RESULTS OF ANALYSIS ON THE DESIGN VARIABLE CELLS

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INTRODUCTION

Sealed Nickel-Cadmium aerospace cells play a very important role in the mission of the satellite. There has been a constant effort to improve the cycle life, energy density, and reliability of these cells by many manufacturers and users. The Design Variable Cell Program is one systematic approach started by NASA in collaboration with General Electric (GE) towards that goal. Nine important designs were selected for evaluation.

Fifty-two nickel-cadmium cells each of 12AH nominal capacity manufactured by GE were sent to the Naval Weapons Support Center for evaluation of different design variables with which these cells were built. Figure 1 shows the different plate treatments and designs of the cells. The evaluation test procedure and the results of evaluation have been documented by Jim Harkness in the report WQEC/C 79-114 in December 1979 [1]. These cells were then life cycled in a Low-Earth Orbit (LEO) regime.

In February 1979 eight 5-cell packs, pack 3D through 3K corresponding to Group 1 to 8, were put on life test. The life test parameters were:

Temperature	20°C
Cycle Period	90 Minutes
Depth-of-Discharge	40 Percent
Charge Rate	9.6 Amps
Discharge Rate	9.6 Amps
Voltage Limit Per Cell	1.453
Percent Recharge	110 to 115

Cells of Group 9, Pack 3L, were put on life test in August 1979 with the same test regime.

A brief description of the design variables for each group of cells is given by George Morrow in his paper in the present proceedings, and, hence will not be repeated here.

After 1 year of cycling, one cell from each pack was removed and the initial evaluation tests were repeated. An update of the results of evaluation test and performance of these cells was presented by David Baer in the 1981 Battery Workshop [2]. The results of chemical and electrochemical analysis of the cells that were pulled out were presented by Kunigahalli Vasanth [3].

The purpose of this presentation is to give an update on the performance of the design variable cells along with the results of chemical, electrochemical analysis and capacity checks performed on cells that were cycled 3 to 4 years.

Experimental Approach

The experimental techniques that have been followed in this investigation are:

- o Visual Inspection
- o Physical Measurements
- o Chemical and Electrochemical Analysis
- o SEM Examination

A teardown analysis of each cell was carried out according to the analysis procedures given in the NASA Document X-711-74-279 Revision A.[5].

Visual Examination

On opening the cells, it was found that the cell pack was usually moist with electrolyte, the extent varying from one cell to another. With the exception of one or two groups, the separators were deteriorated very much and invariably were stuck to the surface of the negative electrode. In other words, the separator bags could not be taken out in one single piece as in the case of uncycled cell. The separator that came off the electrodes had dark to light gray patches due to different extents of cadmium migration. The polypropylene separator group cell showed very heavy cadmium migration although the separators came off in one piece (Figure 3). Strong adherence of the thin film of separator material on the negative electrode is common to all the other groups (Figure 4). The positive electrode could be easily separated from the separator.

One of the cells of Group 2 was found to have a short. The short as one can see from Figure 5 is extended to a couple of plates on either side in the stack. The SEM's in and around the short on the positive plate shows the presence of large crystals of $Cd(OH)_2$ which obviously must have migrated from the neighboring negative plate and pierced the separator material thus causing the cell failure. This particular cell was identified in the life test regime to be one that was not accepting charge. Figures 6 and 7 show the short and crystals on the negative and positive plate, respectively.

Physical Measurement

Each design variable 12AH cell consists of 11 positive and 12 negative plates. The positive plates were housed in a bag of separator material. Physical measurements involve the recording of the weight and thickness of each plate and are given in Table 1. The thickness is measured in three separate places (top, middle, bottom) and later averaged. These measurements were done after the positives, negatives, and the separators were soxhleted separately in order to extract the electrolyte and further dried in an oven at $45^{o}C$ overnight in a nitrogen atmosphere.

For all the groups, the thickness of the positives is plotted versus the number of cycles in Figure 8. The general behavior that can be seen in these curves is that the positive swelling takes place linearly during the first 6,000 cycles finally tending to taper off to a limiting value. In

the case of positives of cells of Groups 2, 3, 4, and 6, the flat part of the curve after about 18,000 cycles indicates that the thickness is reaching a limiting value. As the cell ages, swelling of the positive plate occurs leading to the squeezing of the deteriorated separator material and electrolyte loss between the plates. The dryness of the plates may result in cell failure.

P. McDermott and E. Sommerfeldt [6] reported in the analysis of data from the Accelerated Test Program on 6.0AH aerospace nickel-cadmium cells, that there was a strong negative correlation between interelectrode separation and number of cycles. They also have shown that as the separation decreases, so does the amount of electrolyte in the separators. Our results are in agreement with their observations (see Table 2). Electrolyte decreases in the separator as the positive swells due to cycling. H. Lim [7] 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 shows that at a fixed rate of DOD (40%) the positive swelling is linear with respect to the first few thousand cycles (4000) and is likely to reach a limiting value later on.

Electrolyte Analysis

The results of the electrolyte analysis for all the design variable groups are given in Table 2. Within a given group, the carbonate content generally increases as a function of the number of cycles. This should be expected since the Pellon separator material is a polyamide of the formula $(-NH-(CH_2)_5-CO)_n$. 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 thus increasing the carbonate level. This also leads to the degradation of the properties of the separator. The results also show that the electrolyte distribution follows the same order for all the groups considered and seem to be independent of the number of cycles.

The electrolyte distribution order is NEG>POS>SEP.

Capacity and Utilization (See Table 3)

For purposes of comparison, it may be necessary to divide the groups into three categories:

(1) Groups 2, 3, 4, 6, and 8 that underwent approximately 17,300 cycles
(2) Groups 1, 5, and 7 that underwent approximately 23,000 cycles
(3) Group 9 that underwent approximately 14,827 cycles

Considering the first category the polypropylene group (Group 6) is the one that is hard hit. It not only shows very heavy cadmium migration, but low positive and negative plate capacity and utilization. Among the other groups in this category, Teflon (Group 2) and Light Loading (Group 4) show equal performance with regard to capacity and utilization. But the visual examination of cells show that the teflonated cell separators have cadmium migration higher than that in the case of cells with light loading (Group 4). 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, the Control (Group 1) and No Pq (Group 5) groups performed better than the A.K. Plate Old Process and the other groups as well. SEM's of the sample electrode plates from Group 1 and Group 5 are shown in Figures 13-16. Analysis by George Morrow shows that the No Pq lost only 15% of initial capacity in 3 years of cycling and about 55% by the end of cycling, i.e., 4 years. A first look at the capacities and utilization in Table 4 for the cells in category 2, shows that all three groups seem to have performed equally. However, the A.K. Old Plate Process has large carbonate content compared to control and No Pq groups. But the positive swelling is small (refer to Table 1 and Table 2). Analysis of electrical test results show that the No Pq group lost only 15% of initial capacity in 3 years of cycling, and about 55% by the end of cycling. Further, a comparison of the end-of-eclipse voltages for these design variable groups have shown that the no pq group performed better than the rest of the groups.

It is rather difficult to choose between the Control and No Pq group, in that, the chemical analysis and electrochemical results are almost similar and group 1 shows a higher percent of utilization. A closer analysis between these two groups now becomes necessary to decide one way or the other.

NOTE: The baseline capacity test is designed to determine the actual plate capacity after a 100% overcharge based on the manufacturer's nominal cell capacity.

Cycling test is designed to determine the steady state cycling capacity. The duration of each charge cycle assures an input of 120% of the baseline capacity. The capacity of each cycle is measured at C/2 rate of discharge. The capacity obtained on the third cycle is defined as the steady-state capacity.

The author expresses his appreciation to Sher Khan, Angelie McNair, and Dr. M. Rock of Bowie State College for their help in the analysis, to Diane Kolos and Brad Parker of the Goddard Space Flight Center for pictures and SEM's, and to NASA/Goddard Space Flight Center for the award of Grant NSG-5009.

FIGURES

REFERENCES

1. J. Harkness, "Initial Evaluation Tests of GE 12AH Nickel-Cadmium Spacecraft Cells with Design Variables," WQEC/C 79-114, December 1979

2. D. Baer, "Comparisons of Different Plate Treatments and Designs - An Update," GSFC Battery Workshop Proceedings, NASA CP 2217, p. 435, November 17-19, 1981

3. V. Kunigahalli, "Comparisons of Different Plate Treatments and Designs Analysis," GSFC Battery Workshop, NASA CP 2217, p. 443, November 17-19, 1981

4. G. Morrow, "Nickel-Cadmium Cell Design Variable Program Data Analysis," GSFC Battery Workshop Proceedings, November 13-15, 1984.

5. G. Halpert and V. Kunigahalli, "Procedure for Analysis of Nickel-Cadmium Cell Materials," X-711-74-279, Revision A, December 1980

6. E. Sommerfeldt and P. McDermott, "Analysis of Data from the Accelerated Test Program on Aerospace Nickel-Cadmium Cells," X-711-77-193, July 1977

7. H. Lim, "Expansion of the Nickel Electrode," GSFC Battery Workshop, NASA CP 2177, p. 175, November 18-20, 1980

CELL DESIGN VARIABLES - GE 12 AH CELL

VARIABLE	GROUP #	TYPICAL POSITIVE THICKNESS cm	TYPICAL NEGATIVE THICKNESS cm	POSITIVE LOADING gm/dm^3 OF SINTER	NEGATIVE LOADING gm/dm^3 OF SINTER	FINAL KOH QUANTITY cc N/V3rd**	PRECHARGE ADJUST*** Ah
CONTROL*	1	0.069	0.079	2095	2180	40/40	4.6
TEFLON TREATMENT	2	0.069	0.079	2095	2180	48/49	4.6
SILVER TREATMENT	3	0.069	0.079	2095	2180	43/44	4.6
LIGHT LOADING	4	0.069	0.079	1840	1833	45/46	4.6
NO P.Q. TREATMENT	5	0.069	0.079	2113	2180	40.3/41.5	4.6
POLYPROPYLENE SEPARATOR	6	0.069	0.079	2095	2180	39/40	4.6
A.K. PLATE-1968 DESIGN, NO PQ OLD ECT PROCESS, NO DECARB PROCESS	7	0.081 (UNSIZED)	0.066	2130	2542	38/39	0
A.K. PLATE-1968 DESIGN, NO PQ PRESENT AEROSPACE CELL PROCESSES	8	0.081 (UNSIZED)	0.066	2130	2542	39/40	1.8

*CONTROL CELL REPRESENTS PRESENT AEROSPACE DESIGN AND PROCESSES WITH NO EXTRA TREATMENTS: NONWOVEN NYLON SEPARATOR, P.Q. TREATED POSITIVES, DECARBONATION PROCESS, IUE LOADING LEVELS, 31% KOH.

**TWO CELLS IN EACH GROUP CONTAINED SIGNAL ELECTRODES.

***BASED ON 228 cc O^2/Ah.

Figure 1. Different Plate Treatments and Designs

EXPERIMENTAL TECHNIQUES:

1. VISUAL INSPECTION
2. PHYSICAL MEASUREMENTS
3. CHEMICAL ANALYSIS
4. ELECTROCHEMICAL ANALYSIS

Figure 2. Experimental Techniques

CELL MATERIALS FROM S/N 005, GROUP 6, 17,632 CYCLES, SHOW HEAVY CADMIUM MIGRATION

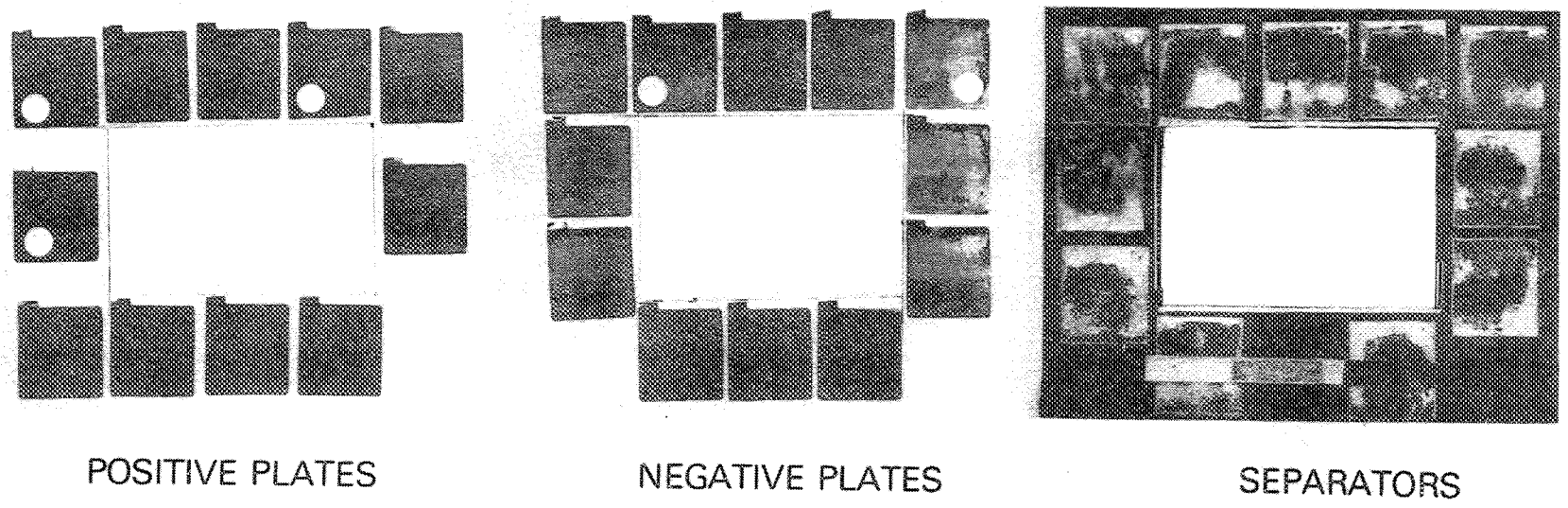


Figure 3. Heavy Cadmium Migration in Polypropylene Group Cell

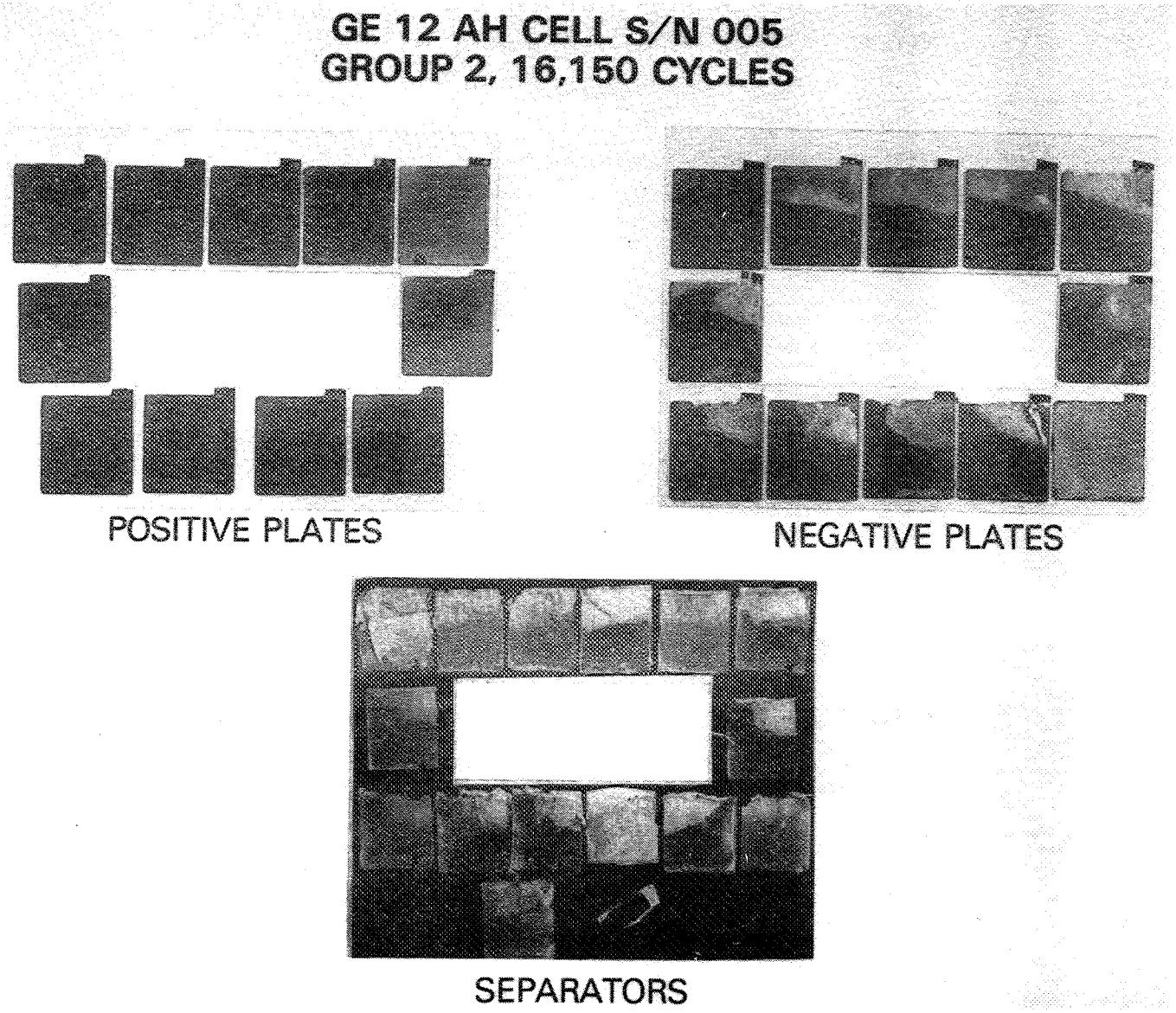


Figure 4. Example of Cell Materials from Teflon Group Show SEP Adhering to NEG

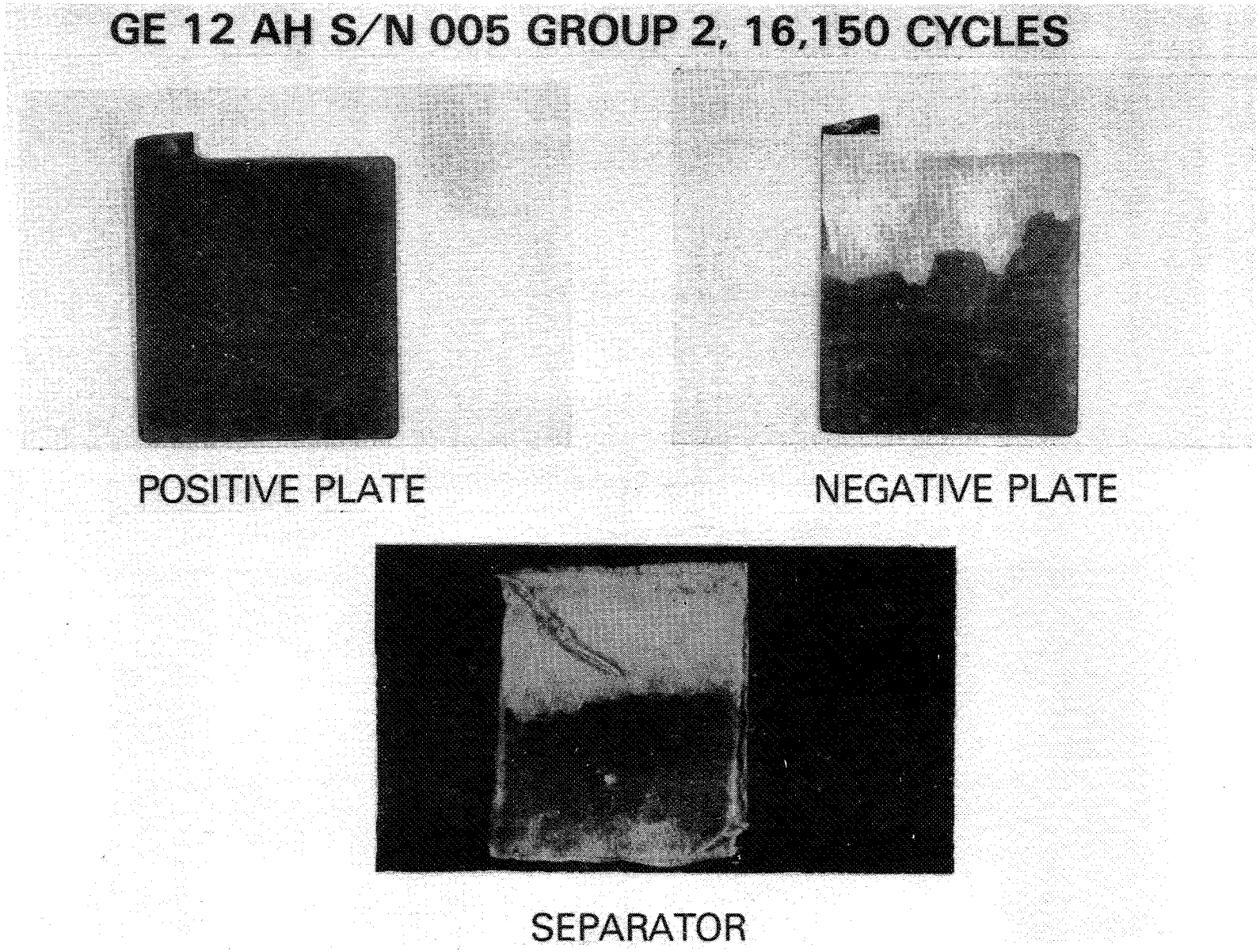


Figure 5. Close-up View of POS, NEG, and SEP in Teflon Group Cell

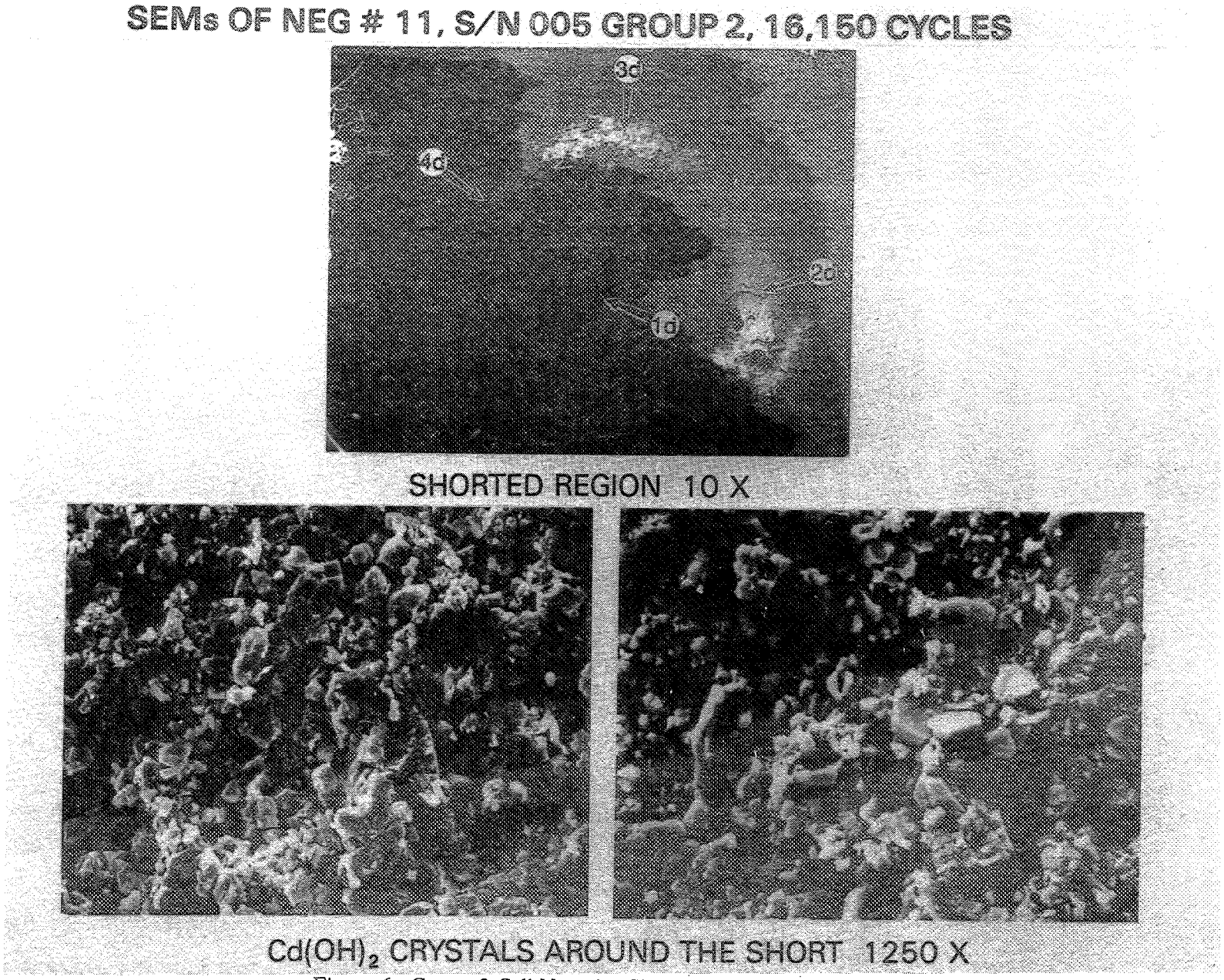


Figure 6. Group 2 Cell Negative Showing the Short and Crystals

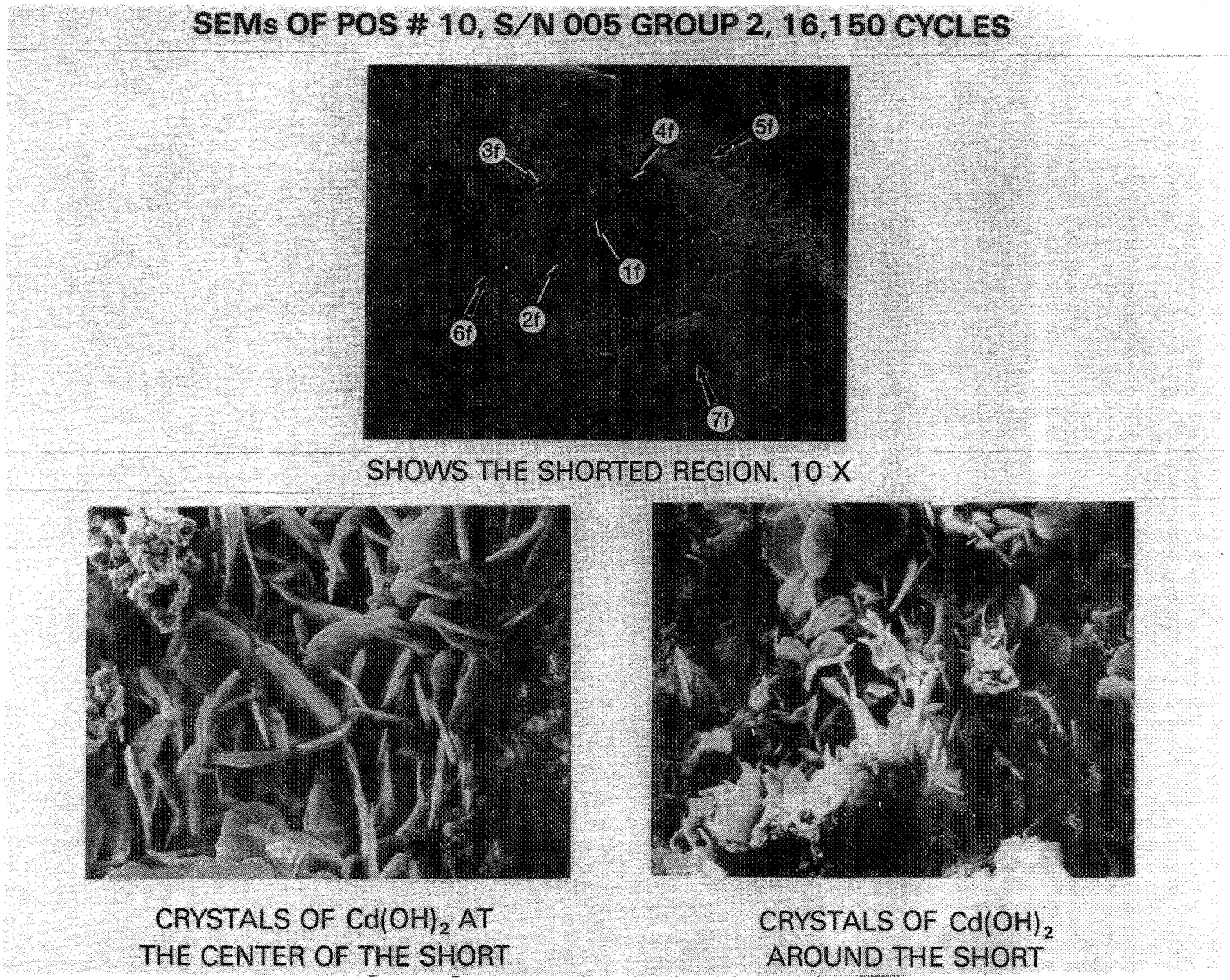


Figure 7. Close-up View of Positive Showing the Short and Crystals

POS. THICKNESS VS NO. OF CYCLES FOR DESIGN VARIABLE CELLS

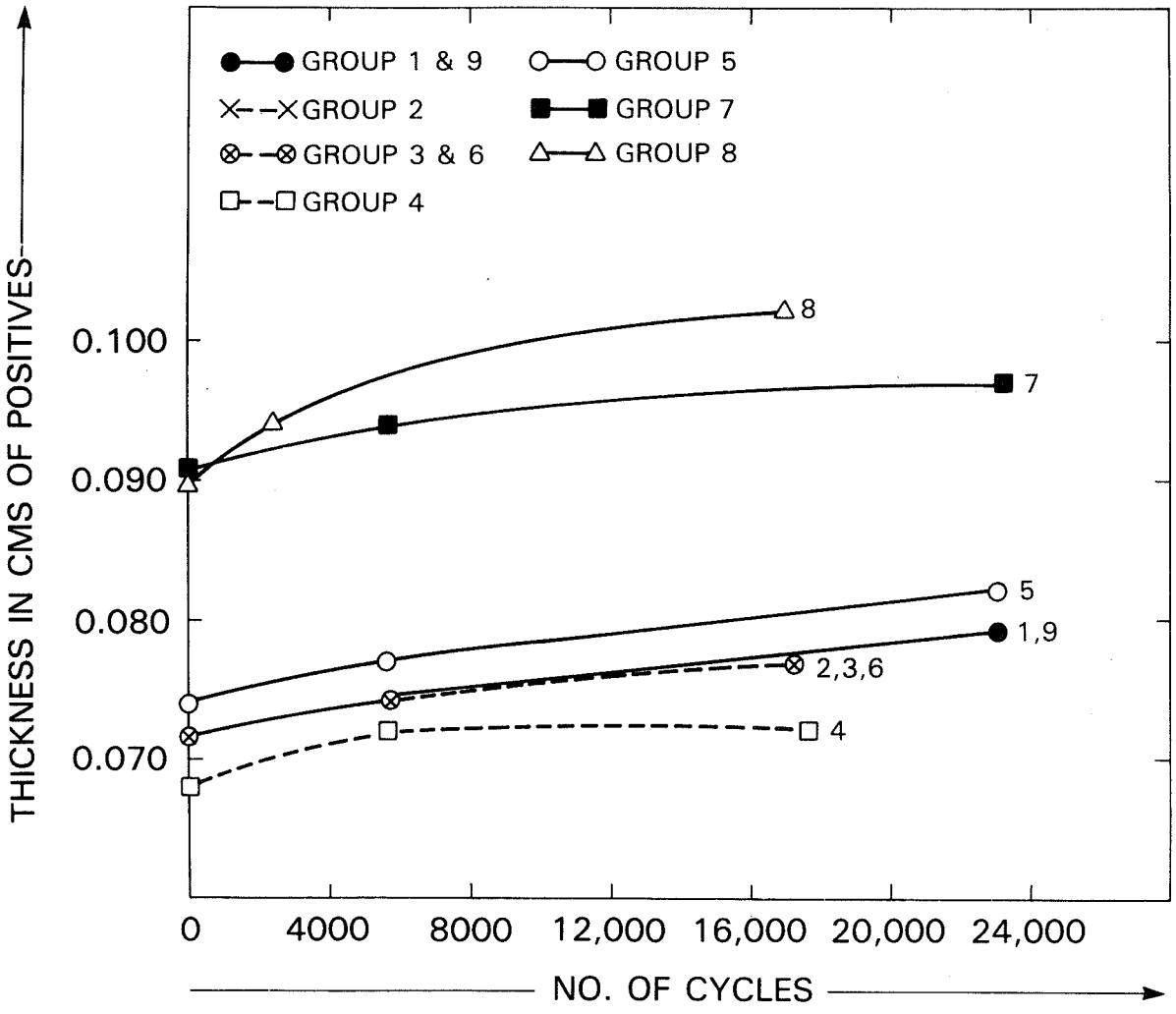


Figure 8. Curves – POS Thickness vs. Number of Cycles

Table 1. THICKNESS AND WEIGHT OF CELLS

GROUP #	S.N. OF CELL	PACK #	NO. OF CYCLES	PLATE THICKNESS (cm) POSITIVE	PLATE THICKNESS (cm) NEGATIVE	PLATE WEIGHT WITH TAB (Gms) POSITIVE	PLATE WEIGHT WITH TAB (Gms) NEGATIVE
1	04	3D	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	3E	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	3F	5844	0.074	0.083	14.03	14.82
	03		17,781	0.077	0.083	13.97	15.46
4	01	3G	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	3H	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

Table 1. (Continued) THICKNESS AND WEIGHT OF CELLS

GROUP #	S.N. OF CELL	PACK #	NO. OF CYCLES	PLATE THICKNESS (cm) POSITIVE	PLATE THICKNESS (cm) NEGATIVE	PLATE WEIGHT WITH TAB (Gms) POSITIVE	PLATE WEIGHT WITH TAB (Gms) NEGATIVE
6	02	3I	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	3J	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	3K	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	02	3L	14,827	0.076	0.072	13.10	15.42

Table 2. RESULTS OF ELECTROLYTE ANALYSIS

GROUP #	NO. OF CYCLES	Gms Electrolyte NEG	POS	SEP	TOTAL	% KOH	% K_2CO_3	ML KOH FOUND	ML KOH 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	40.3/41.5
	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	

Table 2. (Continued) RESULTS OF ELECTROLYTE ANALYSIS

GROUP	NO. OF CYCLES	Gms Electrolyte NEG	POS	SEP	TOTAL	% KOH	% K_2CO_3	ML KOH FOUND	ML KOH ADDED
6	–	21.80	15.41	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	29/40
	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	14,827	29.49	24.37	5.74	59.60	21.41	11.73	45.85	40/40

- $CO_3^{=}$ INCREASES AS A FUNCTION OF NO. OF CYCLES
- GROUP 7 AND GROUP 8 CELLS CONTAIN LARGE AMOUNTS OF $CO_3^{=}$
  - GROUP 7 CELLS NOT DECARBONATED
  - GROUP 8 CELLS HAVE THICKER POSITIVES
- ORDER OF ELECTROLYTE DISTRIBUTION: NEG > POS > SEP

Table 3. CAPACITIES: CHEM AND BASELINE

NAME	GROUP #	S.N. OF CELL	PACK #	NO.OF CYCLES	CAPACITY ON CELL BASIS (AH) CHEMICAL POS	CHEMICAL NEG	BASELINE POS	BASELINE NEG	% UTILIZATION POS	% UTILIZATION NEG
CONTROL	1	04	3D	–	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	3E	–	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	3F	5844	20.86	32.80	15.55	20.14	74.54	61.05
		03		17,781	23.03	31.84	12.89	19.86	55.97	62.37
LIGHT LOADING	4	01	3G	–	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	3H	–	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

Table 3. (Continued) CAPACITIES: CHEM AND BASELINE

NAME	GROUP #	S.N. OF CELL	PACK #	NO.OF CYCLES	CAPACITY ON CELL BASIS (AH) CHEMICAL POS	CHEMICAL NEG	BASELINE POS	BASELINE NEG	% UTILIZATION POS	% UTILIZATION NEG
POLYPROPYLENE	6	02	3I	–	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	7	05	3J	–	25.23	32.54	19.61	24.99	77.70	76.81
OLD PROCESS		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	8	02	3K	–	25.63	32.93	16.52	24.86	64.46	75.52
NEW PROCESS		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
ELECTROCHEM	9	02	3L	14,827	21.19	30.31				

Table 4. Co, Cd, Ni IN THE PLATES

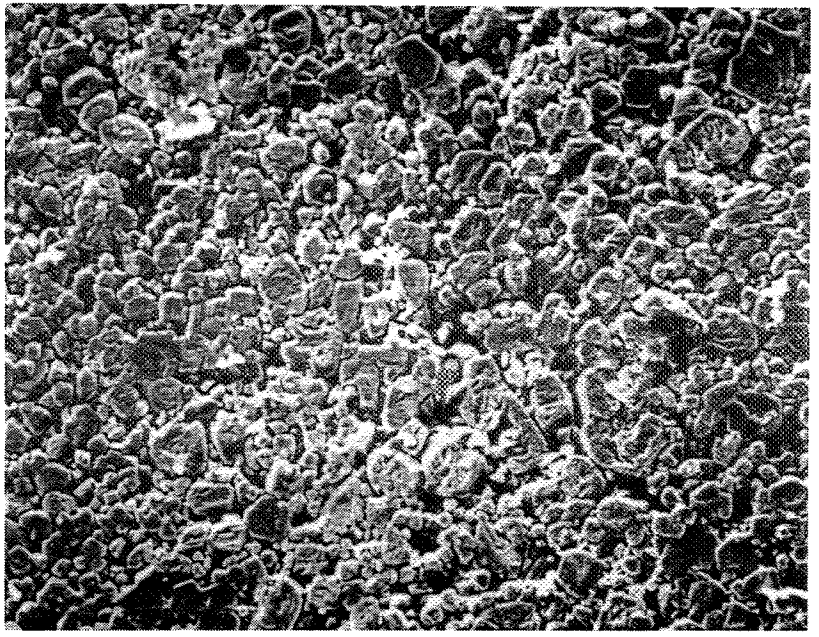
NAME	GROUP	S.N. OF CELL	PACK #	NO. OF CYCLES	% $Cd(OH)_2$ IN POSITIVE	% $Co(OH)_2$ PLATE	AH CHARGED Cd IN NEG	% $Ni(OH)_2$ IN NEG
CONTROL	1	04	3D	UNCYCL	10.74	2.81	0.59	4.04
		01		5833	12.17	2.78	0.75	5.39
		06		23,468	8.57	2.82	0.09	5.57
TEFLON	2	04	3E	UNCYCL	9.49	3.77	1.17	4.14
		01		5841	11.48	2.98	1.20	5.39
		03		17,760	10.12	2.95	1.35	6.06
SILVER	3	01	3F	5844	12.38	3.14	1.84	4.46
		03		17,781	8.91	2.81	2.58	5.82
LIGHT LOADING	4	01	3G	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 TREATMENT	05	01	3H	UNCYCL	6.46	3.20	0.71	4.29
		02		5840	7.31	3.06	1.16	4.32
		03		23,282	8.73	2.31	1.08	4.62

Table 4. (Continued) Co, Cd, Ni IN THE PLATES

NAME	GROUP	S.N. OF CELL	PACK #	NO. OF CYCLES	% $Cd(OH)_2$ IN POSITIVE	% $Co(OH)_2$ PLATE	AH CHARGED Cd IN NEG	% $Ni(OH)_2$ IN NEG
POLYPROPYLENE SEPARATOR	6	02	3I	UNCYCL	8.39	3.22	1.02	4.08
		01		5833	9.63	2.98	0.03	5.06
		05		17,632	9.23	2.30	2.60	6.53
AK PLATE OLD PROCESS NO DECARB	7	05		UNCYCL	2.75	3.56	0.87	4.41
		06		5834	4.92	3.15	0.65	5.40
		01		23,335	7.22	2.92	0.42	6.14
AK PLATE NEW PROCESS	8	02	3K	UNCYCL	4.71	3.79	0.91	4.45
		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
ELECTROCHEM	9	02	3L	14,827	–	1.87	1.23	3.59

GE 12 AH S/N 006 GROUP 1
23,468 CYCLES

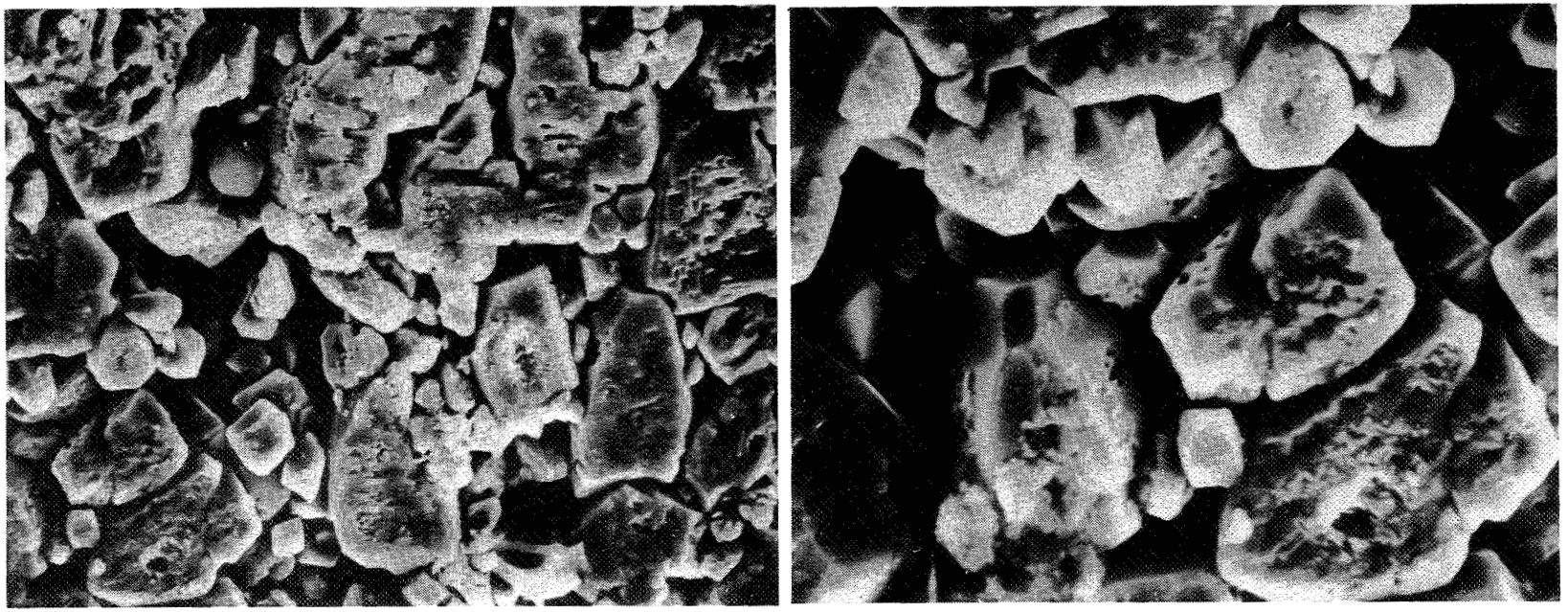
NEG # 3 WITH LAYER OF SEPARATOR (320 X)



NEG # 1 LARGE CRYSTALS OF $Cd(OH)_2$ (320 X)

Figure 9. SEMs of NEG from Group 1 Cell

S/N 006 GROUP 1 NEG #1 23,468 CYCLES
HEXAGONAL CRYSTALS OF $Cd(OH)_2$

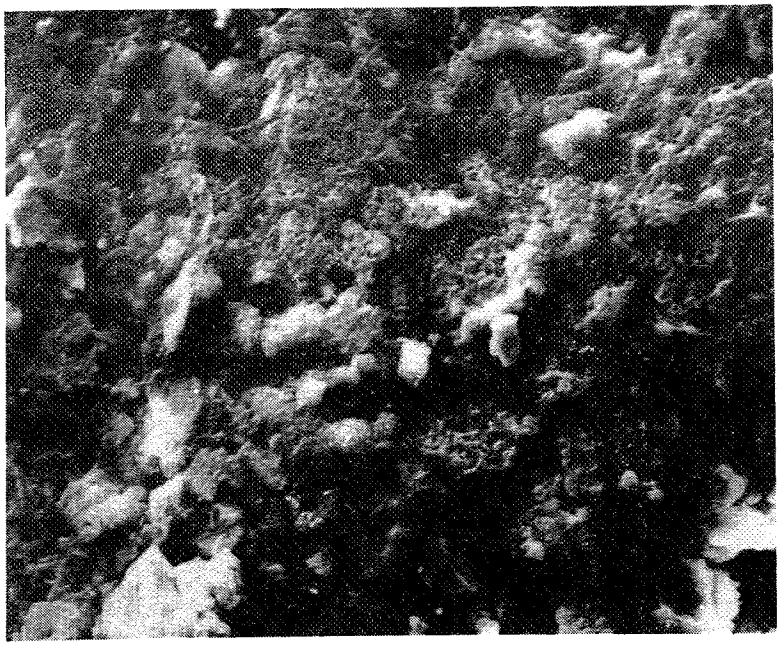


1250 X

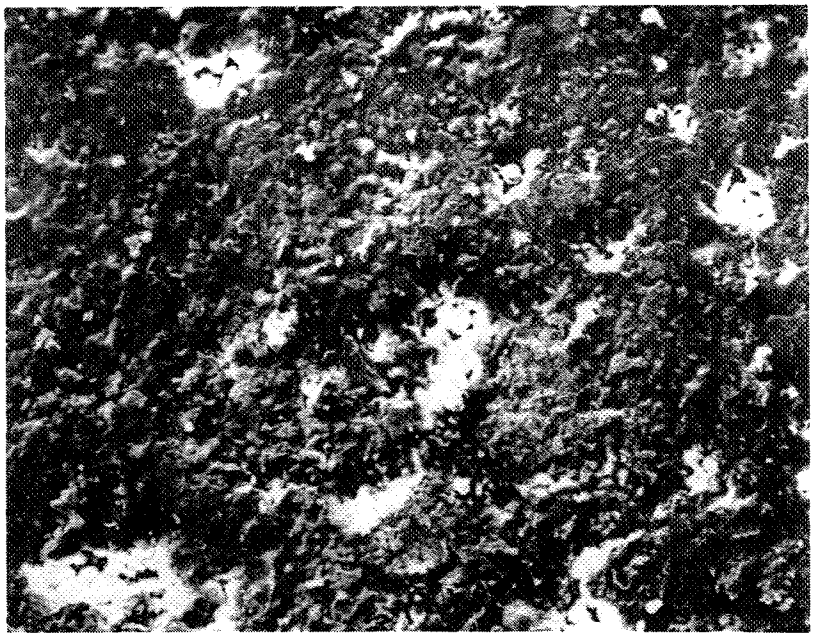
2500 X

Figure 10. SEMs of NEG from Group 1 Cell Showing Large Crystals of Cd $(OH)_2$

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



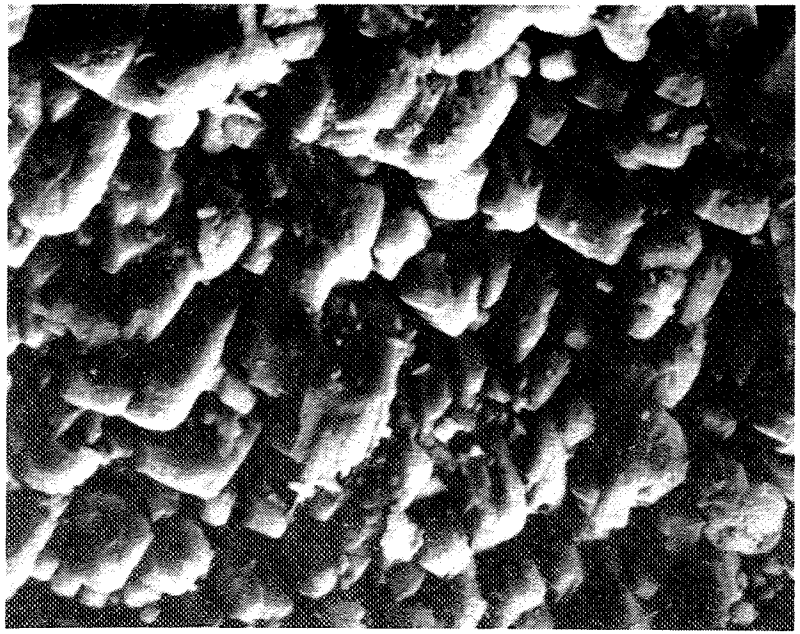
SEM OF POS. # 2 320 X



SEM OF POS. # 2 1250 X

Figure 11. SEMs of POS from Group 5 Cell

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



SEM OF NEG # 1 —
LARGE CRYSTALS 2500 X
OF $Cd(OH)_2$

SEM OF NEG # 3 WITH
SEPARATOR 320 X

Figure 12. SEMs of NEG from Group 5 Cell