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STATISTICALLY DETERMINED NICKEL CADMIUM PERFORMANCE RELATIONSHIPS

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A considerable amount of data are customarily taken on aerospace nickel cadmium cells to control manufacture, to verify that the cells will be acceptable, and to select well-matched cells for assembly into batteries. These data provide an opportunity for statistical analysis on data distribution and the interrelationships between parameters. This information can be helpful in understanding behavior, for use in quality control, and in identifying possible problems with individual cells or with lots of cells, and even for manufacturing process control (Figure 1). This is also a logical approach for analysis of a common data pool for Ni/Cd cells. Since the data required for analysis is already available during manufacture, there is little additional cost involved for data acquisition. In fact, computerized data handling will save money in data processing. Furthermore, data analysis should be able to help screen out unnecessary tests, for additional cost saving.

A statistical analysis was performed on sealed nickel cadmium cell manufacturing data and cell matching data. The cells subjected to the analysis were 30 AH sealed Ni/Cd cells, made by General Electric Co. A total of 213 data parameters was investigated, including such information as plate thickness, amount of electrolyte added, weight of active material, positive and negative capacity, and charge-discharge behavior (Figure 2). Statistical parameters determined include the maximum and minimum values, arithmetic mean, variance, standard deviation, skewness, kurtosis, and data histograms (Figures 3 and 4). Figure 5 shows a typical data histogram with very little skewness or kurtosis, whereas, Figure 6 shows another which is skewed and has a high kurtosis. Statistical analyses were made to determine possible correlations between test events; for example, if there is any connection between end of charge voltage and pressure, or between electrolyte amount and capacity.

The data show many departures from normal distribution. Some departures are inherent in the physical behavior of cells, and others are due to manufacturing bias. For example, in one lot of cells, the data fall in two distinct groups, which were identified as caused by manufacturing variations from batch processing. Skewing of pressure data sometimes occurred very strongly and appeared to be related to removal and rework of the high pressure cells.

Statistical relationships between data obtained during one test event and another were also obtained. The analysis used was the rank-difference method for coefficient of correlation, producing coefficients that can range from -1.0 to +1.0 for perfect positive correlation and perfect negative correlation, respectively. Completely random results would yield a correlation of 0. For example, the relationship between cell pressures for 30 AH cells at two unrelated test conditions was evaluated 20 hours into the charge at 3.0 amperes and 75°F versus 72 hours into the charge at 1.5 amperes and 32°F. Correlation coefficients for five lots averaged 0.62, showing that there is a definite relationship (Figure 7). Pressure at 72 hours of charge also correlates with pressure after two hours of discharge. Pressure does not correlate very well with voltage, however, and its correlation with pressure at the end of charge on the last cycle is good for only one of the four lots.

Sometimes two parameters would show a strong positive correlation for some lots but not for others. This behavior appeared to be the result of important differences between lots. In analyses of five lots, this was found to be the case for correlations of pressure vs. voltage (ranging 0.097 to 0.47), early life pressure vs. pressure after cycling (ranging -0.187 to 0.604), end of charge voltage vs. KOH volume (ranging 0.026 to 0.987), open circuit voltage 24 hours after removing shorting wires vs. 1.0 hours afterwards (ranging 0.306 to 0.972, Figure 8), and also vs. open circuit voltage 24 hours after 15 A/1 minute charge following 16 hours shorting (-0.054 to 0.998, Figure 8).

Occasionally, there are interesting surprises, though upon reflection these are understandable. For example, thickness of the cells, measured at the center, correlates very well with the final cell weight (Figure 9), and also correlates well with the open circuit voltage 24 hours after a 15 A/1.0 min charge following 16 hours shorting. Data are not available to determine whether these correlations would hold also for other lots.

The end of charge voltage after 31 cycles is found to correlate well with that same voltage at the first cycle (Figure 10). It also correlates well with capacity. For only one of the four lots did KOH final volume and end of charge voltage appear to be related.

Capacity to 1.0 V and capacity to 1.15 V were found to be closely related, though with some departure for one of the lots. Interestingly enough, capacity to 1.0 V on one test did not correlate, for three of the four lots, with capacity to 1.0 V for another test (Figure 11). The test conditions for test 7 were C/20 charge for 72 hours at 0°C, and discharge at C/2 at 0°C.

Product consistency from one lot to another is an important attribute for aerospace applications. It is clear from these examples that there are some significant differences between these lots. Statistical analyses are seen to be an excellent way to spot those differences. Also, it is now proven beyond doubt that battery testing is one of the leading causes of statistics.

ACKNOWLEDGEMENT

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TECHNOLOGY

- o Investigate interrelationships between parameters
- o Help understand behavior

MANUFACTURING PROCESSING CONTROL

- o Identify long-term changes in processes
- o Identify batch-to-batch differences
- o Common data pool for Ni/Cd cells

QUALITY CONTROL

- o Identify problems with individual cells
- o Identify problems with cell lots
- o Help select matched cells for batteries

COST

- o Data are already available
- o Computerized data-handling will save money
- o Analysis can help screen out unnecessary tests

Figure 1. Advantages of Statistical Data Analysis.

- o 30 AH sealed NiCd cells
- o Used manufacturing data and cell matching data
- o 213 data parameters were investigated; e.g.,
  - o Plate thickness
  - o Amount of electrolyte
  - o Weight of active material
  - o Positive and negative capacity
  - o Charge-discharge behavior
  - o Many others
- o Multiple manufacturing lots

Figure 2. Basis for Analysis.

- Maximum and minimum values
- Arithmetic mean
- Variance
- Standard deviation
- Skewness
- Kurtosis
- Data histograms
- Correlations between test events

Figure 3. Statistical Analysis.

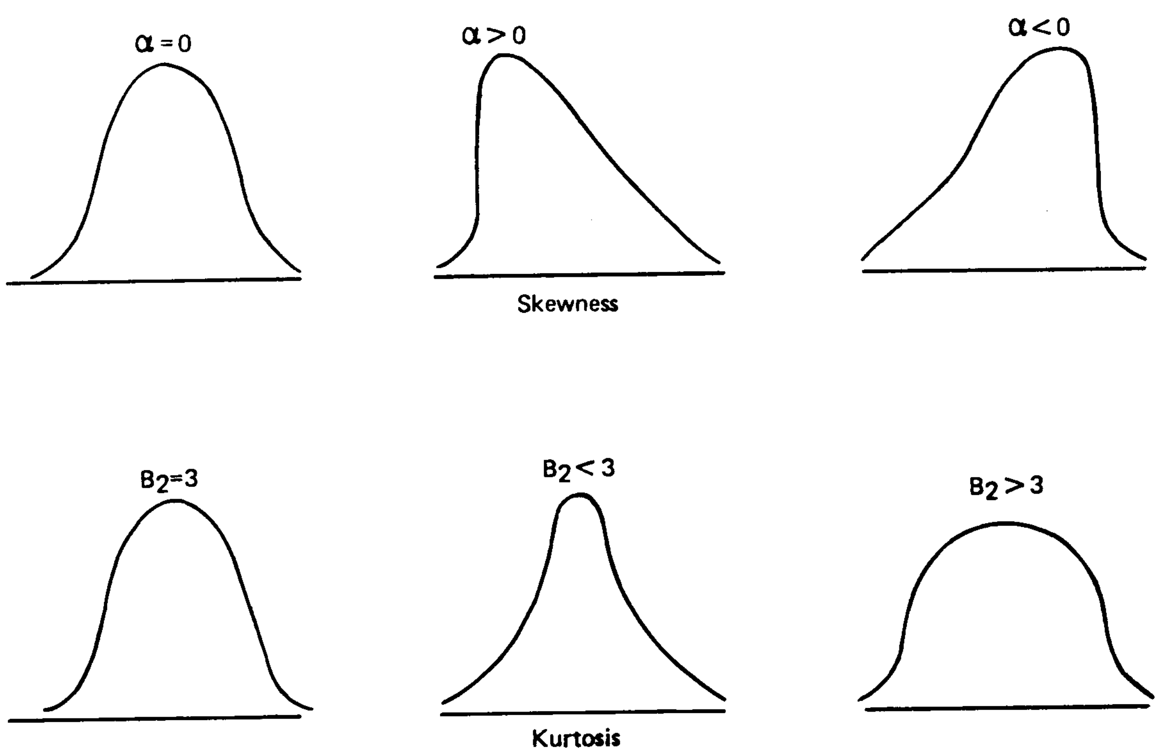

Figure 4. Statistical Terms.

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HISTOGRAM FOR TRW DATA      LOT8     TESTA     VARIABLE D.S.7A        AHIV
NMAX=    95
MINIMUM VALUE=   35.200     MAXIMUM VALUE=   37.500
STANDARD DEVIATION=          .417     VARIANCE=          .174
SKEWNESS=          -.338    KURTOSIS=          3.205
-2 ST. DEV.     -1 ST. DEV.         MEAN         +1 ST.DEV.     +2 ST. DEV.
   35.627          36.044          36.462          36.879         37.296

 35.20  -  35.43    90
              1

 35.43  -  35.66    27  94
              2

 35.66  -  35.89    58  68  85  95
              4

 35.89  -  36.12    37  57  61  62  65  67  69  70  71  87  88  92
             12

 36.12  -  36.35     1   2   3   5  10  12  32  33  38  47  48  50  64  75  80  84  93
             17

 36.35  -  36.58     7   8  16  34  45  46  49  51  52  56  66  72  73  78  79  81  83
             17

 36.58  -  36.81     4  11  13  14  15  20  21  22  23  24  25  26  28  29  31  35  36  39  41  42  43  44  53
                    59  60  63  76  82  86  89
             30

 36.81  -  37.04    18  19  54  55  74  77  91
              7

 37.04  -  37.27    17
              1

 37.27  -  37.50     6  30  40
              3
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Figure 5.   Capacity to 1.0 Volt.

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HISTOGRAM FOR GE DATA     LOT8     TEST7     VARIABLE VSC
NMAX=    95
MINIMUM VALUE=      .001     MAXIMUM VALUE=      .350
STANDARD DEVIATION=          .062      VARIANCE=           .004
SKEWNESS=          2.074     KURTOSIS=            9.141
-2 ST. DEV.     -1 ST. DEV.        MEAN          +1 ST.DEV.     +2 ST. DEV.
  -.65946-01     -.39890-02      .57968-01       .11992         .18188

 .1000-02-  .3590-01    1  13  15  29  34  38  39  40  41  43  44  45  46  51  53  55  56  57  58  60  61  62  63
                       65  66  67  68  69  70  71  73  74  75  76  77  78  79  83  84  85  86  87  91
                    43

 .3590-01-  .7080-01    3   7  12  14  16  17  18  31  32  36  37  47  48  52  72  80  89  90  93
                    19

 .7080-01-  .1057       2   4   5  10  19  20  21  23  25  28  33  35  42  49  54  64  81  82
                    18

 .1057   -  .1406      11  22  24  27  88  92
                     6

 .1406   -  .1755       8  50  94
                     3

 .1755   -  .2104       6
                     1

 .2104   -  .2453      30
                     1

 .2453   -  .2802
                     0

 .2802   -  .3151      26
                     1

 .3151   -  .3500      95
                     1
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Figure 6. Voltage After 16 Hour, One-ohm Short at 0°C.

Pressure at 72 hours of charge versus:

	Correlation Coefficient			
	Lot 5	Lot 6	Lot 7	Lot 8
Voltage at 72 hours	0.097	0.390	0.264	0.255
Pressure at 20 hours	0.663	0.589	0.447	0.792
Pressure at 120 minutes of discharge	0.492	0.582	0.916	0.799
Pressure at end of charge, last cycle	0.484	0.343	0.604	-0.222

Figure 7. Pressure Effects.

Open circuit voltage 24 hours after removing shorting wires versus:

	Correlation Coefficient			
	Lot 5	Lot 6	Lot 7	Lot 8
OCV 1.0 hour after removing wires	0.306	0.319	0.942	0.972
OCV 24 hours after 15A/1.0 min charge following 16 hr shorting	-0.054	0.637	0.003	0.998

Figure 8. Open Circuit Voltage Effects.

Cell center thickness versus:

	Correlation Coefficient
	Lot 8
OCV 24 hrs after 15A/1.0 min charge following 16 hr shorting	0.996
Final cell weight	0.997

Figure 9. Cell Thickness Effects.

End of charge voltage at cycle 31 versus

	Correlation Coefficient			
	Lot 5	Lot 6	Lot 7	Lot 8
EOCV at cycle 1	1.000	1.000	1.000	0.999
Capacity to 1.0V	0.999	1.000	0.871	0.990
KOH final volume	0.131	-0.061	0.186	0.976

Figure 10. End of Charge Voltage Effects.

Capacity to 1.0V (C/10 chg 14 hr, C/2 disch, 75°F) versus:

	Correlation Coefficient			
	Lot 5	Lot 6	Lot 7	Lot 8
Capacity to 1.15V, same test (B)	0.996	0.999	0.912	0.560
Capacity to 1.0V, test 7	0.191	-0.116	0.187	0.811
End of charge voltage, cycle 31	0.999	1.000	0.871	0.980

Figure 11. Capacity Effects.