

SECOND PLATEAU VOLTAGE IN NICKEL-CADMIUM CELLS*

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ABSTRACT

Sealed nickel-cadmium cells having large number of cycles on them were discharged using Hg/HgO reference electrode. It was found that the negative electrode exhibited the second plateau. SEM of negative plates of such cells show a number of large crystals of cadmium hydroxide. The large crystals on the negative plates disappear after continuous overcharging in flooded cells.

INTRODUCTION

Nickel-Cadmium cells are extensively used in satellite power systems. These cells undergo a large number of charge-discharge cycles. The changes in the battery voltage or capacity directly affect the power requirements and control unit function of the satellite power systems. It has been found more often that nickel-cadmium cells after a year's use show a voltage degradation during discharge. Such cells suffering with voltage degradation increases the load on the batteries and may sometimes result in loss of capacity. The voltage degradation during the discharge is commonly referred to as the second plateau or voltage plateau or stepped discharge curve.

Different views have been expressed as to which electrode is contributing and about the mechanisms causing such voltage degradation. One of the mechanisms (Reference 1) suggested is that the recrystallization of cadmium hydroxide at the surface of the cathode during cycling insulates the lower layers of active cadmium, as a result the discharge occurs at a very low rate. It has been reported (Reference 2) that an alloy Ni_5Cd_{21} formed in the negative electrode of nickel-cadmium

cells subjected to continuous charging at elevated temperatures is the cause of voltage degradation. Russian workers (Reference 3) reported that under certain conditions, e.g., if the battery is stored in the charged state or cycled with

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incomplete discharge, some of the cadmium forms the intermetallic compound $\text{Ni}_5\text{Cd}_{21}$ with nickel, and is discharged at a potential on the positive side of the usual potential by 0.1V. Recently, Barnard et al (Reference 4) have reported that the secondary discharge plateau is associated with the inefficient reduction of sintered plate NiOOH electrodes. They point out that the potential of the lower plateau is highly dependent on discharge rate and also to some extent on the charge regime applied to the electrode. Zimmerman and Janecki (Reference 5) also report that the voltage losses result from changes in the nickel electrode potential with cycling.

Gerald Halpert (Reference 6) presented the results of cycling 26.5 AH sealed nickel-cadmium cells. Sealed cells were cycled on a near earth orbit regime at 10°C and to a voltage limit. Cells showed voltage degradation after about 6400 cycles. Pack 26H that was discharged with 25% DOD showed a more significant voltage degradation than pack 26G cells with 20% DOD. In fact, this presentation prompted me to further examine the voltage degradation behaviour of sealed nickel-cadmium cells.

EXPERIMENTAL METHODS

1. Preparation of Hg/HgO Reference Electrode:

- a) Small amounts of mercury and mercuric oxide (red variety) were ground well with 2 to 3 drops of 31% KOH.
- b) The above mixture was put into a piece of teflon tubing of 50mm diameter which had a tiny hole at the bottom that is plugged with separator material.
- c) A few ml of pure mercury was put over the layer of Hg/HgO.
- d) A platinum or nickel wire was stuck in the mercury pool taking care to prevent the wire from touching the Hg/HgO interface.

Such a Hg/HgO electrode served as a stable reference electrode and was used to monitor the potentials versus the negative and positive electrode of the nickel-cadmium cells.

2. Cells Used for the Study:

History of the cells used is given in Table 1.

3. Identification of the Electrode causing the Second Plateau:

A 20 AH cell from pack 12 F was chosen for investigation. The cell had undergone 24958 cycles on a near earth orbit basis at Crane at 16 A of charge and discharge. The cell showed appreciable second plateau. The temperature was at 10°C and 40% DOD.

The following steps were carried out using the above mentioned sealed cell:

- a) The fully charged cell was discharged to 50% and the Hg/HgO reference electrode was carefully introduced by drilling a hole on the top of the cell and sealing the hole all around with putty. Care was taken to prevent the cell from exposure to air by keeping it in a polyethylene bag filled with nitrogen.
- b) The cell was recharged at the same charge regime to the specified voltage limit of 1.458 V and discharged at 10 A rate to 0.5 volt.
- c) During the discharge, the reference versus negative and reference versus positive electrode potentials were monitored and recorded using a two-channel recorder. The cell voltage was also recorded separately. The results obtained from the discharge of the cell from pack 12 F is shown in Figure 1.
- d) The discharged cell was once again cycled 10 times overnight and was discharged at 10 A while still monitoring the potentials of the negative and the positive versus the Hg/HgO reference. As expected, the cell now did not exhibit the second plateau due to earlier reconditioning effect.

I waited another year to confirm the findings by conducting similar experiments using 3 12 AH cells one each from pack 3H, 3J, and 3D and another 20AH cell from pack 1 K. These cells were discharged at Crane, Indiana using the reference electrode technique described earlier. In all the cases, the results show that it is the negative electrode versus reference which exhibit the second plateau.

I appreciate very much the help of Mr. Jim Harkness, Steve Hall, and S. Hammersely in carrying out the tests at NWSC, Crane, Indiana.

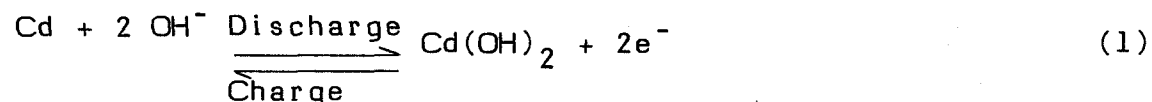
4. Experiments with Flooded Cells:

After discharging the cells using reference electrode these were brought from Crane to Goddard. Flooded cells were assembled in plexiglass cell cases using the negative and positive plates taken out from a cell that showed the second plateau. Each flooded cell consisted of two negatives and one positive separated by pellaon. These flooded cells were charged to different voltage limits. Different charge rates as given in Table 2 were employed to charge the cells. The plateau reappeared in those cases marked with an asterisk and the voltage limit was 1.434 volt per cell.

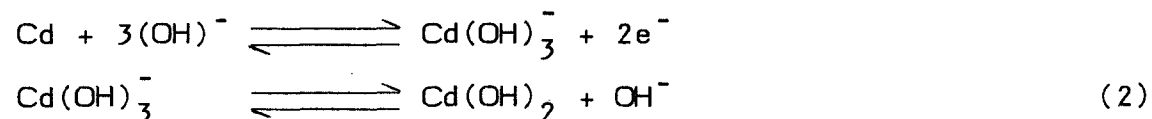
RESULTS AND DISCUSSION

The results of the present investigation indicate that the negative electrode is responsible for the second plateau in nickel-cadmium cells. The negative and positive plates from such cells were used to assemble flooded cells in the laboratory. These were charged at different rates for different durations to a voltage limit and discharged. The second plateau could be induced again in some cases (see Table 2). The discharge profile of one such case is shown in Figure 2. In two cases, however, the reference versus positive potential showed a slight hump, a sample of which is shown in Figure 5. Comparing the positive versus reference electrode discharge profile to the negative versus reference electrode (Hg/HgO) profile in Figures 1 and 3, it can be seen that the magnitude of the second plateau on the negative electrode is larger (300 mv). In agreement with a number of workers, a shift in the second plateau with cycling is demonstrated in Figure 4.

The half-cell reaction at the cadmium electrode is well known:



The Cd(OH)_2 is also known to form through dissolution - precipitation mechanism: (Reference 7)



Reactions (1) and (2) precipitate cadmium hydroxide and migrate to the surface of the electrode, towards the separator and positive electrode. In the initial stages of cycling, the cadmium hydroxide is present as thin film masking some areas of

active cadmium. As the cycling progresses, these films provide convenient sites for crystal growth and thus mask the active cadmium surface with large crystals of cadmium hydroxide. The SEMs of negative plates of cells that showed second plateau show very large crystals of cadmium hydroxide and the positives do not have any crystal growth (see Figures 6 and 7). Ford (Reference 8) demonstrated that the nickel-cadmium cells that had electrolyte starvation suffered both in voltage and capacity. The cells examined by him were Gulton 6 AH cells cycled at 20°C, 25% DOD with a voltage limit of 1.417 and C to D ratio of approximately 115. By simply increasing the electrolyte content the capacity degradation of such cells was overcome but the double plateau effect still existed. Increase of electrolyte seem to dissolve smaller crystals but there is still a bulk of large crystals masking the active surface of the electrode. The experiments in the present work have shown that continuous charging of negative electrodes with large crystal growth in flooded condition almost eliminates the crystals. SEMs of negative plates after gasing by overcharging in excess electrolyte show no trace of large crystals (Figure 8). This is in agreement with the results of Fritzwill and Hess (Reference 9) who pointed out that prolonged reduction leads to the dissolution of crystals of $\text{Cd}(\text{OH})_2$.

The tear-down analysis of cycled cells have shown that the cadmium migration is quite heavy in the areas under compression and quite often the separator sticks strongly to the electrode surface. This may be explained by assuming that in sealed cells the electrolyte is squeezed out from areas where there is more compression and these electrolyte starved areas seem to be good nucleation sites for crystal growth. The crystal size grows as the cycling continues and finally result in loss of voltage and/or capacity. When no effort is made to restore the voltage and capacity by reconditioning, a situation may arise when the cadmium dendrites will pass through the weak separator and lead what is popularly called soft or hard shorts which will cause cell failure. It appears, if one can prevent cadmium migration and suppress crystal growth the voltage degradation i.e., second plateau behaviour is taken care of.

From the Navigation Technology Satellite-2 (NTS-2) nickel-hydrogen battery performance, F.E. Betz, J.D. Dunlop and J.F. Stockel (Reference 10) have reported that the battery voltage level improves with continued cycling as the discharge duration increases. The increase in voltage was related to the positive electrode i.e., the nickel electrode. Stockel in an updated paper (Reference 11) reported that nickel-hydrogens have not shown any voltage or capacity degradation during 3.5 years in orbit and eight eclipse seasons.

CONCLUSIONS

1. The second plateau is exhibited mainly by the negative electrode.
2. Formation of large crystals of $\text{Cd}(\text{OH})_2$ on the negative electrode during cycling is responsible for voltage degradation.
3. Continuous gassing of the negative electrode in flooded cells leads to the dissolution of large crystals of cadmium hydroxide.

FUTURE PLANS

It will be interesting to establish conditions that will minimize cadmium migration. It is planned to investigate the possibility of using some sort of coating, electroplating, or additives that may achieve this purpose. Also plans are underway to look into the effect of varying the compression on the plate stack.

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Table 1
Cell History and Operating Parameters

PACK #	12F	1K	3H	3J	3D
CELL #	3	1	3	3	2
NOMINAL CAP (AH)	20	20	12	12	12
VOL. OF KOH (ml)	85	85	41.5	39	40
POS. LOADING (g/dm ³)	1704	1704	2113	2130	2095
NEG. LOADING (g/dm ³)	1865	1865	2180	2542	2180
SPECIAL TREATMENT	NEG	PELLON	NO PQ	OLD PROC.	CONTROL
	TEFLNTD	2503	TREAT	NO PQ	GROUP
ORBIT PERIOD (HR)	1.5	1.5	1.5	1.5	1.5
TEMP (°C)	10	20	20	20	20
CHARGE RATE (A)	16	16	9.6	9.6	9.6
NO. OF CYCLES	24,958	18,864	23,281	23,334	23,467
DOD (%)	40	40	40	40	40
VOLT. LIMIT (V)	1.457	1.434	1.453	1.453	1.453-1.473
AH-OUT TO 0.5 V (AH)	14.50	10.86	8.19	8.80	8.35
POS. THICKNESS (IN)	0.027	0.027	0.027	0.032	0.027
NEG. THICKNESS (IN)	0.0315	0.0315	0.031	0.026	0.031

Table 2

Conditions of Charge/Discharge for Flooded Cells

DISCHARGE RATE: C/2			ROOM TEMP
VOLT LIMIT	NASA LEVEL #	CHARGE RATE	# HRS CHARGED
1.475	V8	C/2	288
1.455	V7	C	288
1.434*	V6	C/2	480
1.434*	V6	C/2	672
1.434	V6	C	714
1.434*	V6	C	912
1.434*	V6	C	1248
1.414	V5	C/2	176
1.414	V5	C/2	288
1.414	V5	C/2	720

*SECOND PLATEAU APPEARED IN THESE CASES.

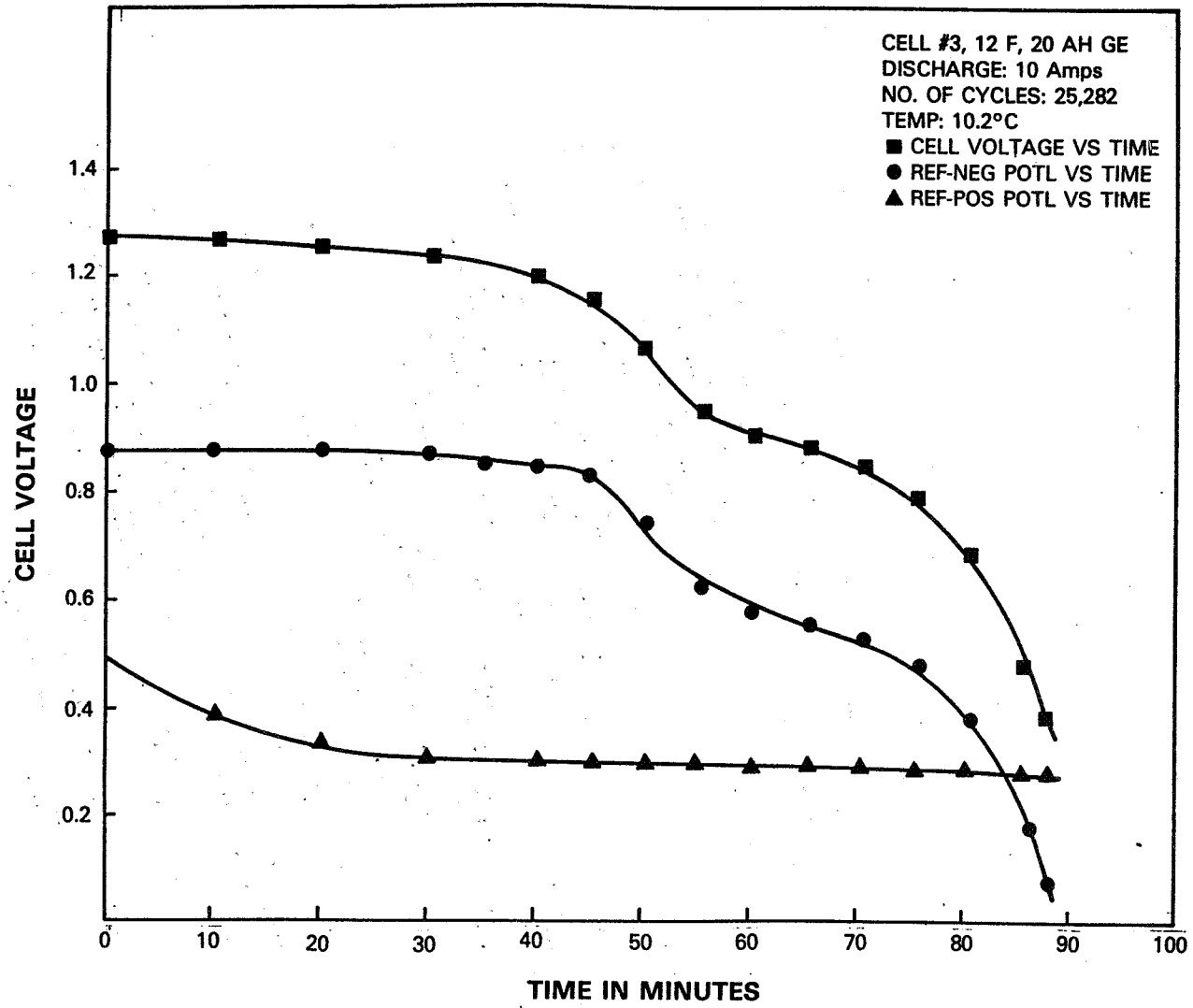


Figure 1

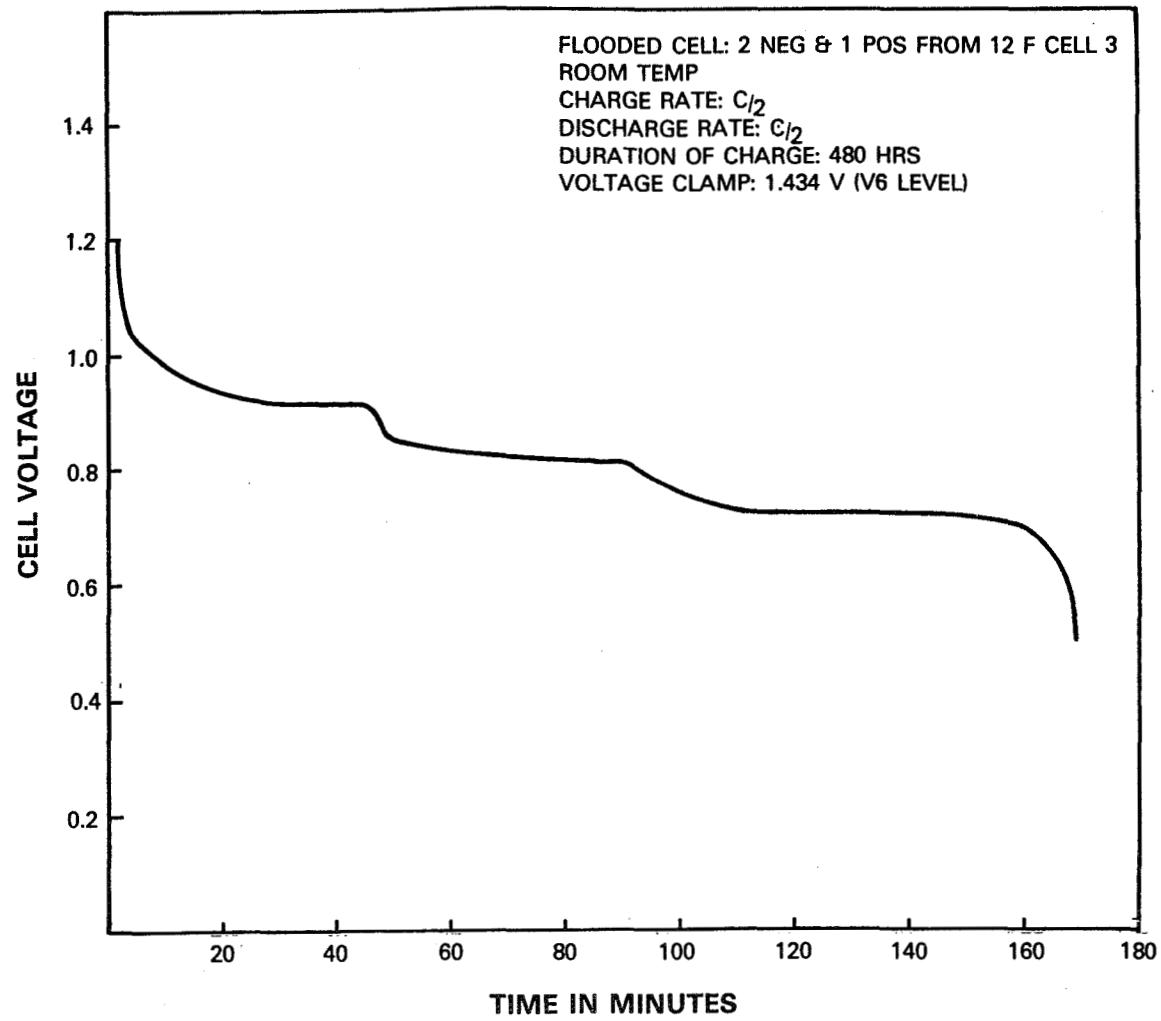


Figure 2

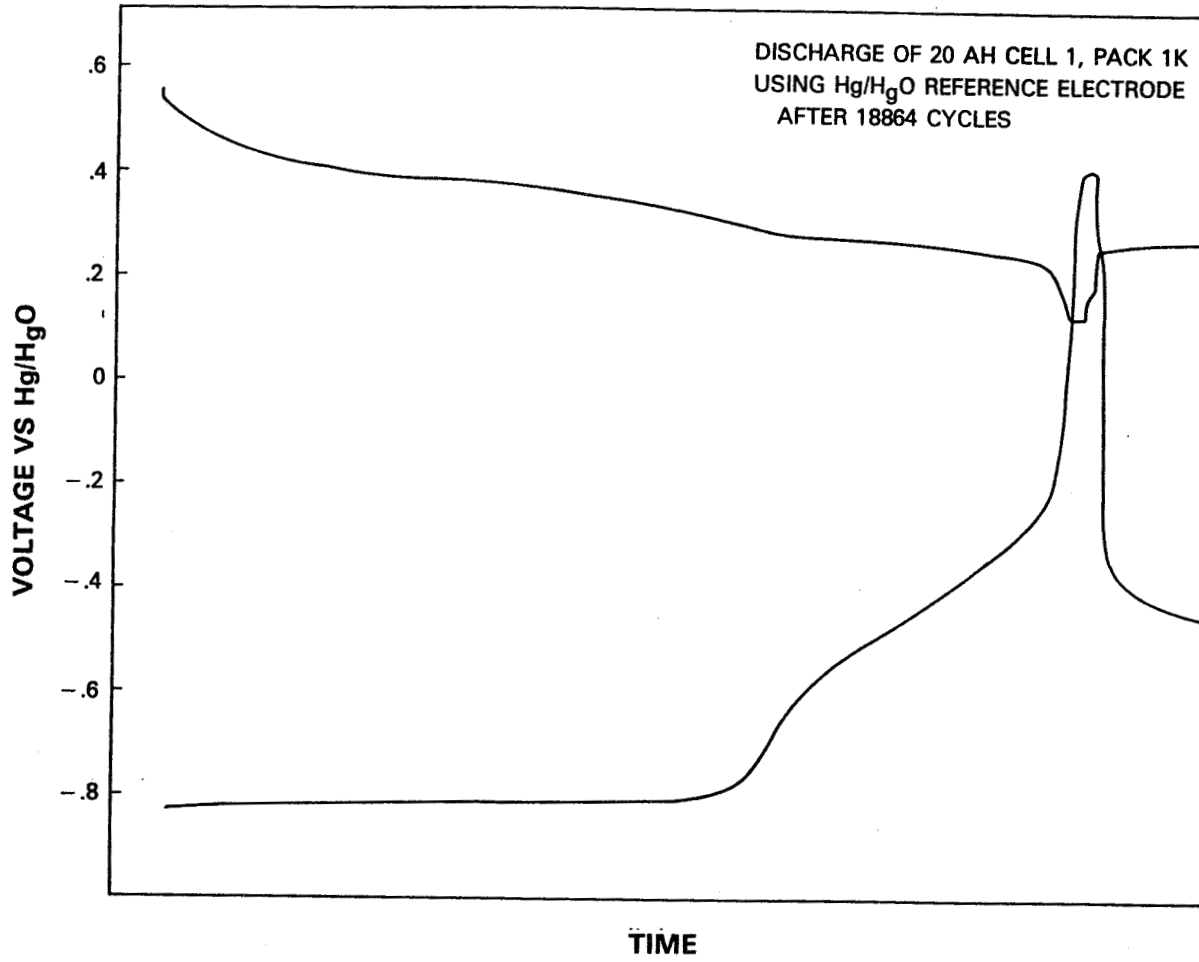


Figure 3

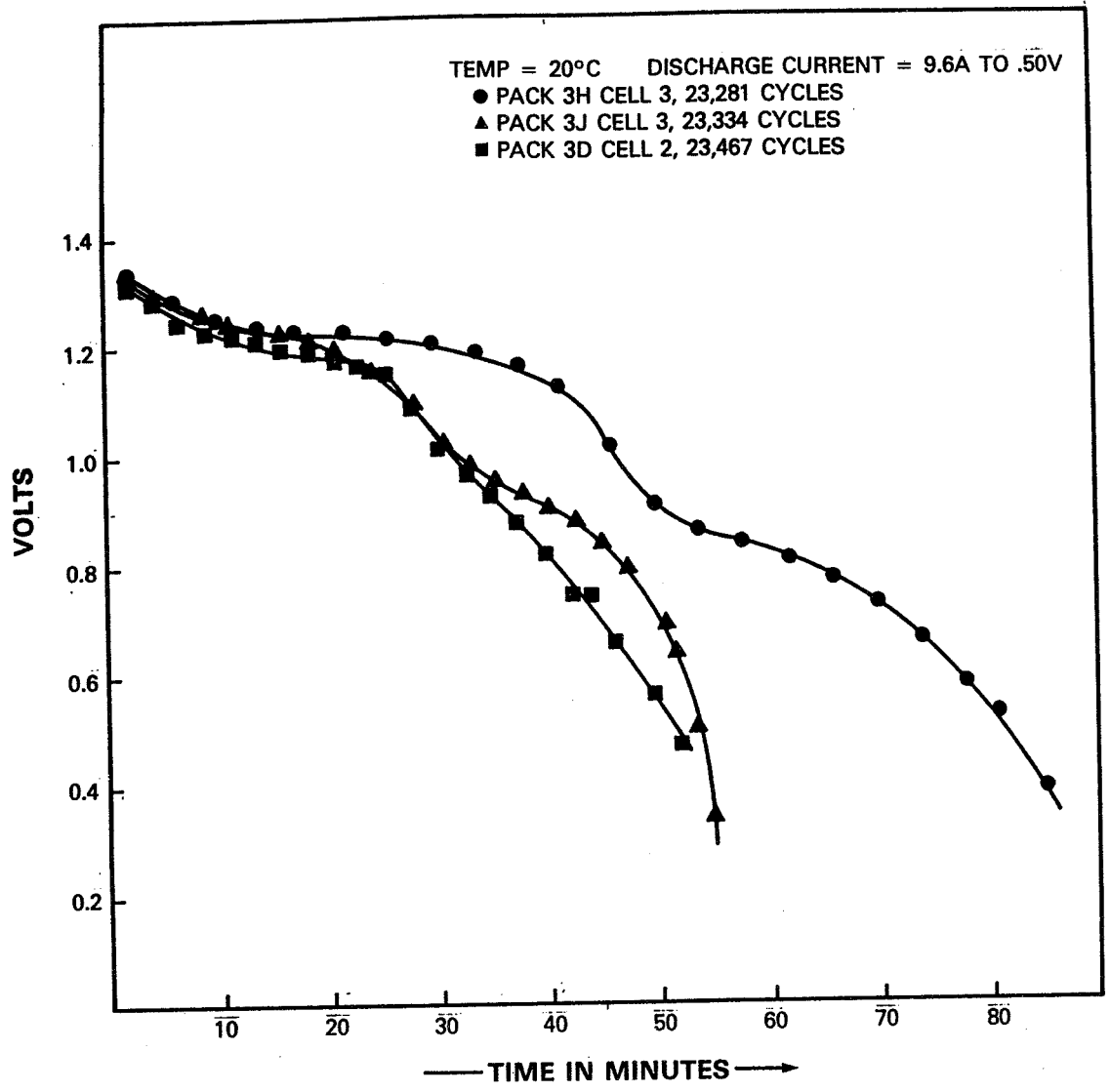


Figure 4

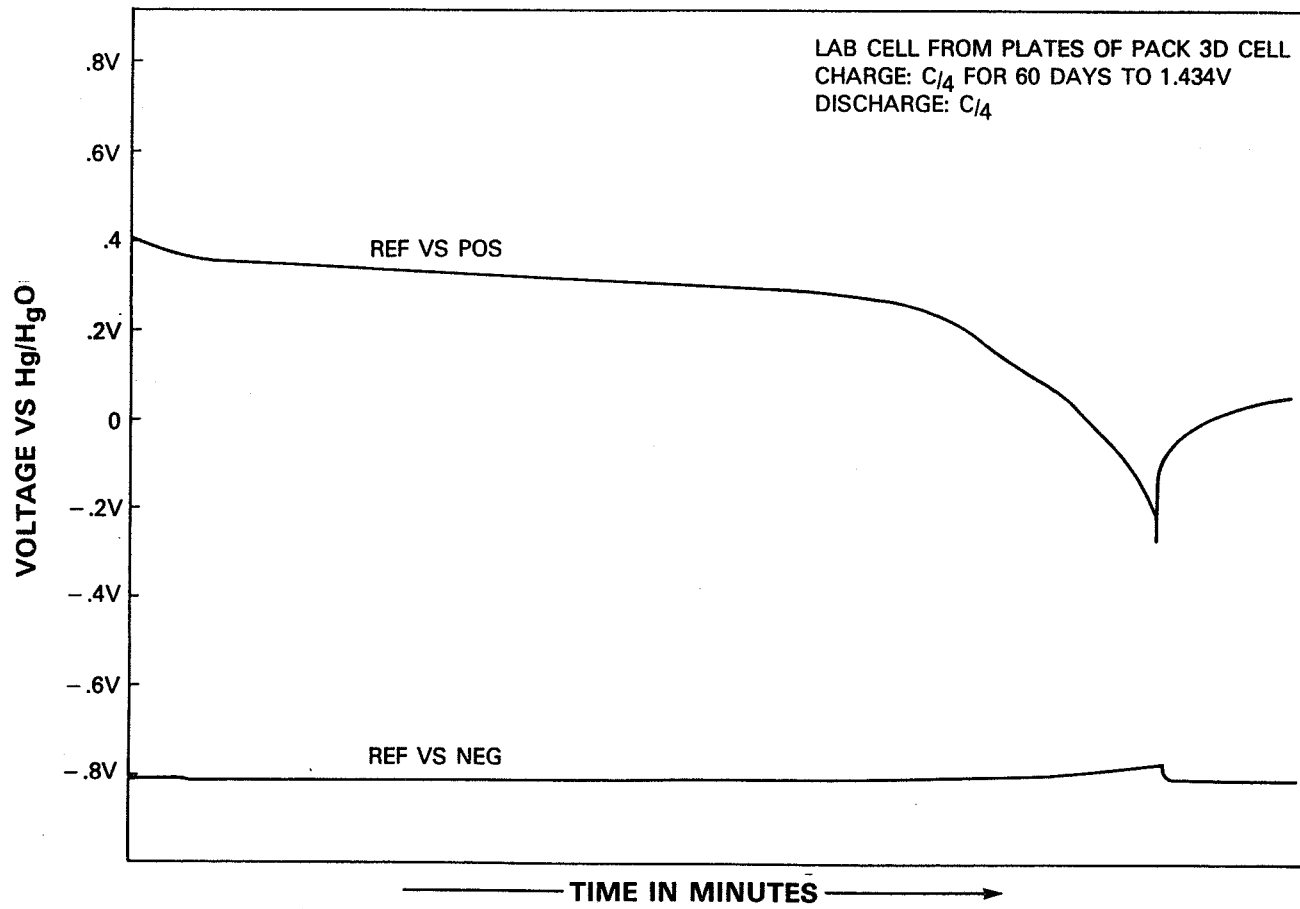
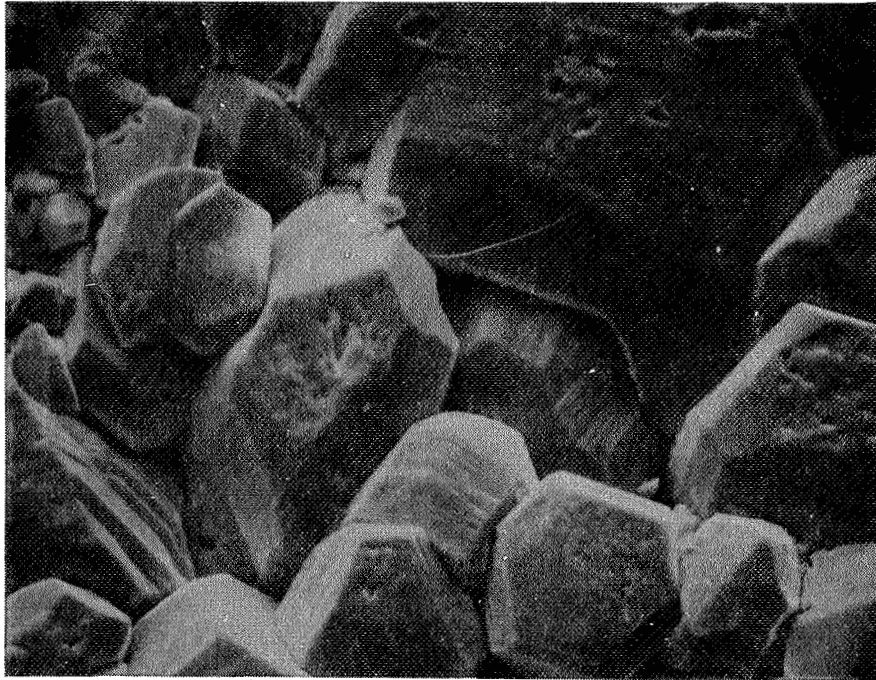
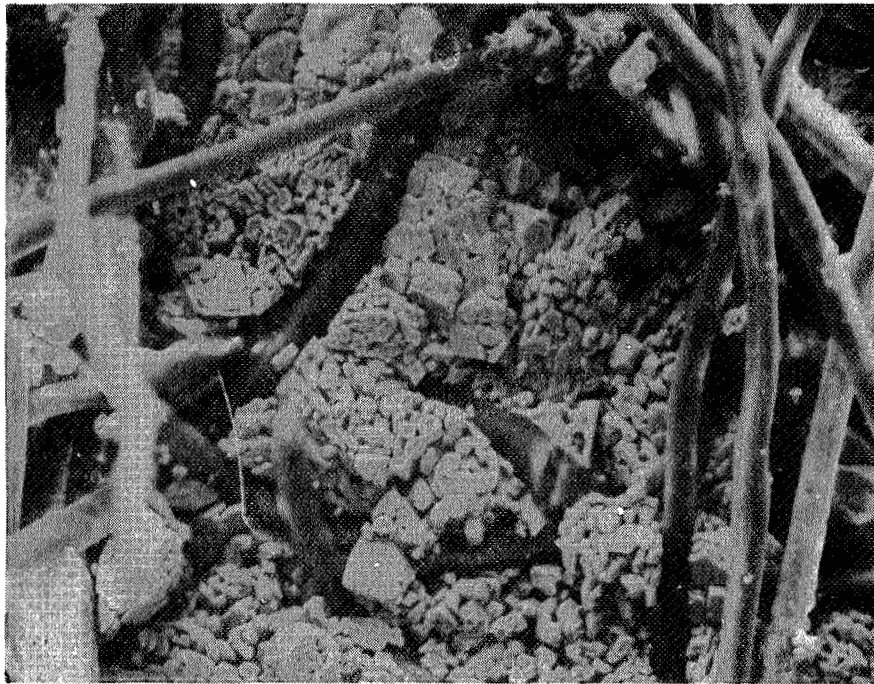


Figure 5



SEM of neg of cell 2, pack 3D at 640X show large crystals of β -Cd(OH)₂.



SEM of neg of cell 2, pack 3D at 340X show crystals of β -Cd(OH)₂ and fibers of separator.

Figure 6

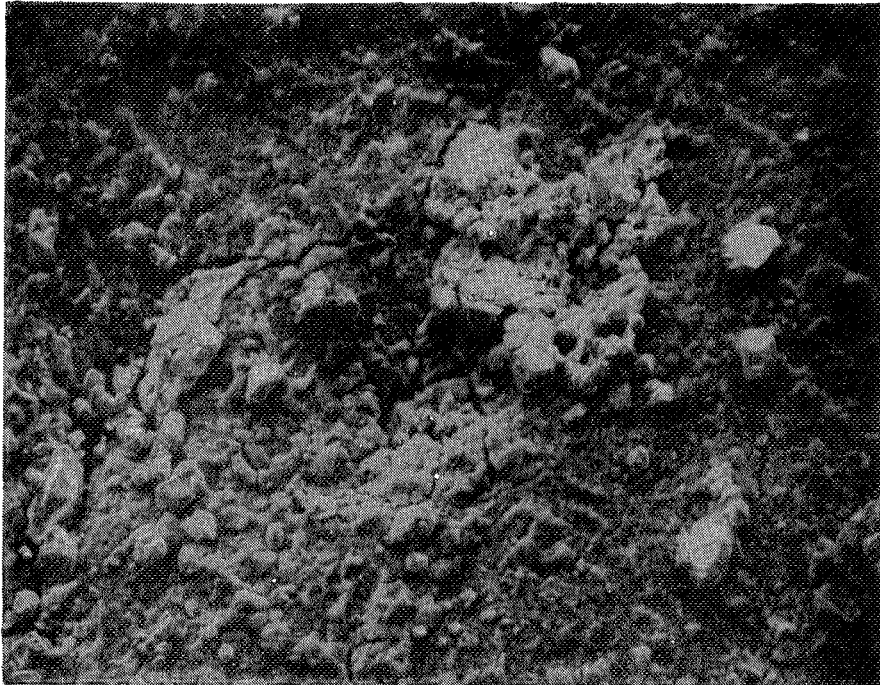
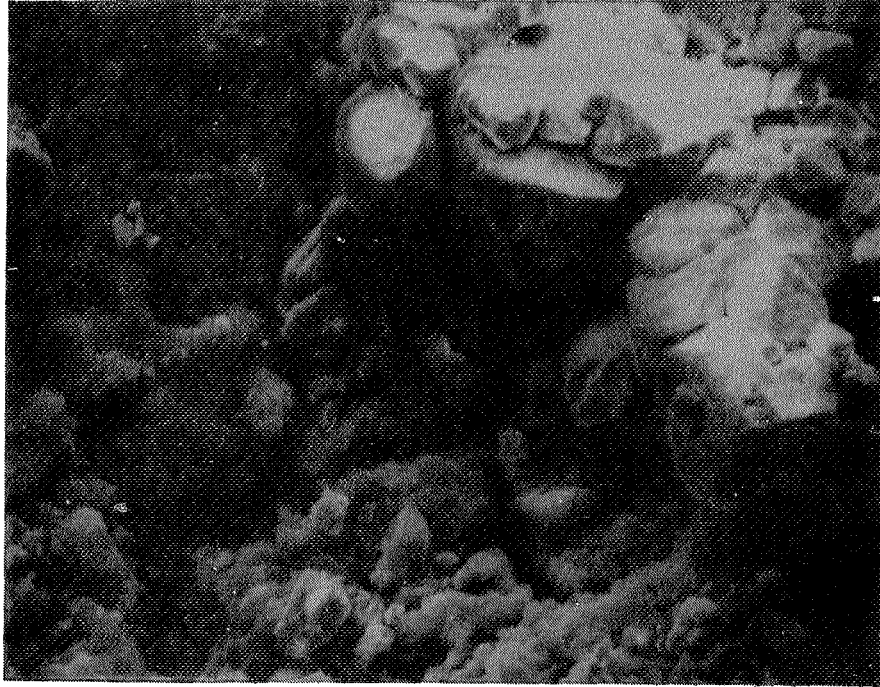


Figure 7. SEMs of POS of cell 2, pack 3D at 640X and 160X amorphous surface of POS with a lump of β -Cd(OH)₂ collected due to a short.

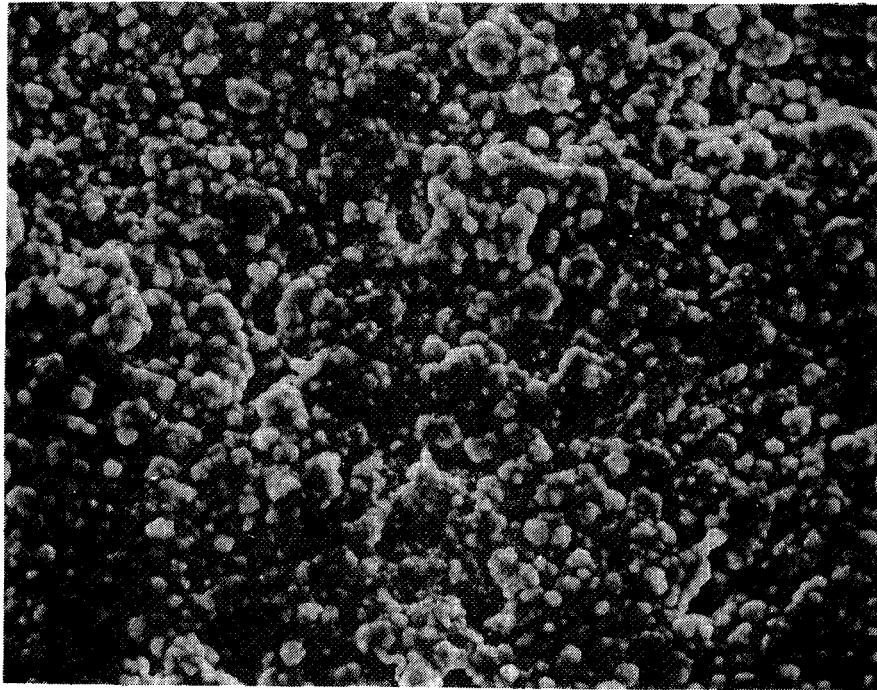


Figure 8. SEM of neg of cell 3, pack 12F at 320X after overcharging show absence of crystals.

- Q. Unidentified: Do you observe a rate dependence or are those crystals different than the normal crystals that discharge or are they bigger?
- A. Kunigahalli, Bowie State College: They are bigger.
- Q. Unidentified: And then if you do it a very low rate you should not see a voltage plateau?
- A. Kunigahalli, Bowie State College: If you do it.
- Q. Unidentified: If you discharge at a very low rate you should not see a voltage plateau. Is that correct?
- A. Kunigahalli, Bowie State College: Right. That's what I would expect. The higher rate suddenly drops to the plateau.
- A. Unidentified: The reason why I asked that was reconditioning in space is where you see the voltage depression at very low rates, which suggests they are not just depending on the crystal size there has to be more to it than that because the current densities are dropped.
- Q. Hendee, Telesat Canada: There were sealed cells you were working with?
- A. Kunigahalli, Bowie State College: Right sir.
- Q. Hendee, Telesat Canada: When you put the teflon tube in there with the mercury and you seal it how did you keep the balance of a cell? I noticed actually that you were negative limited on discharge which means that it's a considerably different cell. Am I correct on that?
- A. Kunigahalli, Bowie State College: We took only about 1 or 2 minutes to drill the hole and we introduced the teflon tubing which is the reference electrode. Okay?

COMMENT

Hendee, Telesat Canada: Something happened I think when you charged because you are a negative limited on discharge, definitely you were. The other comment I guess I would like to make: Why do we see this same plateau occasionally on different cells of nickel hydrogen which have no negative.

Kunigahalli, Bowie State College: I know I'm aware of that. Some people have indicated that second plateau has occurred in the work of Fred Burns and Dunlop Burns who reported earlier that reconditioning would actually improve the voltage cycling in nickel hydrogens.

- Q. Hendee, Telesat Canada: Have you done any kind of continuous impedance checks on discharge?
- A. Kunigahalli, Bowie State College: No sir.
- A. Hendee, Telesat Canada: I'm going to run right home and do that.
- A. Kunigahalli, Bowie State College: Thank you.
- Q. Sullivan, APL: Some of the recent satellites have been designed with discharge resistors so we can completely discharge a battery in orbit over a period of about a month and we've been wondering - the frequency with which we should do that. Would your studies indicate that we should be doing it frequently or infrequently? It sounds like to me it's something that should be done often.
- A. Kunigahalli, Bowie State College: You mean the reconditioning?
- Q. Sullivan, APL: The reconditioning cycle?
- A. Kunigahalli, Bowie State College: I cannot suggest anything.
- A. Sullivan, APL: Okay.

COMMENT

Maurer, AT&T Bell Labs: I guess I have a problem with the cadmium hydroxide crystal explanation. The plateau occurs on the discharge and on discharge you are going from the cadmium metal to the cadmium hydroxide and the cadmium hydroxide precipitating to the cadmium hydroxide crystal. So it's an end product of the reaction and not the electro-chemical step part of the reaction. So the size of the cadmium hydroxide crystals shouldn't have anything to do with the electro-chemical voltage. Also you haven't commented on the nickel cadmium intermetallic explanation for the same phenomena.

Kunigahalli, Bowie State College: Yes, I am aware of that. The mercury indicates that the intermetallic compounds are a large formation as Bernard puts it. That's the compound that they have examined formation. But I have a feeling this compound or crystal whatever is just insulating the active cadmium and that's maybe the reason then they will discharge the lower voltage.

Ford, NASA/GSFC: Ed, I'm surprised that you were surprised that these cells were negative limited on discharge. I've never seen cells cycle at this depth in LEO orbit that weren't negative limited on discharge after 20,000 cycles. Addressing Ralph's question, I don't think this gives you any insight into the effects of reconditioning per say. I recall though a few years

Ford, NASA/GSFC (Con't): back Dr. Will Scott had done some work at TRW. He showed I believe if you are going to recondition you have to start off early and continue it throughout the life and fairly frequent. That was my recollection.

- Q. Jagielski, GSFC: I was wondering would you assume that this same mechanism would cause the third plateau that's been observed or would you assure that some other type of mechanism maybe precipitated by this growth of the large crystals?
- A. Kunigahalli, Bowie State College: I can't answer unless I investigate what is the possible cause for the third plateau. I don't know but I have seen in many other cases the discharge curve showing more than two plateaus. So it needs some investigation.
- Q. LaFrance, Aerospace Corporation: I thought I heard you say the prognosis for this problem to cure the large cadmium hydroxide crystals were overcharged and gassed. Did I hear you say that?
- A. Kunigahalli, Bowie State College: Pardon me.
- Q. LaFrance, Aerospace Corporation: You can eliminate these large crystals with gassing on overcharge?
- A. Kunigahalli, Bowie State College: Yes in flooded cells but that's not in real sealed Ni-Cd cells.
- A. LaFrance, Aerospace Corporation: Oh I see. Okay.
- A. Kunigahalli, Bowie State College: In short what I found was gassing has eliminated those.
- Q. Lim, Hughes Research Lab: Are any of your parameters a direct measure of the capacity?
- A. McDermott, B&K Dynamics, Inc.: The reason I say it's what I would call apparent capacity is if you cut the rate of discharge down I think that would go off into another second plateau and you would get more capacity out of the cell. So it's not the absolute capacity of the cell. But what I think it's measuring is the quote memorized capacity of the cell that is after you've cycled the cell for a number of cycles you will find that tailoring off at the far region of the discharge due to changes or whatever in the cell. I'm not going to hazard a guess as to why that happens but it means at that depth of discharge and that rate that discharge rate you should expect that curvature of that nature and so you would call it the capacity of the cell at that rate of discharge and that age.

- Q. Lim, Hughes Research Lab: Second question. Have you tried to determine whether that voltage you are analyzing is due to positive electrode voltage or negative electrode?
- A. McDermott, B&K Dynamics, Inc.: No. It's just strictly, I'm looking at the cell as a black box. I'm just taking the voltage out but I'm saying that the equation itself is not totally a statistical analytical tool that I think the C parameter is related to capacity and I think Shepherd in his work around the 65 time frame actually was arguing for some physical chemistry behind some of these fit coefficients, he does some explaining with regard to electro-chemical reactions but I'm using it strictly as an analytical tool at this point.
- Q. Hafen, Lockheed: Concerning the charge voltage you seem to be mostly concerned. On the charge voltage does that work as well and what is the meaning of x in that equation? Is it taken into account for the charge efficiency or?
- A. McDermott, B&K Dynamics, Inc.: Yeah, that's the problem. X there is simply current passing through the cell and so as a tool we haven't actually used that in interpreting for life prediction. You could use it for interpreting or for predicting this voltage characteristic. I'd say it would be very good for that once you've established the slopes and the turning point when you go from phase 1 to phase 2 and phase 3. But as a life predictor when we haven't looked into that yet.
- Q. Bell, Hughes Aircraft: Dr. McDermott the matrix you showed there has relative high depth of discharge high operating temperatures, does this model apply equally well to some of the Crane data in excess of 70 and 80,000 cycles at low temperatures and low depths of discharge?
- Q. McDermott, B&K Dynamics, Inc.: Are you talking about the prediction equation?
- A. Bell, Hughes Aircraft: The prediction equation, yes.
- A. McDermott, B&K Dynamics, Inc.: Yes it does pretty well on that. I have given papers in the past here using that prediction equation for a broader set of conditions than this. I'm just I was using that equation relative to this data because we were doing this data analysis. But yes, the equation works. I can give you several references to other data that we have used it on.
- A. Bell, Hughes Aircraft: Thank you.