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TITLE

PERFORMANCE OF LOW MERCURY ZINC/MANGANESE DIOXIDE ALKALINE CELLS

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PERFORMANCE OF LOW MERCURY ZINC/MANGANESE DIOXIDE ALKALINE CELLS

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Abstract

The Canadian armed forces use large quantities of alkaline cells, often in cold field conditions. In recent years the manufacturers of alkaline cells have been gradually lowering the mercury content of these cells, primarily because of the environmental hazards of mercury. The present study was undertaken because of the concern that the removal of mercury might adversely affect performance, especially in the cold, and also diminish the resistance to mechanical shock and vibration, and shelf life. This investigation of some of the performance characteristics of alkaline cells was conducted in comparison with older cells which contained higher levels of mercury. It was found that the room temperature performance of alkaline cells was excellent. However, between 5°C and -20°C, low-mercury cells manufactured since 1992 had performance that was inferior to the older cells.

Introduction

The zinc/potassium hydroxide/manganese dioxide cell, commonly referred to as the alkaline cell, became a widely available consumer product during the 1970's. It is estimated that worldwide annual use is more than five billion cells.(1) Historically, mercury has been an important additive in the manufacture of these cells, being amalgamated at up to 8% by weight with the zinc anode. The use of mercury resulted in less zinc corrosion and extended shelf life compared to the zinc/carbon Leclanche cell.(2,3) There was also enhanced interparticulate contact in the zinc powder, producing better electrode conductivity(4,5) and improved resistance to mechanical shock and vibration.

In recent years, primarily in response to environmental pressure, manufacturers have been reducing the amount of mercury contained in alkaline cells,(6,7) some of which are now advertised as being "environmentally-friendly" and containing less than 0.001% Hg. Consumers have been assured that the mercury removal program has not caused any loss in cell performance. Notwithstanding these claims, it was decided to conduct an objective assessment of the effects of moving to low-mercury alkaline cells.

Experimental Program

In February 1993 it was learned that a large military stock of AA-size and C-size cells had been declared "time-expired" and was slated for disposal. The military supply system considers alkaline cells to be "time-expired" when they have been stored for 30 months from their date of manufacture (DOM). The only D-size cells in stock were manufactured in 1992. For comparative purposes, a quantity of commercially available, "mercury-free" D cells was purchased locally: DOM - June 1992.

In all, six groups of cells were available for the study:

1. AA size - DOM 01/92 - military stock
2. AA " - DOM 03/89 - military stock

3. C size - DOM 01/92 - military stock
4. C " - DOM 05/89 - military stock

5. D size - DOM 02/92 - military stock
6. D " - DOM 06/92 - commercial

It was verified that all cells in the test program were produced by the same manufacturer. The following measurements were made on the cells in each group: open circuit voltage, resistance (ac value at 1 kHz) and mass.

Undischarged cells from each group were dissected and samples of the zinc anode were removed, weighed and dissolved in concentrated HCl/HNO_3. The concentration of mercury in each of these solutions was then determined using inductively-coupled argon plasma atomic absorption spectrophotometry. The dry mass of the anode sample was used to calculate the mercury content as a percent by weight.

In a typical alkaline cell application, such as operating a flashlight, the rate of discharge is approximately 250 milliamperes, corresponding to a load of about 5 ohms. Thus the majority of cells from each group was resistively discharged at this load. Some additional experiments were conducted using 1Ω and 10Ω loads. Cell capacity was determined to the industry standard end of test voltage: 0.8 volts, although in many cases discharging was continued to below 0.1 volts.

For each experiment, cells were equilibrated prior to discharging for a minimum of four hours in an environmental test chamber at the desired temperature, between -40°C and 60°C. A 12 W resistor was then connected across each cell. The voltage drop across the load was measured every two minutes throughout the discharge period using a PC-controlled data acquisition unit. The capacity was determined by integrating the computed current over the elapsed time using Simpson's rule.

Results and Discussion

There were only minor differences between the open circuit voltages of cells of each size group and no significant differences in weights. The two groups of D-size cells had very similar impedance values. However, the impedance of the AA- and C-sized cells that were manufactured in 1989 was significantly lower than those manufactured in 1992. The mercury content of the anode in the 1989 cells was found to be about 0.8% and that of the 1992 cells was approximately an order of magnitude lower. During a subsequent conversation with the manufacturer, it was learned that all alkaline cells made by this company since 1990 were "ultra-low mercury", (i.e. less than 0.025% mercury).(8) Our analyses indicated that the mercury content stated by manufacturers must be relative to the total cell mass rather than the mass of the zinc anode. These results are summarized in Table I.

TABLE I

MERCURY CONTENT OF ANODES AND
MEAN IMPEDANCE MEASUREMENTS

Group	Cell Size	DOM	Mercury Content (%w/w anode)	Mean Impedance (mohms)
1	AA	01/92	0.10	165 ± 7.4*
2	AA	03/89	0.74	89 ± 5.1
3	C	01/92	0.07	131 ± 11.9
4	C	05/89	0.82	79 ± 6.5
5	D	02/92	0.08	96 ± 15.1
6	D	06/92	0.07	98 ± 19.0

* standard deviation

Since one of the effects of amalgamating mercury with the zinc anode is to increase the conductivity of the electrode, the impedance data confirmed that 1992 cells contained less mercury than the 1989 cells. The impedance data also suggested that the mercury content of the military D cells was similar to that of commercial "low-mercury" cells.

Typical results for the discharge of alkaline C cells at 25°C are given in Figure 1. In this experiment, two 1989 cells and three 1992 cells were discharged simultaneously. During the first several minutes after the load was applied, voltages dropped quickly from about 1.5 volts to 1.3 volts. After this initial period, the voltage curve sloped gradually, taking between 25 and 30 hours to fall to 0.8 volts. It then quickly decreased to a minimum value of about 0.1 volts. At temperatures above 10°C, the newer cells outperformed the older cells by about two to fours hours. This was expected on the basis of the reported 3% to 4% annual loss of capacity for storage of alkaline cells at 20°C.(5,9) It was also noted that the voltage of the 1989 cells was marginally higher than the 1992 cells during the first 15 hours of the experiment. Similar comments pertain to the groups of AA-size cells.

The typical discharge curves obtained for a similar experiment which was conducted at 0°C are shown in Figure 2. In this experiment the output of the 1989 cells remained above 0.8 volts for about twice as long as for the 1992 cells (19.5 h vs 9.2 h) and on average their capacity was twice as great (3.8 Ah vs 1.9 Ah). These results were unexpected, thus prompting a more detailed evaluation of low temperature performance.

Numerous discharge experiments at 1Ω, 5Ω and 10Ω were conducted to compare the performance of the two groups of C cells over a range of temperatures between -40°C and 60°C. The capacity results for these experiments are given in Table II (5Ω only) and in Figure 3 in slightly different representations. The data were averaged over at least five replicate cell discharge experiments at each temperature. Above 5°C, the capacity, as represented by the time to reach 0.8 volts, of the 1992 cells was about 10% more than that of the 1989 cells, but between 5°C and -20°C the capacity of the 1989 cells was significantly greater (in some cases more than 100%) than that of the 1992 cells (e.g. see Table II). Table II also indicates that there was a substantial increase in standard deviations for the data between 5°C and -5°C and at 45°C, most notably for the 1992 cells.

TABLE II

MEAN CAPACITY OF C CELLS
DISCHARGED THROUGH 5 OHM LOAD

Temperature (°C)	Time to 0.8 v (hours)	
	1989	1992
60	32.0 ± 0.5*	35.1 ± 0.3*
45	28.7 ± 1.1	32.6 ± 1.1
30	28.5 ± 0.3	30.5 ± 0.2
20	25.6 ± 0.3	28.5 ± 0.1
10	23.6 ± 0.3	25.9 ± 0.5
5	22.2 ± 0.2	23.9 ± 0.8
0	19.7 ± 0.4	12.6 ± 4.4
- 5	16.0 ± 0.9	7.1 ± 1.6
-10	11.2 ± 0.1	5.5 ± 0.1
-15	7.8 ± 0.1	4.5 ± 0.1
-20	5.2 ± 0.1	4.2 ± 0.1
-30	2.3 ± 0.0	2.4 ± 0.1
-40	1.0 ± 0.0	0.4 ± 0.0

* standard deviation

The difference in the capacity for higher versus lower mercury-content cells was plotted in Figure 3 against the test temperature for C-size cells that were discharged at 1Ω, 5Ω and 10Ω. It shows that the cells with higher mercury content performed better overall, but there was a rate dependence for the magnitude of the difference which varied with the temperature. At the 1Ω rate the older, higher mercury-content cells were better at all temperatures, but excelled in the 10°C-30°C range.

A comparison of the performance of AA cells manufactured in 1989 and in 1992 indicated a similar, but less pronounced discrepancy at temperatures between 0°C and -30°C.

For the D-size cells discharged on a 5 ohm load, the only significant difference between the capacity of the two groups of cells occurred at -5°C. This anomaly is illustrated in Figure 4 which shows the very dissimilar discharge curves for commercial and military cells. At this temperature, the difference in time to reach 0.8 volts was almost 60% while at all other temperatures this difference was always less than 7%. The discrepancy at -5°C was verified as significant by repeating the experiment on 10 additional cells from each group. There was only a small difference in the mercury content of the anodes for these two groups of cells (see Table I) and the impedance values were also indistinguishable. This suggests that only a small change in the mercury content of the zinc electrode can have a profound effect on performance at certain temperatures. Why this should occur at temperatures near to or just below 0°C is unknown and may warrant further study. Except for -5°C, there would appear to be no significance performance differences between cells produced for the military and those for the consumer market.

At temperatures below approximately 0°C there were notable irregularities in the discharge curves for all of the low-mercury alkaline cells. Figure 4 shows this behaviour for D cells from both groups as indicated, and Figure 5 for C-size cells discharged in this case at 0°C. What was typical of the low mercury cells of all sizes, as shown by the examples in Figures 4 and 5, was the instability of the voltage below approximately 0.8 volts and the tendency for the cell voltage to increase after several hours of discharging below 0.4 volts. The voltage fluctuations may be caused by a loss of electrical continuity in the anode. None of the 1989-dated cells exhibited these features.

The effects of low-mercury on the shelf life and resistance to mechanical shock and vibration are currently being studied and will be the subject of a future publication.

Conclusions

At temperatures above 5°C the performance of each of the three sizes of alkaline cells used by the Canadian military was found to be excellent, often exceeding the manufacturer's performance claims. However, between 5°C and -20°C, AA-size and C-size cells that were procured since 1992 had performance characteristics which were inferior to those of older cells. The older cells contained more mercury in the zinc anode and despite the marginal loss of capacity over three years of storage, still produced more energy at lower temperatures than the newer, low mercury cells. The lower mercury content of 1992 cells compared to 1989 cells was confirmed by chemical analysis of the anode. Lower mercury cells also had higher impedance values.

The performance of the military stock of D cells and commercial D cells with comparable DOM was only different at -5°C. The slight differences in composition of the zinc/mercury anode may have been responsible.

Acknowledgements

The authors would like to acknowledge the continued support of the Directorate of Research and Development Air, Canadian Armed Forces and the Electrochemical Science and Technology Centre, University of Ottawa.

References

1. K. Kordesch, Ch. Faistauer and J. Daniel Ivad, 8th International Battery Symposium, Brussels, May 9-13, 1993.

2. C. Huang, et al, "A new type of nonpoisonous addition agent for substituting mercury in zinc/manganese dry cells", J. Power Sources, 45 (1993) 169-175.

3. K.V. Kordesch, "Alkaline manganese dioxide cells", in "Handbook of Batteries & Fuel Cells", (D. Linden, ed.), McGraw-Hill, 1984.

4. J.Y. Huot, "Resistivity and anodic discharge of mercury-free gelled zinc anodes", Power Sources **14** (1993) (A. Attewell and T. Keily, eds.).

5. K.V. Kordesch, "Alkaline manganese dioxide zinc batteries", in "Batteries, Vol 1", K.V. Kordesch (ed.), Marcel Dekker, Inc., New York, 1974.

6. D. Spahrbier, "Mercury reduction programme for primary batteries", Chemistry & Industry, July 1990.

7. M. Meeus, et al, "New Developments in Reduction of Mercury Content in Zinc Powder for Alkaline Dry Batteries", Power Sources 11 (1986), (L. J. Pearce, ed.).

8. Private communication; manufacturer's representative and author (RWN), 30 Sept 1993.

9. Manufacturer's Battery Engineering Data, published 1992.

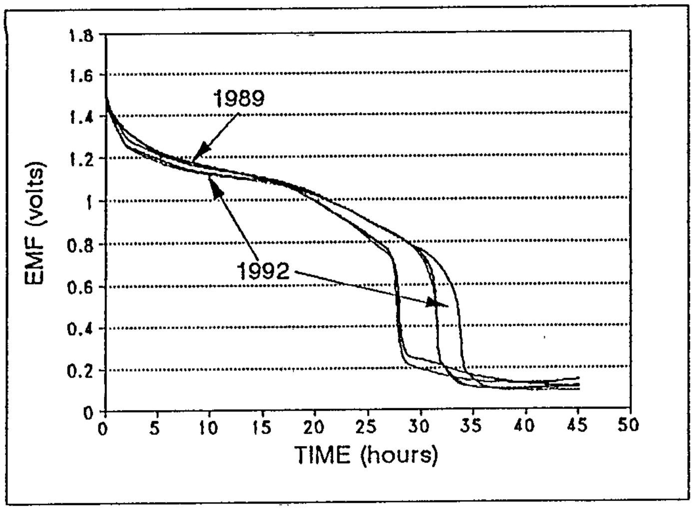

Figure 1. C Cells: Discharge Curves @ 20°C, 5 ohm Load.

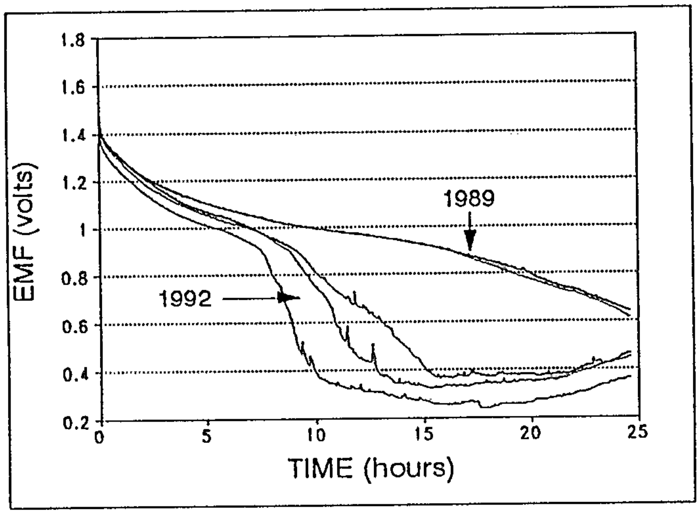

Figure 2. C Cells: Discharge Curves @ 0°C, 5 ohm Load.

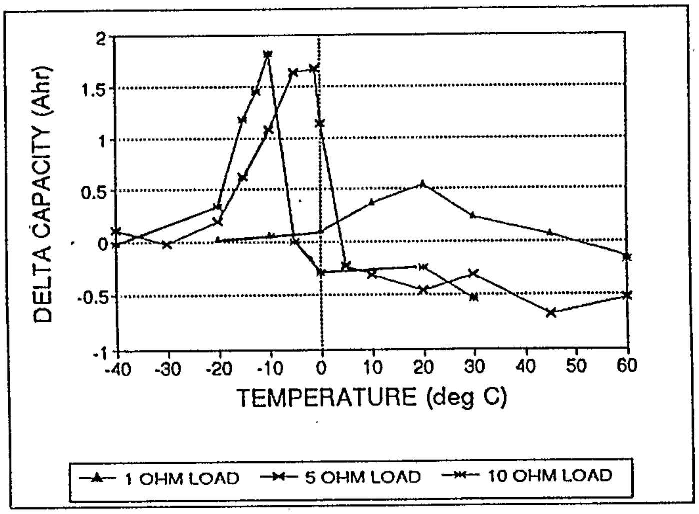

Figure 3. Mean Difference in Capacity: High Mercury - Low Mercury C Cells versus Load and Temperature.

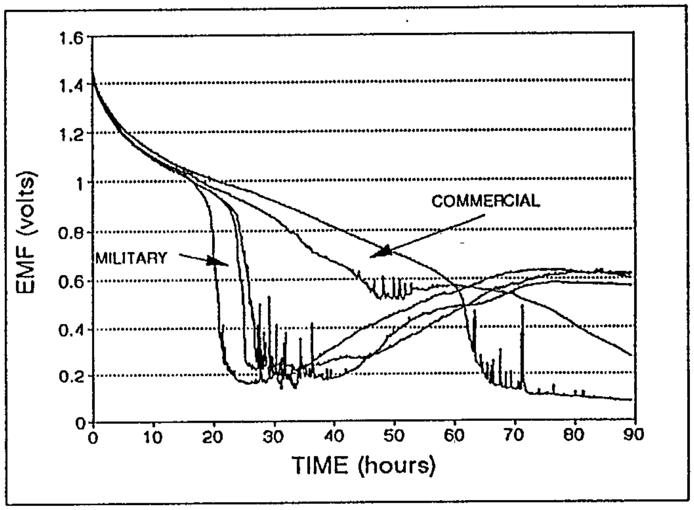

Figure 4. D Cells: Discharge Curves @ -5°C, 5 ohm Load (Discharging continued beyond 0.8 volts).

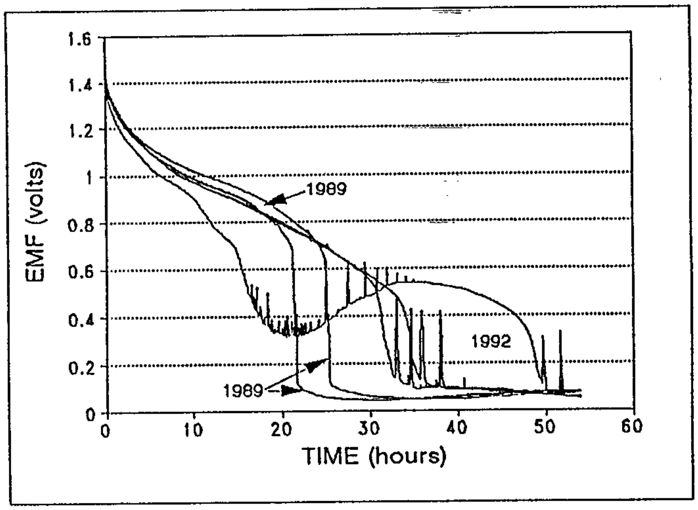

Figure 5. C Cells: Discharge Curves @ 0°C, 5 ohm Load (Discharging continued beyond 0.8 volts).

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