468	8.57	2.82	0.09	5.57

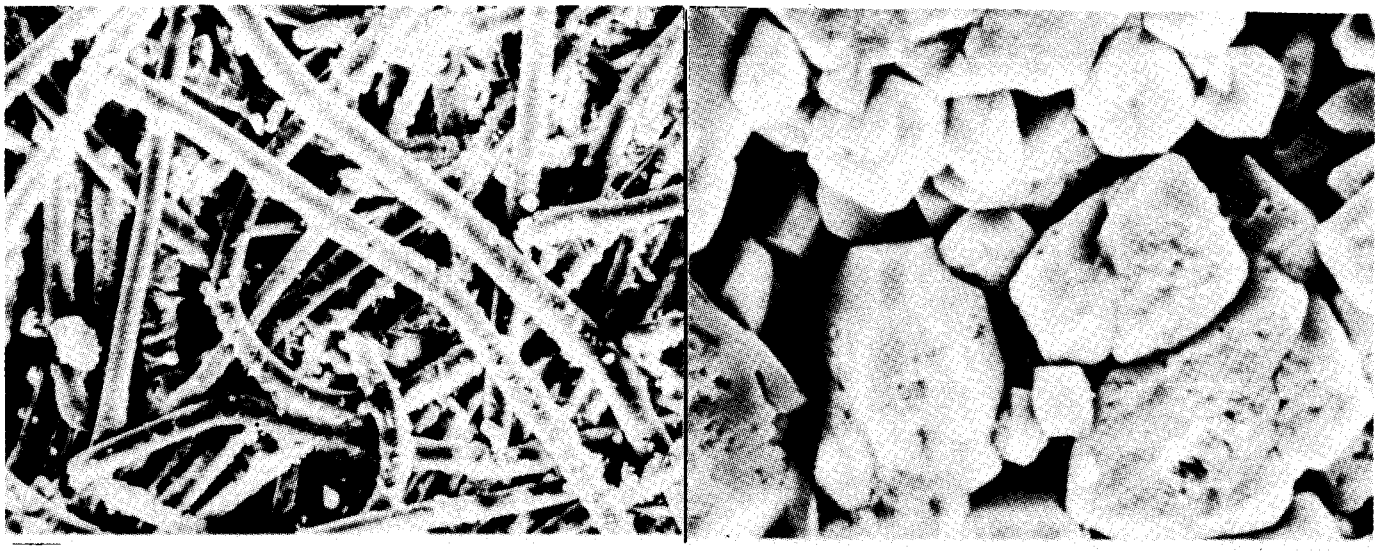
Continue Table 11.

NAME	GROUP	S.N. OF CELL	NO. OF CYCLES	% $Cd(OH)_2$ IN POSITIVE	% $Co(OH)_2$ PLATE	AH CHARGED Cd IN NEG	% $Ni(OH)_2$ IN NEG
TEFLON	2	04	UNCYCL	9.49	3.77	1.17	4.14
		01	5841	11.48	2.98	1.20	5.39
		03	17,760	10.12	2.95	1.35	6.06
SILVER	3	01	5844	12.38	3.14	1.84	4.46
		03	17,781	8.91	2.81	2.58	5.82
LIGHT LOADING	4	01	UNCYCL	11.52	3.12	0.71	4.23
		02	5844	13.27	2.70	0.35	4.14
		05	17,855	8.15	2.11	1.21	4.37
NO PQ	5	01	UNCYCL	6.46	3.20	0.71	4.29
TREATMENT		02	5840	7.31	3.06	1.16	4.32
		03	23,282	8.73	2.31	1.08	4.62
POLYPROPYLENE	6	02	UNCYCL	8.39	3.22	1.02	4.08
SEPARATOR		01	5833	9.63	2.98	0.03	5.06
		05	17,632	9.23	2.30	2.60	6.53
A.K.-PLATE OLD	7	05	UNCYCL	2.75	3.56	0.87	4.41
PROCESS		06	5834	4.92	3.15	0.65	5.40
NO DECARB		01	23,335	7.22	2.92	0.42	6.14
A.K.-PLATE	8	02	UNCYCL	4.71	3.79	0.91	4.45
NEW PROCESS		06	2008	5.36	2.57	0.89	4.37
		05	2459	4.55	2.53	0.78	4.47
		03	17,300	9.26	2.57	0.13	4.71
ELECTROCHEMICAL	9	03	5818	7.68	5.40	3.04	4.07
		02	14,827	12.11	1.87	1.23	3.59

In the first category, polypropylene group (Group 6) showed the worst performance. It not only showed heavy cadmium migration, but also low positive and negative plate capacity and utilization. Teflon (Group 2) and Light Loading (Group 4) groups showed equal performance with regards to capacity and utilization. But visual examination showed that the separators of Teflon group had cadmium migration higher than the Light Loading group. In addition, one of the teflonated cells failed at 16,150 cycles due to severe shorting which can be related to cadmium migration.

In the second category, Control (Group 1) and No PQ (Group 5) groups performed better than the A.K. Old Process group and outperformed all the groups in the other two categories as well. SEMs of cycled and uncycled sample plates from Control and No PQ groups are shown in Figure 15 and 16 respectively. It has been observed that the negative from an uncycled cell of Control has a small number of crystals (Fig. 15) while that from an uncycled No PQ is free from such crystals on its surface.

Results of capacity checks made at an interval of 6 months through 2 years, and then on a yearly basis till the end-of-cycling have been documented (Ref. 10). These capacity checks consisted of a discharge at the nominal cycling discharge rate of 9.6 Amperes to a voltage of .75 Volts. Results indicate that the No PQ group outperformed the other groups. Table 10 indicates that all the three groups in the second category performed well in maintaining a reasonably good base line capacity. It has been documented (Ref. 10) that No PQ group lost only 15 per cent of its initial capacity over 3 years of cycling and 55 per cent by the end-of-cycling which was 4 years.



NEG # 3 With Layer of Separator (320 X)

NEG # 1 Crystals of $Cd(OH)_2$ 2500 X

SEMS OF NEG. GE 12 AH S/N 006 GROUP 1 23,468 CYCLES

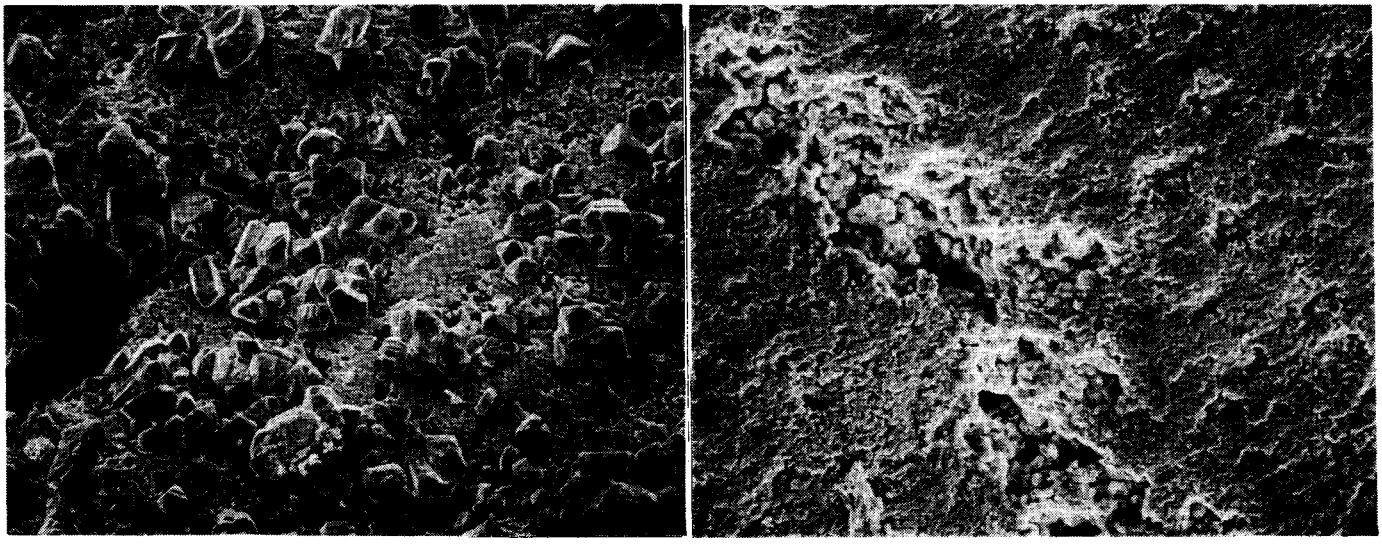
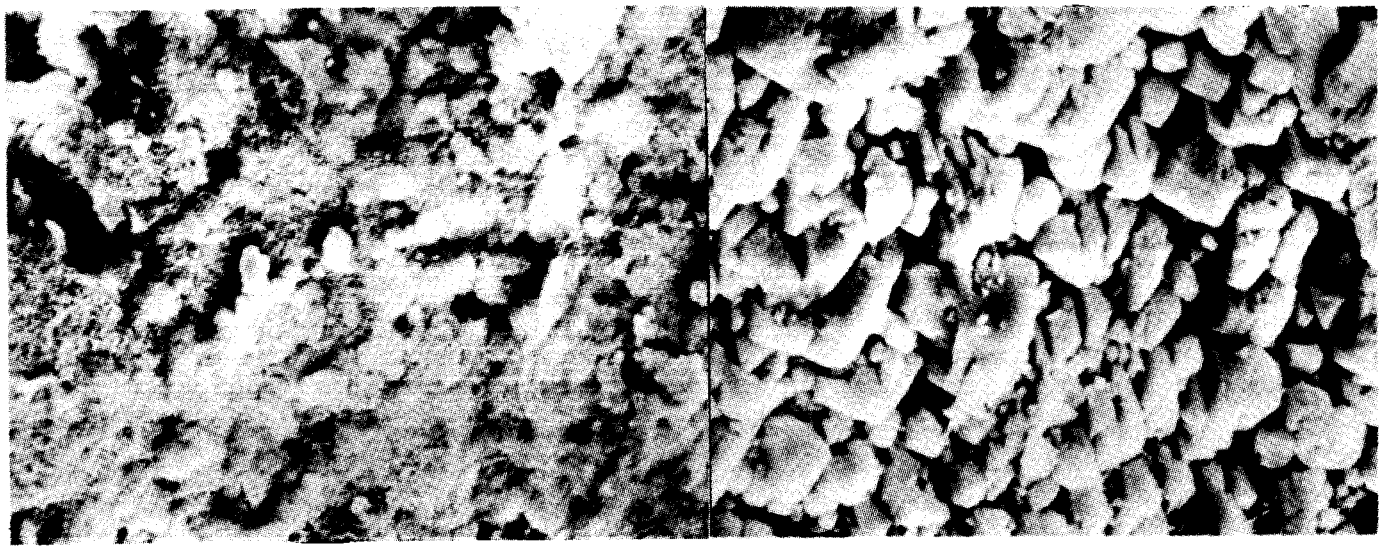


Figure 15. SEMS of NEG from Group 1.



SEM of POS # 2 1250 X

SEM of NEG # 1 – Large Crystals 2500 X of $Cd(OH)_2$

GE 12 AH S/N 003, GROUP 5 23,282 CYCLES

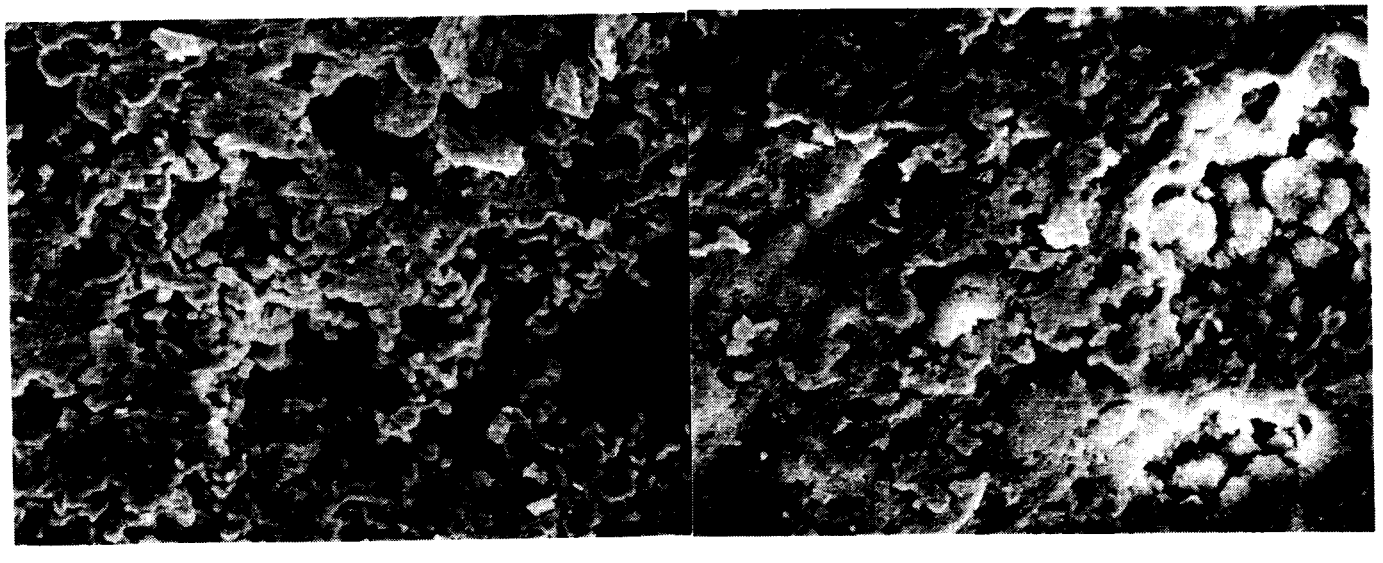


Figure 16. SEMs of NEG and POS from Group 5.

A.K. Old Process Group had high carbonate content compared to the Control and No PQ groups, although positive swelling was small.

CONCLUSIONS

The No PQ group showed good overall performance in terms of capacity, utilization, cadmium migration and visual inspection. The Control group which had PQ treatment and the A.K. Old Process group which did not have PQ, but had high carbonate content, performed equally well. In particular, a selection between the Control and No PQ group is difficult without further work such as, longer period of cycling, capacity test and final tear-down analysis.

RECOMMENDATION

It is recommended that the remaining cells of A.K. Old Process, Control and No PQ groups be cycled for one or two years, and the capacity test and tear-down analysis be performed.

ACKNOWLEDGEMENT

The author extends his gratitude to Mssrs. Floyd Ford and Michael Tasevoli at the NASA/GSFC, Greenbelt, MD 20771 for the support of NASA Grant NSG5009. He would like to acknowledge Mssrs. George Morrow and Thomas Yi for useful comments in preparing this document. The author also expresses his appreciation to Dr. Michael Rock, Mr. Sher Khan and Miss Angelie McNair of Bowie State College for their help in the analytical work, to Mr. Brad Parker and Miss Diane Kolos of Code 313, GSFC for SEMs and pictures of cell materials.

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BIBLIOGRAPHIC DATA SHEET

1. Report No.	2. Government Accession No.	3. Recipient's Catalog No.
NASA TM-87774		

4. Title and Subtitle	5. Report Date
Analysis of 12 AH Aerospace Nickel-Cadmium Cells From the Design Variable Program	APRIL 1987
	6. Performing Organization Code

7. Author(s)	8. Performing Organization Report No.
Kunigahalli L. Vasanth and George Morrow	86B0186

9. Performing Organization Name and Address	10. Work Unit No.
Goddard Space Flight Center Greenbelt, Maryland 20771	11. Contract or Grant No.
	13. Type of Report and Period Covered
12. Sponsoring Agency Name and Address	Technical Memorandum
National Aeronautics and Space Administration Washington, DC 20546	14. Sponsoring Agency Code

15. Supplementary Notes

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16. Abstract

The Design Variable Program of NASA/GSFC provided a systematic approach to evaluate the performance of 12 Ampere-Hour Nickel-Cadmium cells of different designs. Design Variables tested in this program included teflonated negative plates, silver treated negative plates, lightly loaded negative plates, positive plates with no cadmium treatment, plate design of 1968 utilizing old and new processing techniques and electrochemically impregnated positive plates. These cells were life cycled in a Low-Earth Orbit (LEO) regime for 3 to 4 years. Representative cells taken from the Design Variable Program were examined via chemical, electrochemical and surface analyses. The results indicate:

1. positive swelling and carbonate content in the electrolyte increase as a function of number of cycles,
2. electrolyte distribution follows a general order NEG > POS > SEP,
3. Control and No PQ groups outperformed the rest of the groups, and
4. the polyproylene group exhibited heavy cadmium migration and poor performance.

17. Key Words (Selected by Author(s))	18. Distribution Statement
Nickel-Cadmium Cells	Unclassified - Unlimited Subject Category 33

19. Security Classif. (of this report)	20. Security Classif. (of this page)	21. No. of Pages	22. Price*
Unclassified	Unclassified	31	A03

*For sale by the National Technical Information Service, Springfield, Virginia 22161

NASA-Langley, 1987