NWSC NICKEL CADMIUM SPACECRAFT CELL ACCELERATED LIFE TEST PROGRAM DATA ANALYSIS

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This topic will deal with the accelerated life test program which is being conducted experimentally at the Naval Weapons Support Center, Crane, Indiana, and we will talk about analysis and accelerated life testing.

One of the objectives of the program was to learn how to do accelerated testing to enable projection to ultimate life under spacecraft usage conditions. The program is essentially complete now in terms of affording the data for analysis to leading to a proposed accelerated life test scheme of affording the data for analysis to accomplish this particular objective. An analysis of the data leading to a proposed accelerated life test scheme is the subject of this paper. And I say " a proposed scheme" because I am sure the data can be worked over in at least several different ways.

(Figure 5-1)

This test plan and its rationale have been presented in detail in reference 1. That's the recent NWSC report. On this program five stress factors were selected for evaluation; DOD, temperature, amount of recharge, discharge and charge rates.

In addition, three cell internal design variables were investigated. These showed low or no effects on cycle life except perhaps in the very extremes, and moreover, they have no effect on accelerated life test design, so they won't be treated here.

(Figure 5-2)

In references 1 and 2, that's the Crane report I mentioned, and also one of mine, there are complete tables of data showing the individual cycle life values for each cell of the five-cell packs, and the stress and design factor conditions.

The data for factorial design prior to the program are shown as averages for several sets of DOD T and percent R combinations. Percent R is recharge in this table. These data have had early-failing cells eliminated from the calculated averages. I don't think we have to dwell on this table at any particular length because I am going to show you plots and tables of condensed data which come out of this.

(Figure 5-3)

Let's talk about the early failures for a moment. An analysis was made of the failure data which showed that there were 15 percent early failures in the fractional factorial experiment, and 29 percent in the star point experiment due to early high pressure.

A chemical analysis showed this to be due to the accumulation of hydrogen. The data showed it was associated with high-overcharge rates and large amounts of overcharge. It is my feeling — I think it is a little bit more than a feeling — that this result was actually induced by the constant current charge procedure which was employed for the test to simplify handling of charge rate and amount of overcharge variables both equipmentwise and data analysiswise.

In retrospect, I think it is obvious that some of this was bound to happen. When the reserve cadmium hydroxide is used up due to positive plaque corrosion and separator degradation, hydrogen has to be produced at the negative plate on overcharge. For high rates of overcharge and large amounts of overcharge, the oxygen recombination rate couldn't handle it at the surface of the negative plate, and when hydrogen gets into the head space it is difficult to recombine.

We had a program in our laboratory and also an accelerated life test program. We also chose the constant current charge procedure.

When high pressures occurred, the charge mode was changed to a modified constant potential. The pressures came down and the cells failed thousands of cycles later due to other causes.

Now, on the NWSC test program, pressure failures also occurred at about the same number of cycles as capacity failures. When this happened, these were counted in the group average which I showed you on the previous table.

Early failures due to internal cell shorting and low capacity amounted to about three percent of the large number of cells that were cycled on this program.

(Figure 5-4)

As early as 1973, a theoretical equation had been derived for cycle life as a function of percent DOD and temperature, which predicted cycle life to be a linear function of the expression shown on this graph.

Now the star point experiment, part of the Crane program, provided the first opportunity to check this particular function. It provided data at three-percent DOD values at 40° C. This data was shown to be linear, and moreover the line passed through the origin if percent DOD was based on the actual capacity of 7.4 ampere-hours rather than the nominal six-ampere hour capacity.

This provided for a point on the curve. The data will be shown later.

This result was one of the more important ones to come out of the star point experiment.

(Figure 5-5)

Now let.s look at the effect of percent recharge.

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Inspection of the data on the previous table shows that percent recharge has a definite effect on life. The high value, 200 percent, results in shortening life. This might have been expected if failure by loss in capacity is life limiting because corrosion of the positive plaque material and separator degradation both proceed during overcharge, especially at the higher temperature. Also, the greater the depth of discharge, the more the amount of overcharge. So that you have those factors working.

(Figure 5-6)

The average cycle-life values as a function of percent recharge from Table II are shown in Table III together with their reciprocals.

We have used the reciprocal life as a function of temperature to good advantage in data analysis on other programs.

(Figure 5-7)

The reciprocals are plotted as a function of temperature in this figure. The effect appears to be nonlinear and the plot indicates that by the time temperature becomes as low as 20° C, the effect of percent recharge might very well disappear. This will be an important result when temperature effect is considered later.

(Figure 5-8)

Let's look at charge-discharge rate combinations. Now we are going to treat these as combinations, not as individual effects. In this table, the averages across all groups shown in Table II data are given for the charge-discharge rate combinations: 4C, 2C, C, C/2, 4C, C/2 and C, 2C. The data shows that there is no essential difference among the combinations except for 4C, 2C, which yield appreciably higher cycle volume.

(Figure 5-9)

In this figure, the 4C, 2C averages are plotted as a parameter in a graph of cycle life versus temperature.

The averages of all the other combinations are lumped together at salient points on the basis of the Table IV data which showed that there are essentially no differences among the other combinations.

Also shown is data from the star point experiment for the 2C, C combination which is interpolated from Figure 5-11. Clearly this combination belongs not with the 4C, 2C combination but with the others, all the others.

The data are limited to the 140-percent recharge groups.

It is clear that the 4C, 2C combination results in high values of cycle life, while the other combinations result in values which are essentially equivalent. The conclusion is that the high-rate combinations of discharge-charge are not effective in accelerating failures. Consequently, they are of no value in accelerated test design.

This conclusion had been reached earlier, as long ago as 1973, on another program where the rate differences, however, were not so widespread.

In actual space application, nothing like a 4C, 2C combination was possible, even in orbits as low as 90 minutes. So, in considering the temperature effect a little bit later, the 4C, 2C data will be eliminated.

Now, the fact that the 2C, C combination does not give different results compared to the others, except for 4C, 2C, is a valuable bit of information and will be used later in accelerated test design.

Now let's look at the temperature and percent DOD combination.

(Figure 5-10)

For this analysis, the 200-percent recharge data and the 4C, 2C data will not be used.

In this figure, cycle life is plotted against the percent DOD which we showed earlier, with temperature as the parameter. And where 100-percent DOD is based on the actual capacity of 7.4 ampere-hours.

The star point and the fractional factorial experimental data are shown. Linearity of the star point data is clear. Convergence of the curves for the different temperatures at the origin results is to be expected.

(Figure 5-11)

The star point data is all for the 2C, C rate combination; however, as we showed earlier, its use is justified.

In preparation of working graphs for data analysis, it had been shown that the 200-percent recharge data also show convergence near the origin. On this basis, it seems reasonably well established that the function of percent DOD is that which we have used for the abscissa, and it remains now only to describe the temperature effect.

In the original derivation of the theoretical equation for the cycle life versus percent DOD and temperature, which will be presented a little later, it was considered that the degradation processes might double in rate per $10°$ C increment as temperature increases.

In this figure it is shown that cycle life more than doubles in the intervals 50 to 40. The 40 to 30 difference is 2.54 times the 50 to 40 difference.

In a previous treatment of the incomplete data it was indicated that cycle life might almost be trebling for 10° C increments as temperature comes down.

Now, at this time we have one cell group, which is No. 86, nearing completion of its test life. It is being cycled at 20° C, 40-percent DOD, and 105-percent recharge. Its average life can be estimated now, it has had three cell failures, to be in the neighborhood of 22,000 to 23,000 cycles. This gives us a fourth point on the cycle-life temperature curve for 40-percent DOD.

While the percent recharge for this group, that is 86, is 105 percent and not 140 as for the other 40-percent DOD data points, the previous figure which showed conversion of the reciprocal of the percent discharge data indicated at 20 degrees, differences in percent recharge may vanish. If so, we can make a plot of the temperature data as shown in this figure.

(Figure 5-12)

For the moment, let us consider only the actual data. That is group 86 in the figure. Then there is the fractional factorial data and the star point data. We will talk about the rest of the curve a little bit later.

(Figure 5-13)

Now, if the temperature effect were allowed to treble, then cycle life would be expressed as a functional table as shown in this vugraph.

(Figure 5-14)

The table in Figure 5-13 yields this table, and here we have the expression $-(T-50)/10$ showing values of 1, 2, 3, 4 for those temperatures. The cycle life for trebling as shown in the previous figure will give us these values of cycle life for those temperatures.

Now this table leads to this equation for cycle life as a function of percent DOD and temperatures. For X and A we have the values shown.

The values of cycle life for 40-percent DOD calculated from the previous equation are plotted. That's this X value which comes from the empirical equation just shown.

This really isn't a bad fit considering that the cycle-life averages have about a plus or minus 10 percent average deviation.

While based on the data of Figure 5-5 for the effect of percent recharge — where we showed the reciprocal with the conversion — it may be satisfactory to draw the curve of this figure, as

representative of the temperature situation for 140-percent recharge. But it would not be correct for 105-percent recharge, which is what that data point is. That's a condition for that data point.

This is because the lower amounts of recharge result in higher cycle life at the higher temperatures as shown in Table II data.

To complicate this situation even further, it is probable, as temperature increases, that 105-percent recharge would be insufficient to maintain capacity. On the test in our laboratories, 110-percent recharge was insufficient at 43° C, but 120 percent was sufficient. So if we used 120 percent rather than 140 percent, the resulting curve would look something like that dashed line curve providing we get convergence at 20° C for the percent recharge function.

Even the dashed line curve would yield a pretty good fit to the empirical equation, which we showed, with modest changes in the constant 3, A, and X.

The temperature curve is shown with a dotted continuation which plunges towards zero-cycle life around 60 degrees. This is on the basis that star point data show this cell design to be incapable of cycling at 60° C, 60-percent DOD, and 140-percent recharge.

(Figure 5-15)

We can use the equation to predict cycle-life values through the three remaining cell packs which are all cycling at 105-percent recharge as shown in this table.

The conditions are 0 and 40 degrees temperature to 40 percent depth; 20 and 20, and 0 and 20. And these values of cycle life result from the equation.

The value of 50,000 cycles for pack 84N seems to be reasonable enough; however, the other two results represent a very high extrapolation of the data. We have no idea of the validity of such a projection on the low temperature end. Moreover, whether it is realistic or not, we are striving for ten-year life in orbit now, with the best break on DOD and temperature that we can get.

If we talk about a 90-minute orbit, only 58,400 cycles are required for a 10-year life. So, speculation about the two zero-degree values on that table seems rather idle.

It appears that a 10-year life in such an orbit could be achieved with this cell design for these combinations of temperature and percent DOD, where percent DOD now is based on a nominal value of six-ampere hours capacity.

This says, for a goal of 10-year life, the usable energy could be doubled by controlling temperatures at 10 degrees rather rather than 20. Operation at temperatures only slightly over 20 degrees will result in large increases in battery weight.

On the face of it, the design could be operated at 70-percent DOD nominal by increasing temperature to zero. And this would give us a factor of about three times weight reduction.

However, reliability of the empirical equation is involved as well as reduced energy availability at the lower temperatures. Change of failure-mode is a possibility also, perhaps resulting in earlier than predicted failures; especially lowered rates of oxygen recombination.

Now let's look at accelerated test design.

(Figure 5-16)

We have talked about a low earth orbit, specifically in 90 minutes.

With the failure of the discharge-charge rate combinations as failure-accelerating vehicles, we are left with percent DOD, temperature, and percent recharge as variables which we can experiment with through design or accelerated testing.

A percent DOD and temperature have been used commonly in the past. There is no doubt that large amounts of overcharge, that's percent recharge, in combination with high temperatures and percent DOD, accelerates failure but in a nonlinear fashion, even perhaps with the effect disappearing at about 20° C.

Now, with both temperature and percent recharge being highly nonlinear, it seems best not to try to work them both into test design, aside from the probability that we don't have enough information about the percent recharge variable to enable adequate treatment.

While use of the rate combinations did not work out, at least it told us that we could go as high as the 2C, C rate combination. This will enable achievement of time acceleration on testing. We must, however, eliminate premature hydrogen pressure failures. This is to be done by going to modified constant potential charging where voltage is limited to 1.53 volts or less.

Now, let's talk about the 90-minute orbit, and discuss the 30-minute discharge, and 60-minute charge in terms of 100-percent DOD based on the actual ampere-hour-cell yield. Now obviously for the 100-percent DOD situation on a 30-minute discharge, the discharge rate would be 2C, and for 50 percent DOD it would be C.

On a constant potential charge mode, the charge rate for a nominal six-ampere hour cell would start around 2C and taper to values of about C/7 during orbit charge.

On the basis of our tests at AFAPL the 110-percent recharge is adequate at 27° C and 120 is adequate at 43° C.

In service we want to achieve a 10-year life or a 58,000 plus cycles. For a test time acceleration factor of 10X, that is one year, we would be limited to 5900 test cycles if we were constrained to use the 90-minute cycle.

(Figure 5-17)

We show representative data for the GE cell design, which we are dealing with here, assuming that our empirical equation holds under all the temperature, and depth-of-discharge conditions shown.

Let's look at the 50-percent DOD which is 1.0 on the abscissa. Using a 90-minute cycle and a C, C/2 rate combination, testing would be constrained on the basis of 5900 cycles to a temperature of no lower than slightly under 30° C.

However, if we can use the 2C, C rate combination allowed by our analysis, the cycle duration would be halved by 45 minutes allowing 10,700 cycles per year. This allows testing at 20° C and a spread of 20° to 40° C gives an adequate range for extrapolation of time or zero or whatever.

At the same time, using a temperature of 30° C, 23 can go as low as 30-percent DOD. We want to do this to check out linearity of the percent DOD function on this cell design, or whatever.

Now this scheme would require a minimum of five cell groups and one-year test time to establish the 10-year service life at 30-percent DOD and 10° C. We probably would be right about in there.

We probably can achieve much faster acceleration without sacrificing prediction reliability by rendering extrapolations unduly formed or by forcing into higher discharge-charge rate combinations leading, perhaps, to spuriously high-cycle life values.

(Figure 5-18)

To summarize, the conditions for accelerating testing could be as follows for a 10X acceleration factor for demonstration of a 10-year life on a 90-minute orbit.

We used the CP recharge mode. We would have five cell packs minimum. We probably ought to use five cells as just a minimum per pack. Temperatures to be used would be 20°, 30°, and 40° C, percent DOD of 50, 40, 30 based on actual capacity. Using a 120-percent recharge to accommodate this 40° C temperature, and a 45-minute cycle we would use 2C discharge rate and a CP recharge mode.

Now I'd like to talk about the theoretical equation.

(Figure 5-19)

Originally in 1973, we derived a theoretical equation for cycle life where m is descriptive of the degradation rate, n is a number which is descriptive of the temperature effect on the degradation rate, and if the degradation rate doubles, the n equals 2.

You can think about it doubling on the basis of the old chemical rule of thumb that chemical reaction rates double for each 10° C rise in temperature.

(Figure 5-20)

In this last figure we have plotted the data for the empirical equation from the previous graph and superimposed on it data calculated from the theoretical equation for m and n combinations of 0.01, 2.1, 0.09 and 2.1. These are shown as gaps in the equation.

The empirical equation is shown as circles. The theoretical equation for these two sets ofc common measurements is shown as X's and squares.

Inasmuch as we have no data yet for 10° C, that 50° C point for the actual data is not too helpful in describing what cycle life will be at the lower temperatures. This is true because in going from 50 to 40 we are not beginning to feel the full upsweep of that curve.

We submit that the theoretical equation with m equal to 0.09 to 0.1 and n equal to 2.1 is not a bad fit to this situation. Therefore, the original theoretical equation may give us a good foundation for more intensive development relating theory more intimately to the degradation process.

I think it can be said that this program not only was the most comprehensive accelerated life test program ever undertaken for NiCad spacecraft cells, but it has been very instructive. In retrospect, experimental design might have been modified. That is, we could have used the CP recharge mode rather than constant current and eliminated the very large amounts of overcharge. But it is a very good program to have behind us.

DISCUSSION

HESS: Can you give us the report number of that NWSC report you mentioned?

LANDER: I am sure you can get it from Harry Brown from NWSC who is here, and maybe if you are lucky, he will have the report to give you.

ROGERS: I am wondering whether the number of cycles, in a 45-minute cycle at the higher rates, compared to a 90-minute cycle at equivalent lower rates, would give you the same length of time in cycle life?

LANDERS: The answer to that is no, it will give you half the time and that's why we can get as many as 10,000 plus cycles in a year instead of only 5900 cycles in a year.

ROGERS: I think what I was driving at was the life of the cell would be 5000 cycles in the 90-minute orbit, or 10,000 in a 45-minute with the same DOD. Would it be the same elapsed time period?

LANDERS: It should be the same according to this data analysis, if you want to believe the data analysis.

ROGERS: The same number of cycles.

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LANDERS: Right.

SEITZ: Would this empirical equation be generalized to commerical nickel cadmium batteries, particularly in smaller sizes, rather than portable type?

LANDERS: What we would hope is that in the event that we wanted to test a new design or a different design, for example, the general shape of the equation would hold. But the constants in the equation would change on the basis of whatever the design might be.

TEST VARIABLES

ENVIRONMENTAL

    1. DEPTH-OF-DISCHARGE (DoD)
    2. TEMPERATURE (T)
    3. AMOUNT OF RECHARGE (% R)
    4. DISCHARGE RATE (MULTIPLES OF C)
    5. CHARGE RATE (MULTIPLES OF C)
       DISCHG.-CHG.-CONSTANT CURRENT

DESIGN

    1. AMOUNT OF ELECTROLYTE
    2. CONCENTRATION OF ELECTROLYTE
    3. AMOUNT OF NEGATIVE PRECHARGE

DESIGN FACTORS: NOT CONCERNED IN ACCELERATED TEST DESIGN

Figure 5-1

Table II

Life Cycle Data, Factorial Design Experiment

	30°C				50°C		
40% DOD		80% DOD		40% DOD		80% DOD	
140%R	200%R	140%R	200%R	140%R	200%R	140%R	200%R
10,600 (1)	10,800+ (5)	3010 (7)	1630 (3)	4200 (8)	3260 (4)	930 (2)	720 (6)
15,500 (9)	11,500 (13)	2970 (15)	2200 (11)	5360 (16)	2040 (12)	1320 (17)	450 (21)
8440 (18)	3060 (22)	2860 (32)	2270 (28)	4610 (23)	2700 (19)	1900 (24)	550 (40)
12,400 (20)	5600 (30)	1320 (36)	2060 (33)	4620 (31)	2580 (27)	2510 (44)	750 (48)
11,600 (26)	7300 (39)	1290 (37)	670 (41)	6520 (38)	3100 (34)	1560 (59)	400 (55)
4700 (35)	7540 (47)	1700 (45)	1700 (50)	3110 (46)	860 (42)		1030 (63)
10,200 (43)	4930 (56)	1640 (54)	1670 (58)	5950 (53)	3350 (49)		
9720 (52)	6340 (64)	2840 (62)		2350 (61)	2680 (57)		
8410 (60)							
10,200±20%	7200±29%	2200±33%	1900±23%	4600±22%	2600±21%	1620±27%	650±18%

numbers in ( ) = cell group numbers.

Figure 5-2

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EARLY FAILURES

- DUE TO HIGH HYDROGEN PRESSURES

- ASSOCIATED WITH HIGH ~~DISCHARGE~~-CHARGE RATES AND LARGE
  AMOUNTS OF OVERCHARGE

- INDUCED BY CONSTANT CURRENT CHARGE MODE

- ACCOUNTED FOR 15% OF FRACTIONAL FACTORIAL AND 29% OF
  STAR POINT EXPERIMENTS

- CULLED FROM DATA AVERAGES

Figure 5-3

% DoD FUNCTION

CYCLE LIFE
LINEAR WITH

$$\frac{100 - \% \, DoD}{\% \, DoD}$$

AS PREDICTED IN 1973

Figure 5-4

EFFECT OF % RECHARGE

- LARGE AMOUNTS ACCELERATE FAILURE ESPECIALLY FOR HIGH DoD's, T's

- NON LINEAR - EFFECT COULD VANISH AT T's BELOW ABOUT 20°C

Figure 5-5

TABLE III

THE % RECHARGE EFFECT

TEST CONDITION

T °C	% DOD	% R	AVERAGE LIFE	1/AVG LIFE (x10^{4})
30	40	140	10,200	1.0
30	40	200	7,200	1.4
30	80	140	2,200	4.5
30	80	200	1,900	5.3
50	40	140	4,600	2.2
50	40	200	2,600	3.9
50	80	140	1,600	6.2
50	80	200	650	15.0

Figure 5-6

Figure 5-7

RECIPROCAL OF LIFE
VS TEMPERATURE

(1/CYCLE LIFE) x 10⁴

200% R, 80% DOD

140% R, 80% DOD

200% R, 40% DOD

140% R, 40% DOD

T (°C)
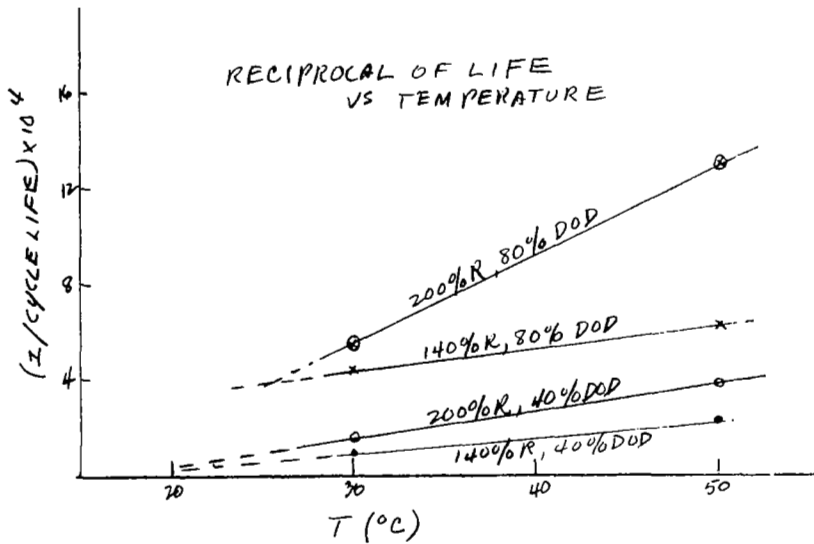
Figure 5-7

Figure 5-8

THE DISCHARGE - CHARGE RATE COMBINATION

AVERAGE CYCLE LIFE FROM TABLE II

4C, 2C	7500
C, C/2	4100
4C, C/2	4300
C, 2C	4000

CONCLUSION: VARIATIONS ARE NOT
EFFECTIVE IN ACCELERATING FAILURE

THE 2C, C COMBINATION BELONGS WITH
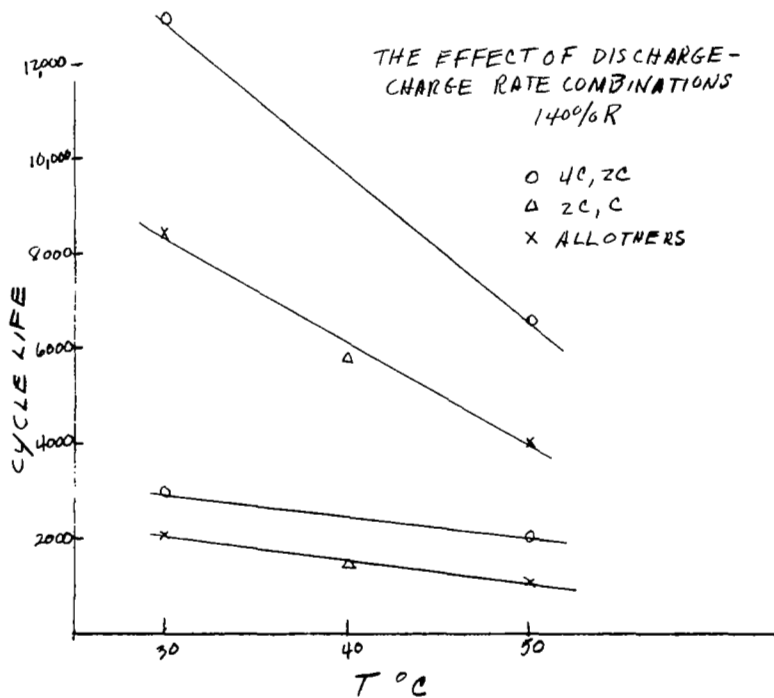THE C, C/2; 4C, C/2; C, 2C GROUP. (NOT 4C, 2C)
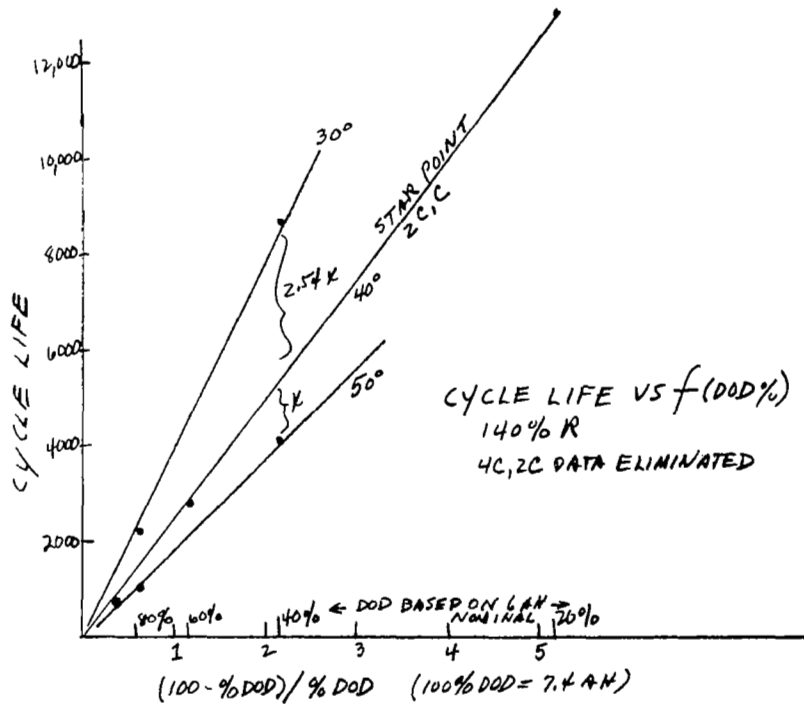
Figure 5-8

Figure 5-9

THE EFFECT OF DISCHARGE-
CHARGE RATE COMBINATIONS
140% R

O 4C, 2C
△ 2C, C
X ALL OTHERS

CYCLE LIFE

T °C

Figure 5-9

Figure 5-10

CYCLE LIFE

30°

STAR POINT

2C, C

2.54 K

40°

K

50°

CYCLE LIFE VS f (DOD%)
140% R
4C, 2C DATA ELIMINATED

80% 60% 40% ← DOD BASED ON LAH → 20%
NOMINAL

(100 - % DOD) / % DOD   (100% DOD = 7.4 AH)

Figure 5-10

THE TEMPERATURE - % DoD COMBINATION

CYCLE LIFE VS. (100 - % DoD) / % DoD

T = PARAMETER

LINEAR IN f(% DoD), CONVERGANCE AT ORIGIN

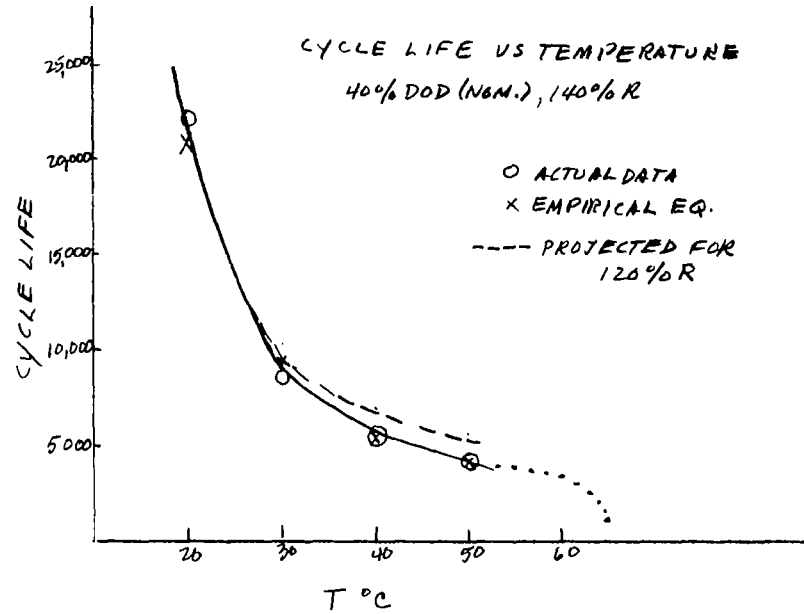WHEN f(% DoD) IS BASED ON ACTUAL CAPACITY
(NOT NOMINAL)

Figure 5-11

Figure 5-12

THE TEMPERATURE EFFECT

A POSSIBLE RELATIONSHIP

ΔT	Δ CYCLE LIFE
50 - 40°C	X
40 - 30	3X
30 - 20	9X
20 - 10	27X

Figure 5-13

T°C	- (T-50)/10	CYCLE LIFE
50	0	A
40	1	A + X
30	2	A + 4X
20	3	A + 13X
10	4	A + 40X

$$C.L. = \left[1/2 \ (3^{-(T-50)/10} -1) \ X + A \right] \ (\frac{100 - \% \ DoD}{\% \ DoD})$$

X = 600   A = 1900

Figure 5-14

PREDICTED LIFE

PACK #	T°C	% DoD	CYCLE LIFE
83N	0	40	156,000
84N	20	20	50,000
85N	0	20	373,000

7 *CELL* $\overline{VII}$

CONDITIONS FOR 10 YEAR LEO LIFE

T°C	% DoD *(NOM.)*
0	70
10	39
15	26
20	~~13~~/8

Figure 5-15

ACCELERATED TEST DESIGN

● DISCHARGE-CHARGE RATE COMBINATIONS DO NOT ACCELERATE FAILURE

● % RECHARGE ACCELERATES FAILURE BUT NON-LINEARLY. EFFECT
   VANISHES AT 20°C AND LOWER. TOO LITTLE INFORMATION

● % DOD, T REMAIN FOR TEST DESIGN

● 2C, C RATE COMBINATION CAN BE USED (2C DISCHARGE, c.p. CHARGE)
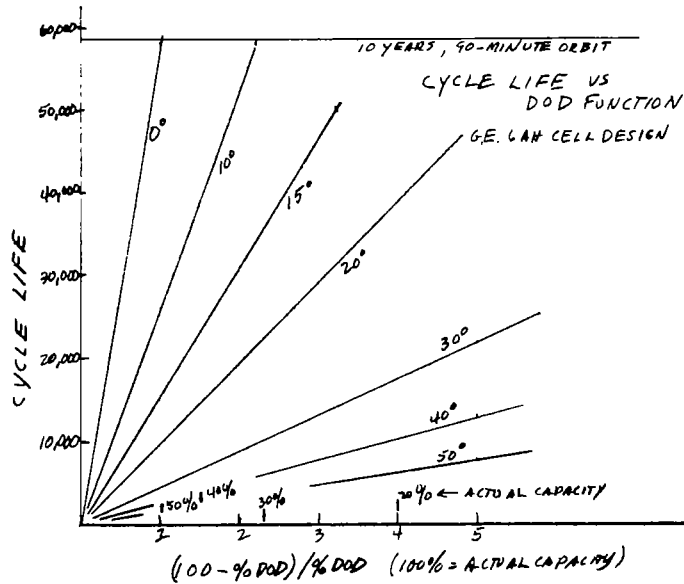
Figure 5-16

Figure 5-17

ACCELERATED TEST DESIGN
(90 - MINUTE ORBIT)

FOR DEMONSTRATION OF 10-YEAR LIFE -- 10 X ACCELERATION

   ● C.P. RECHARGE MODE
   ● 5 CELL PACKS , *MIN.*
   ● T's: 20, 30, 40°C
   ● % DoD's: 50, 40, 30 (ACTUAL CAPACITY)
   ● 120% R
   ● 45-MINUTE CYCLE (2C, C)

Figure 5-18

THEORETICAL EQUATION - 1973

$$\text{CYCLE LIFE} = \frac{1000}{M \times N^{(T-20)/10}} \left(\frac{100 - \% \text{ DOD}}{\% \text{ DOD}}\right)$$

M IS DESCRIPTIVE OF DEGRADATION RATE

N IS A NUMBER DESCRIPTIVE OF TEFFECT;
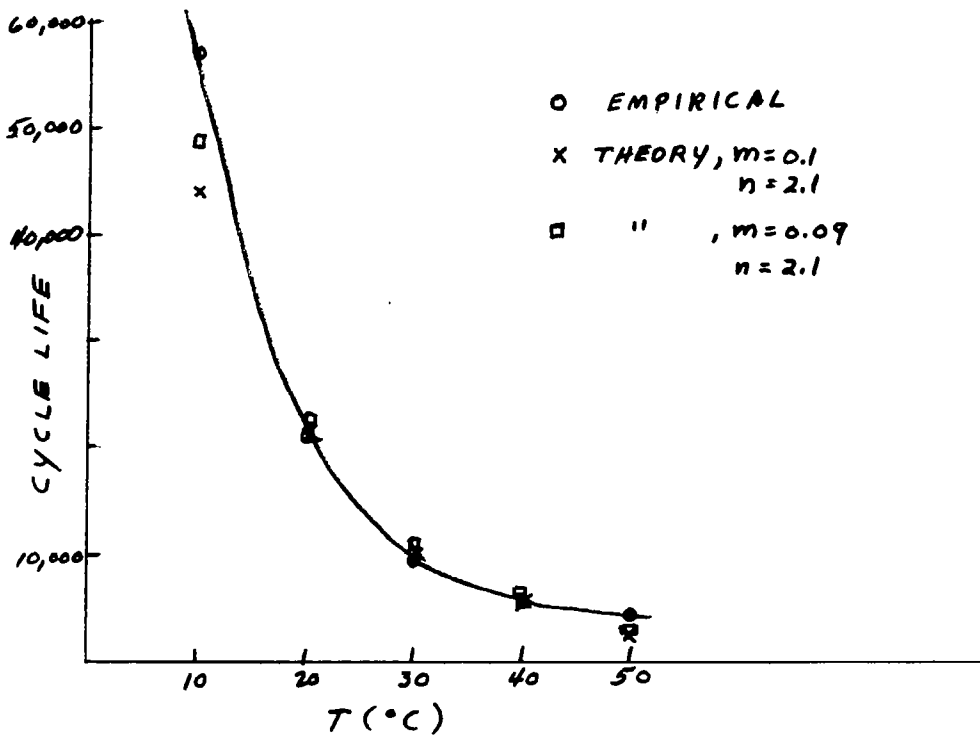IT = 2 IF DEGRADATION RATE DOUBLES PER 10°C INCREASE IN T

Figure 5-19

Figure 5-20

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