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LITHIUM AA-SIZE CELLS FOR NAVY MINE APPLICATIONS: II - EVALUATION OF COMMERCIAL CELLS

BY W. P. KILROY, J. A. BANNER, G. F. HOFF, K. A. JOHNSTON, AND W. A. FREEMAN

WEAPONS RESEARCH AND TECHNOLOGY DEPARTMENT

24 FEBRUARY 1994

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NAVAL SURFACE WARFARE CENTER

DAHLGREN DIVISION • WHITE OAK DETACHMENT

Silver Spring, Maryland 20903-5640

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FOREWORD

The Navy is interested in developing a standard family of cells to be used in power supplies for Naval mine warfare applications. The AA-size cell is one of the component cells under consideration.

One goal of this program is to evaluate the performance of several commercial AA-size cells under conditions applicable to mine requirements. This report compares the discharge behavior of four $Li/SOCl_2$ cells and one Li/MnO_2 cell. The cells were tested according to the plan described in NSWCDD/TR-92/210.

Funding for this effort was provided by the Naval Sea Systems Command, PMO 407, under tasking N0002492WR10247, funding element 64601N. We wish to thank Mr. G. Leineweber and Mr. A. Suggs for their continued interest and support in developing lithium battery technology. We also wish to acknowledge Mr. F. Visk for assistance in planning the test program.

Approved by:

Carl E. Mueller

CARL E. MUELLER, Head
Weapons Materials Division

ABSTRACT

The discharge performance of five commercial AA-size lithium cells has been evaluated to determine the feasibility of incorporating them into various battery packages for future Naval mine applications.

Fresh cells and cells stored for varying durations at high temperature were discharged at (1) ambient room temperature at a low rate (3 mA) and (2) at a low temperature (-2°C) and 3 mA, 20 mA, and 50 mA rates including some with pulse applications.

The $Li/SOCl_2$ cells generally met all of the stringent performance requirements for mine operations. Specific test results often varied from manufacturer to manufacturer. The Li/MnO_2 technology failed to provide sufficient capacity when discharged at -2°C at 20 mA after high temperature storage and was also unable to provide high current pulses at -2°C.

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CHAPTER 1

INTRODUCTION

Currently there are four dozen different batteries with more than a dozen different chemistries available for applications in Navy mines. To reduce the expense of procurement and the logistics associated with this inventory, the Navy is developing a standard family of lithium primary cells for use in developing batteries for mine warfare and mine countermeasure systems. The lithium/thionyl chloride ($Li/SOCl_2$) electrochemical system was selected in the early eighties from the available battery technologies. This chemistry has been developed and qualified for the CAPTOR and QUICKSTRIKE mine battery programs. Criteria that were important in the selection process included the following: high energy density, long shelf life, and low temperature operation.

The standard family of cells includes the #6, C, and A sizes. The fourth member will be developed as a AA-size cell for eventual assembly into batteries for Navy mines. The development will be carried out in the following tasks: (1) establish a test program to evaluate the ability of AA-size cells to meet the performance requirements of several mine system batteries; (2) purchase commercially available, low cost, AA-size cells for comparison; (3) discharge and compare the behavior of the cells as a function of storage, resistive load, and temperature; (4) develop and evaluate the performance of the AA-size cell configured in various mine battery systems; (5) conduct safety and shelf life/storage tests on the batteries; (6) identify logistics issues such as acquisition, handling, and storage.

Figure 1 is the Test Plan for Evaluation of AA-Size Lithium Cells for Navy Mine Batteries from NSWCDD/TR-92/210. This report summarizes data from performance testing of five commercial AA-size cells (task 3). These data will serve as a baseline for the performance expected from a low magnetic signature AA-size cell technology planned for future development.

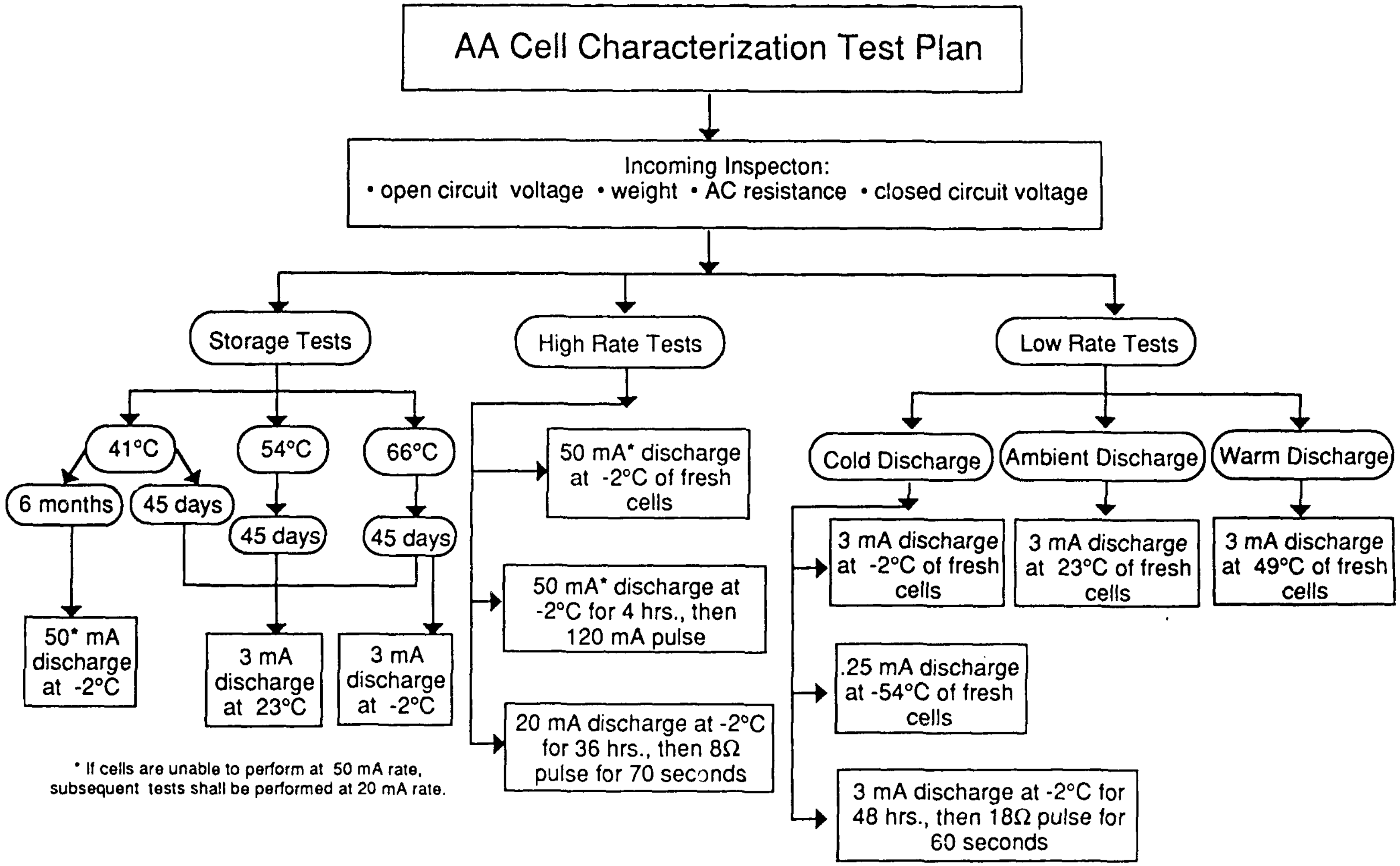

FIGURE 1. TEST PLAN FOR EVALUATION OF AA-SIZE LITHIUM CELLS FOR NAVY MINE BATTERIES

CHAPTER 2

EXPERIMENTAL EVALUATION

Five AA-size cells were evaluated: a Li/MnO_2 cell, series CR AA, from Varta and four $Li/SOCl_2$ cells. The $Li/SOCl_2$ cells include the following: Hitachi Maxell series ER6C purchased from Electrochem Industries (E.I.) as series QTC85-3B940; SAFT France series LS6BA; Power Conversion Inc. (PCI) series T06/41; and an Eagle-Picher "Keeper" cell, series LTC-30P. The Keeper cell is a prismatic design. The other cells are a bobbin design. The Eagle-Picher and PCI cells contain more than 0.5g of lithium and thus require a DOT exemption for shipping.

The cells were weighed upon receipt, serial numbers were recorded, and open circuit voltages (OCV) were measured. The cells were then placed in a refrigerator at 10°C. Fresh cells were stored in this refrigerator prior to evaluation. Cells requiring high temperature storage were transferred to Tenny Jr. environmental chambers set at the prescribed storage temperatures.

Prior to discharge, the OCV and AC resistance of the cells were measured. Cells were mounted horizontally in AA-size cell holders on a board and allowed to equilibrate to the desired discharge temperature in a Tenny Jr. chamber. Each cell was discharged individually at constant resistance. Data were collected on a Fluke Data Logging System.

The planned storage and discharge conditions of the AA cell test program are shown in Table 1. The actual discharge current varied slightly from cell to cell, depending on the discharge conditions and the resistive load. The Varta Li/MnO_2 cells, which exhibited a lower OCV than the $Li/SOCl_2$ cells, were discharged at a lower resistance in order to achieve the same discharge current. In the 3 mA cell tests, the Varta cells were discharged with a resistance of 1000 ohms; all the $SOCl_2$ cells were discharged with a 1200-ohm load. The 50 mA discharge testing was performed using 50 ohms for the Varta cells and 65 ohms for the others. The 20 mA test employed a 125-ohm resistor for the Varta cells and a 175-ohm load for the others. The low-rate discharge (Test P) was carried out using 12.735 Kohm for the Varta cells and 15.08 Kohm for the other cells.

TABLE 1. SUMMARY OF STORAGE AND DISCHARGE CONDITIONS FOR AA-SIZE CELL EVALUATION

TEST	STORAGE		DISCHARGE*	
	TIME (days)	TEMP. (°C)	CURRENT (mA)	TEMP. (°C)
A	45	41	3	23
B^	45	54	3	23
C^	45	66	3	23
D	fresh	23	3	23
E	fresh	23	3	49
F	fresh	23	3	-2
G	fresh	23	20	-2
H	fresh	23	50/20	-2
I^	45	41	50/20	-2
J^	100	41	50/20	-2
K	135	41	50/20	-2
L	180	41	50/20	-2
M	45	66	3	-2
N	fresh	23	3 (48 hr)	-2
O	fresh	23	20 (48 hr)	-2
P	fresh	23	50 (4 hr)	-2
Q	fresh	23	0.25	-54

* Cell tests H-L were carried out at either 50 or 20 mA. SAFT and PCI cells were discharged at the 50-mA rate. The E.I., Eagle-Picher, and Varta cells could not sustain the 50 mA rate and were discharged at the 20-mA rate.

^ After high temperature storage, the cells were stored an additional three to six weeks at ambient room temperature.

CHAPTER 3

RESULTS AND DISCUSSION

CHARACTERISTICS OF AA-SIZE CELLS DISCHARGED AT 3 MA AT AMBIENT ROOM TEMPERATURE

Effects of Storage on AA-Size Cells.

The effect of high temperature storage on the performance of AA-size cells was examined. Fresh cells and cells stored for 45 days at temperatures of 41°C, 54°C, and 66°C were discharged at constant resistive loads equivalent to ~3 mA at 23°C. Each test was performed on five cells from each manufacturer. A summary of the average capacity to a 2.0V cutoff is shown in Figure 2. The data show that fresh cells experience only a minimal loss in capacity after 45 days storage at high temperature. Except for the PCI cells, there was no appreciable additional loss in cell capacity by increasing the storage temperature from 41°C to 66°C.

Consistency of Performance.

In all cases, the PCI cells were the least consistent performers after high temperature storage, with one cell delivering less than one-half its rated capacity after 45 days storage at 54°C. Figure 3 shows the ambient temperature discharge behavior of the best performing cell from each manufacturer after the 45-day storage at 66°C. All of the Varta, SAFT, and Eagle-Picher cells had almost identical discharge characteristics to those illustrated in Figure 3. Both the PCI and E.I. cells exhibited large variability in capacity, especially after storage. The SAFT and Varta cells, either fresh or stored, displayed the most consistent behavior at 3 mA.

Fresh Cell Capacity.

The fresh cell capacity delivered to a 2.0V cutoff was compared with the capacity reported by the manufacturers. The SAFT and Eagle-Picher cells delivered about 11 and 18 percent more capacity, respectively, than advertized. The Varta and E.I. cells delivered the manufacturer's quoted nominal capacity, whereas the PCI cells fell 16 percent short of the 2.2 Ah indicated by the manufacturer.

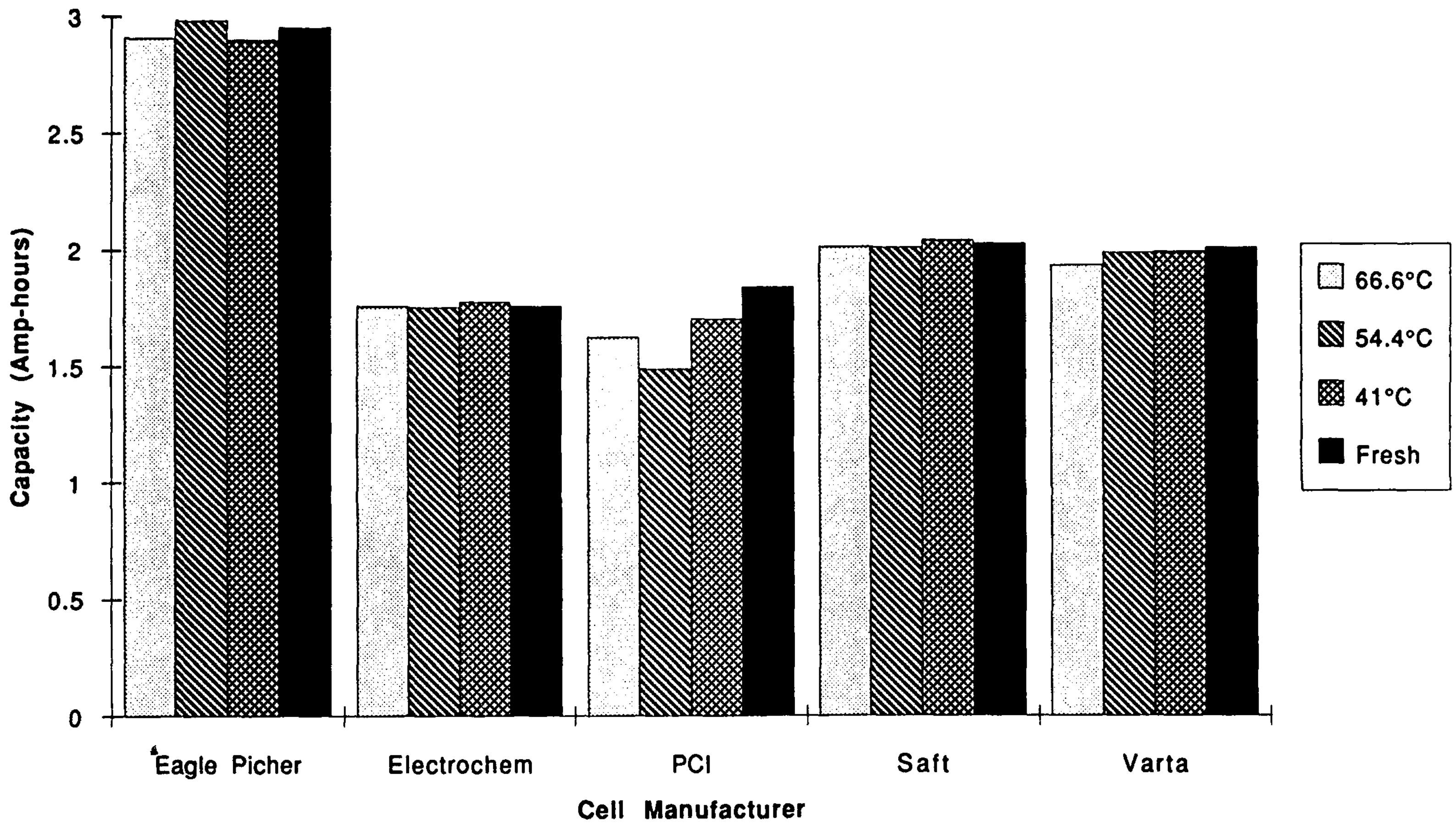

FIGURE 2. EFFECT OF HIGH TEMPERATURE 45 DAY STORAGE ON THE CAPACITY OF AA CELLS DISCHARGED AT 3 mA TO 2.0V

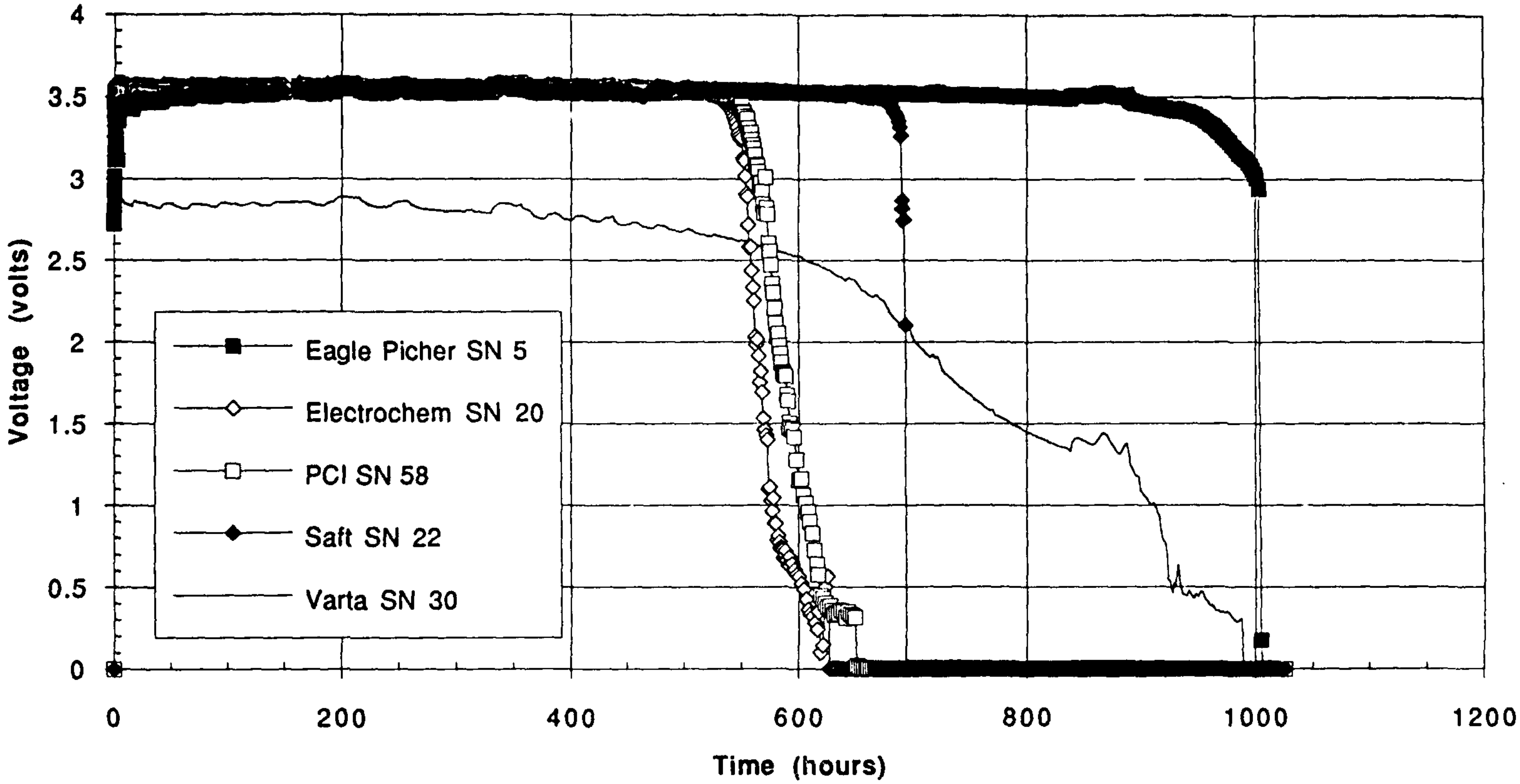

FIGURE 3. PERFORMANCE BEHAVIOR OF AA CELLS DISCHARGED AT 3 mA AT 23°C AFTER 45 DAY STORAGE AT 66°C

Voltage Delay.

The ambient temperature start-up performance of all the fresh cells was excellent. None of the Li/$SOCl_2$ cells dropped below 3.3V at the 3 mA rate. The Li/MnO_2 Varta cells showed no delay but characteristically discharged below 3.0V.

After high temperature storage, the start-up performance of the Eagle-Picher cells was generally poor compared with the other manufacturers' cells. At the lower storage temperatures, the cell voltage usually dropped to 1.5V prior to recovery. After 66°C storage, the cell voltage dropped to 1.3V and required from 15 min. to >3 hours to reach 3.0V when discharged at 3 mA at 23°C.

Voltage Regulation.

The voltage regulation of the cells displayed in Figure 3 was characteristic of the behavior of both the fresh and stored cells. The mid-discharge voltage of all the Varta Li/MnO_2 cells was 2.8V. The mid-discharge voltage of the $SOCl_2$ cells was 3.5V.

During discharge of fresh cells, the PCI cells exhibited a large knee (25 percent of the capacity) at the start of polarization. This behavior was not observed in the cells that were discharged after storage at high temperatures.

DISCHARGE PERFORMANCE OF FRESH CELLS AT 49°C

A comparison of fresh cells discharged at 23°C and 49°C reveals notable differences in performance. The discharge behavior characteristic of fresh cells discharged at 3 mA at 49°C is shown in Figure 4. Figure 5 compares the average capacity of cells discharged at 49°C with the baseline performance at 23°C. The mid-discharge voltage increases about 0.1V when the cells are discharged at the higher temperature. As Figure 6 illustrates, the Li/$SOCl_2$ cells lose some capacity at the higher temperature, presumably due to faster kinetics (non-passivated corrosion) occurring at the higher temperature during the prolonged slow discharge. However, a comparable increase in temperature of 25°C, i.e., when cells were discharged at 23°C relative to discharge at- 2°C, reveals that a similar loss of capacity was not observed. The SAFT cells demonstrated the best capacity retention. In contrast, the Li/MnO_2 cell capacity improved at the higher discharge temperature because the kinetics of the solid cathode system is favored at higher temperatures.

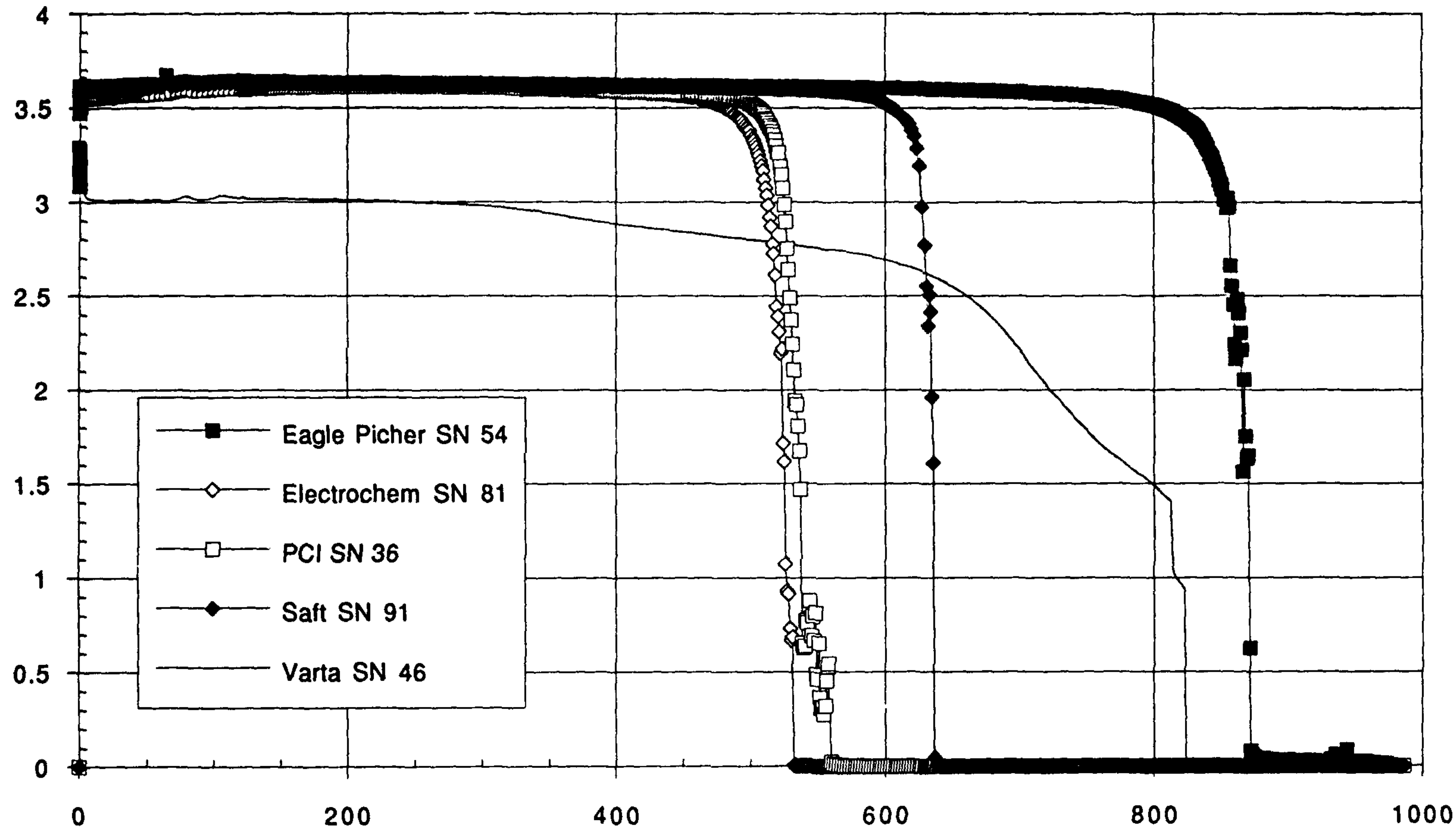

FIGURE 4. PERFORMANCE OF REPRESENTATIVE FRESH AA CELLS DISCHARGED AT 3 mA AT 49°C

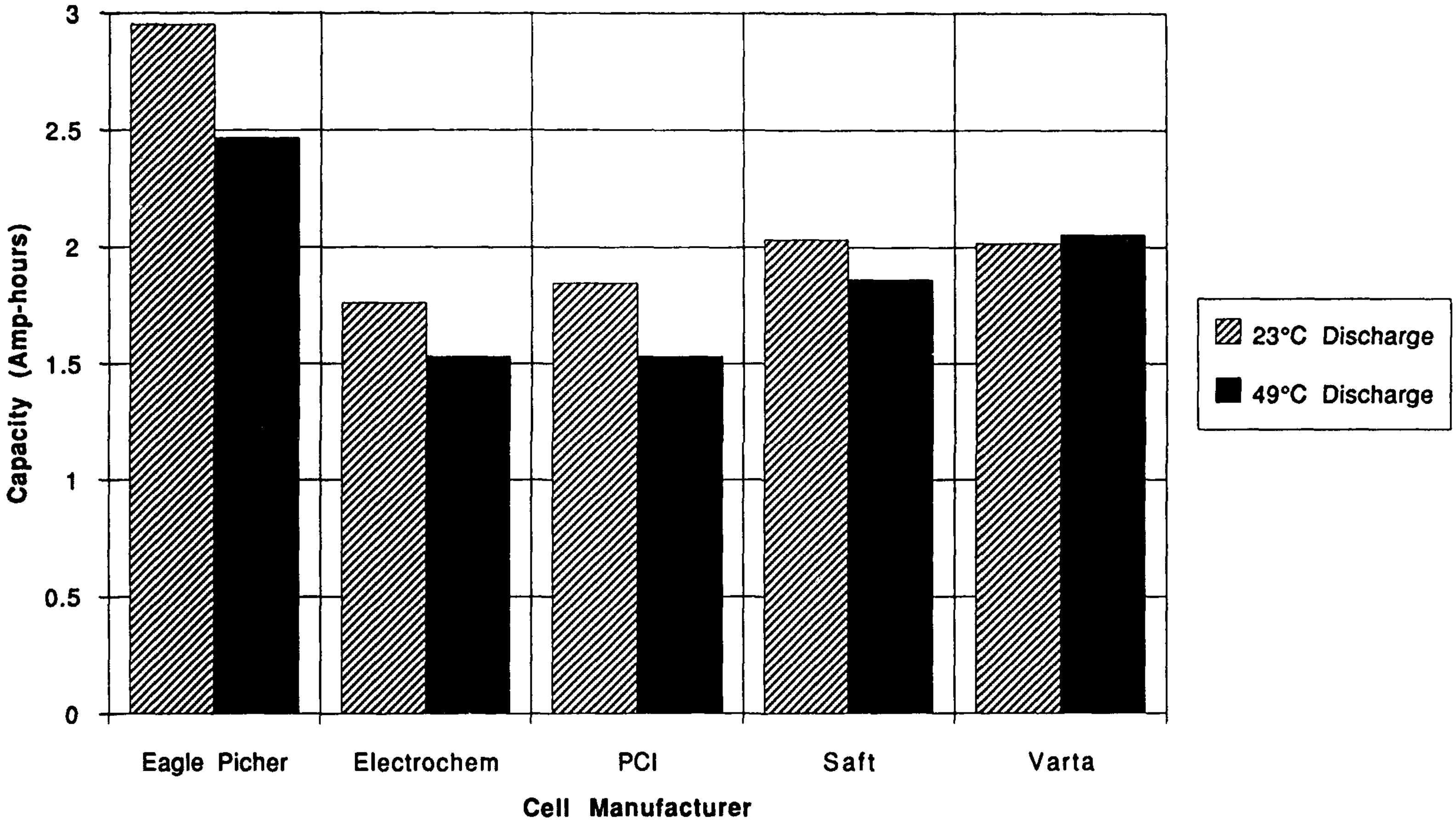

FIGURE 5. EFFECT OF HIGH TEMPERATURE 49°C DISCHARGE ON THE CAPACITY OF AA CELLS DISCHARGED AT 3 mA TO 2.0V

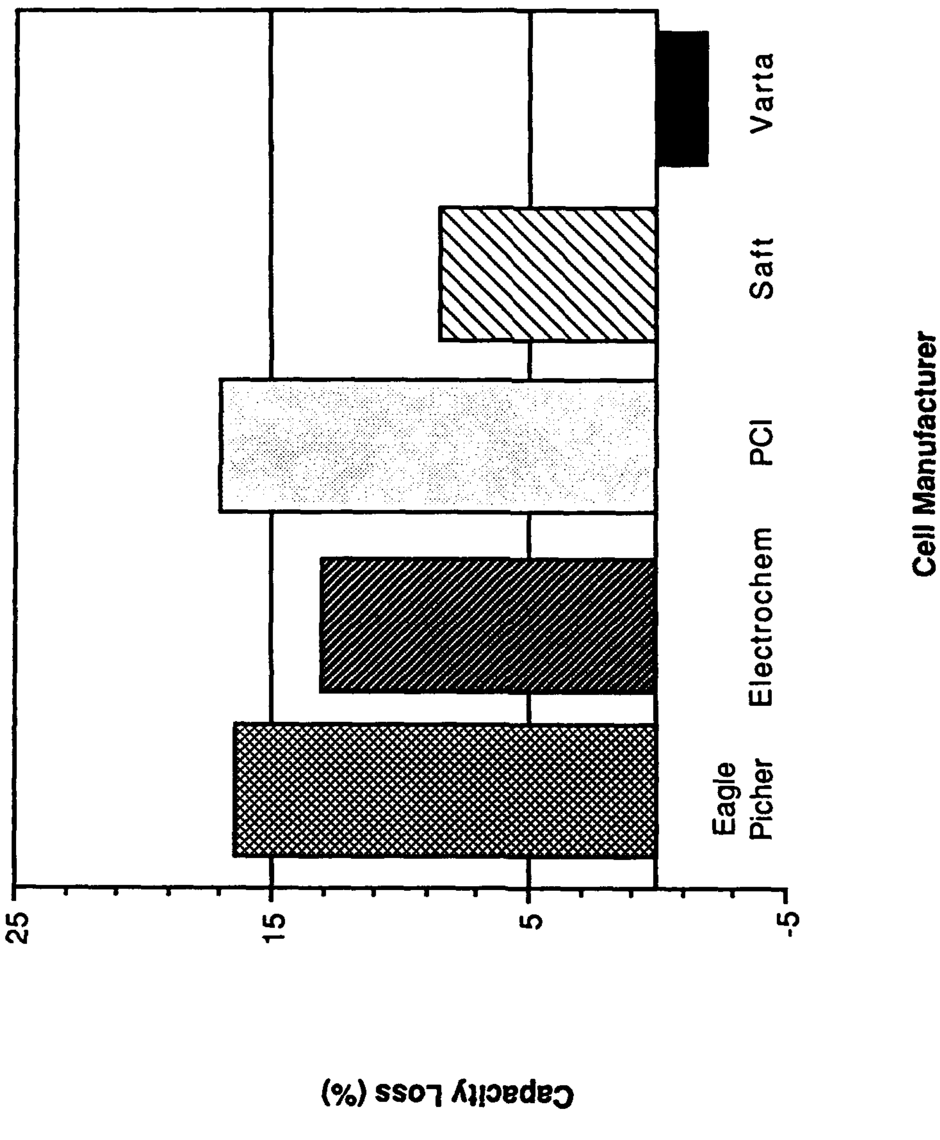

FIGURE 6. CAPACITY LOSS OF AA CELLS DISCHARGED AT 49°C AT 3 mA TO 2.0V RELATIVE TO CAPACITY AT 23°C

DISCHARGE PERFORMANCE OF AA-SIZE CELLS AT LOW TEMPERATURE

Fresh Cells at Very Low Rate.

For some applications, during the deployment phase of mine operation, the batteries are required to provide 0.25 mA at -54°C for approximately one day. The $Li/SOCl_2$ cells easily met these requirements. The cells were still discharging at 3.3V when the tests were terminated after 120 hours. The Li/MnO_2 cells were adequate - providing an average 30 hours to 2.0V with a mid-discharge voltage of 2.6V.

Fresh Cells At Low Rates (3 mA).

Figure 7 shows the discharge behavior of the best performing cells from each manufacturer at 3 mA at -2°C.

The cell performance at -2°C was similar to that observed at 23°C with the following exceptions: (1) at -2°C, the Varta and Eagle-Picher cells exhibited lower capacity and a 0.25V lower mid-discharge voltage; (2) the PCI and E.I. cells displayed a greater spread in delivered capacity at -2°C compared with their behavior at 23°C; (3) the Eagle-Picher cells discharged at -2°C revealed a peculiar voltage delay, manifested by an initial depression to zero voltage upon activation, followed by a rapid rise to 3.3V with subsequent loss of voltage over a 20 hour period to 3.05V where it remained for 35 hours before rising to the mid-discharge voltage of 3.3V. It is possible that this behavior is characteristic of the prismatic cell design, since none of the bobbin cells of the same chemistry exhibited this type of performance.

The average capacities of the AA cells discharged at 3 mA are compared at -2°C and ambient temperature (~23°C) in Figure 8.

Fresh Cells Discharged With Intermittent Pulse.

All the cells were placed in controlled storage at 10°C for one year. The cells were equilibrated at -2°C and discharged at a constant load equivalent to either ~20 mA or ~3 mA.

20 mA Discharge. After 36 hours, the discharge was interrupted by application of a pulse for 20 seconds with an 8-ohm load. The performance under this test regime could be characterized by capacity to 2.0V, voltage regulation, and pulse capability. Perhaps the best indicator of overall reliability was the voltage profile. Only two of the Eagle-Picher cells discharged above 2.0V. Four of the E.I. cells discharged above 3.2V; the fifth took 60 hours to reach 3.0V. All of the PCI cells discharged above 3.2V. The SAFT cells discharged above 3.1V, however, all had positive voltage spikes during the polarization at the end of cell life. The Li/MnO_2 cells discharged consistently; all polarized severely from the start. The time of discharge was ~5 hours above 2.0V.

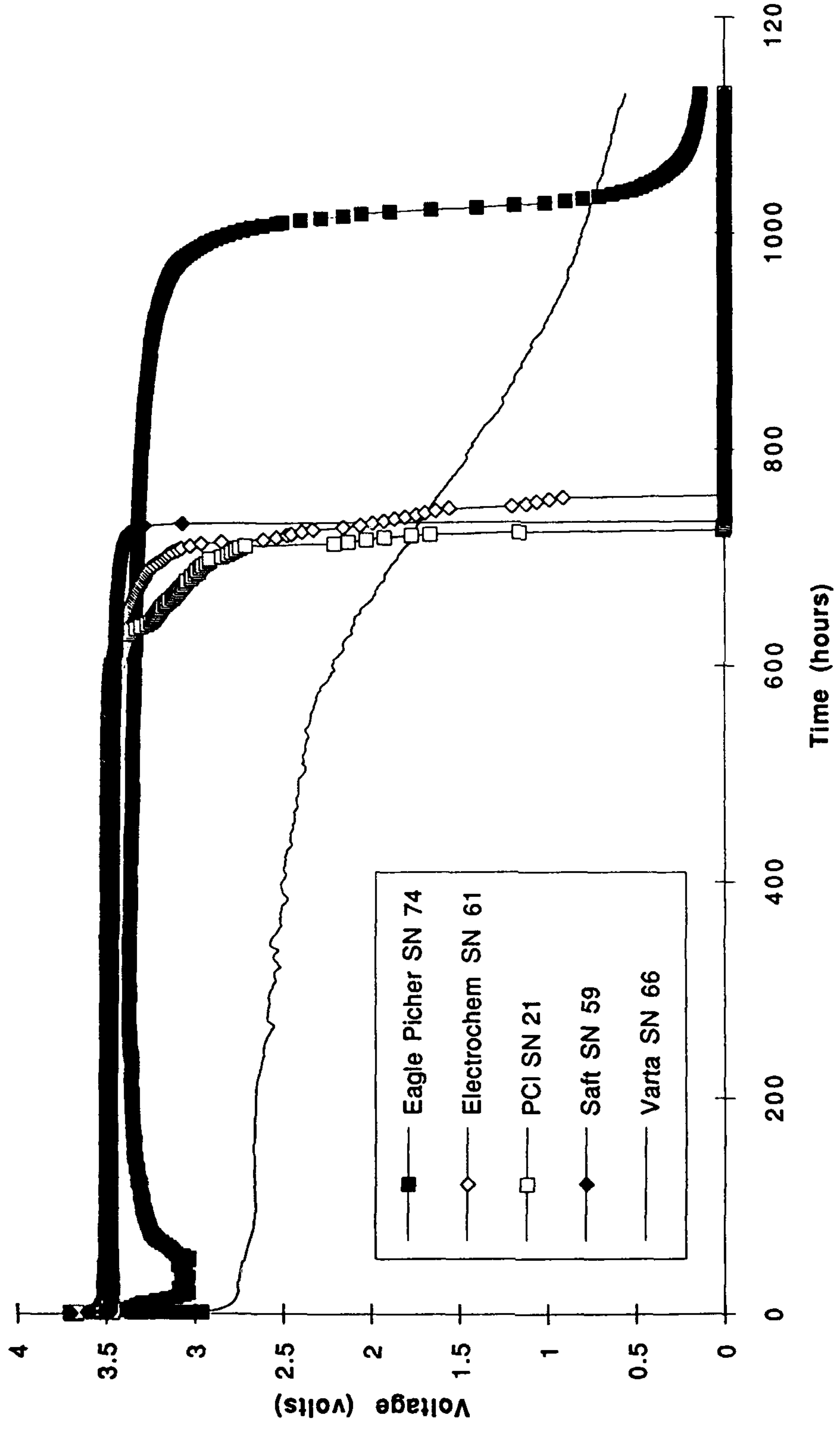

FIGURE 7. PERFORMANCE BEHAVIOR OF FRESH AA CELLS DISCHARGED AT 3 mA AT -2°C

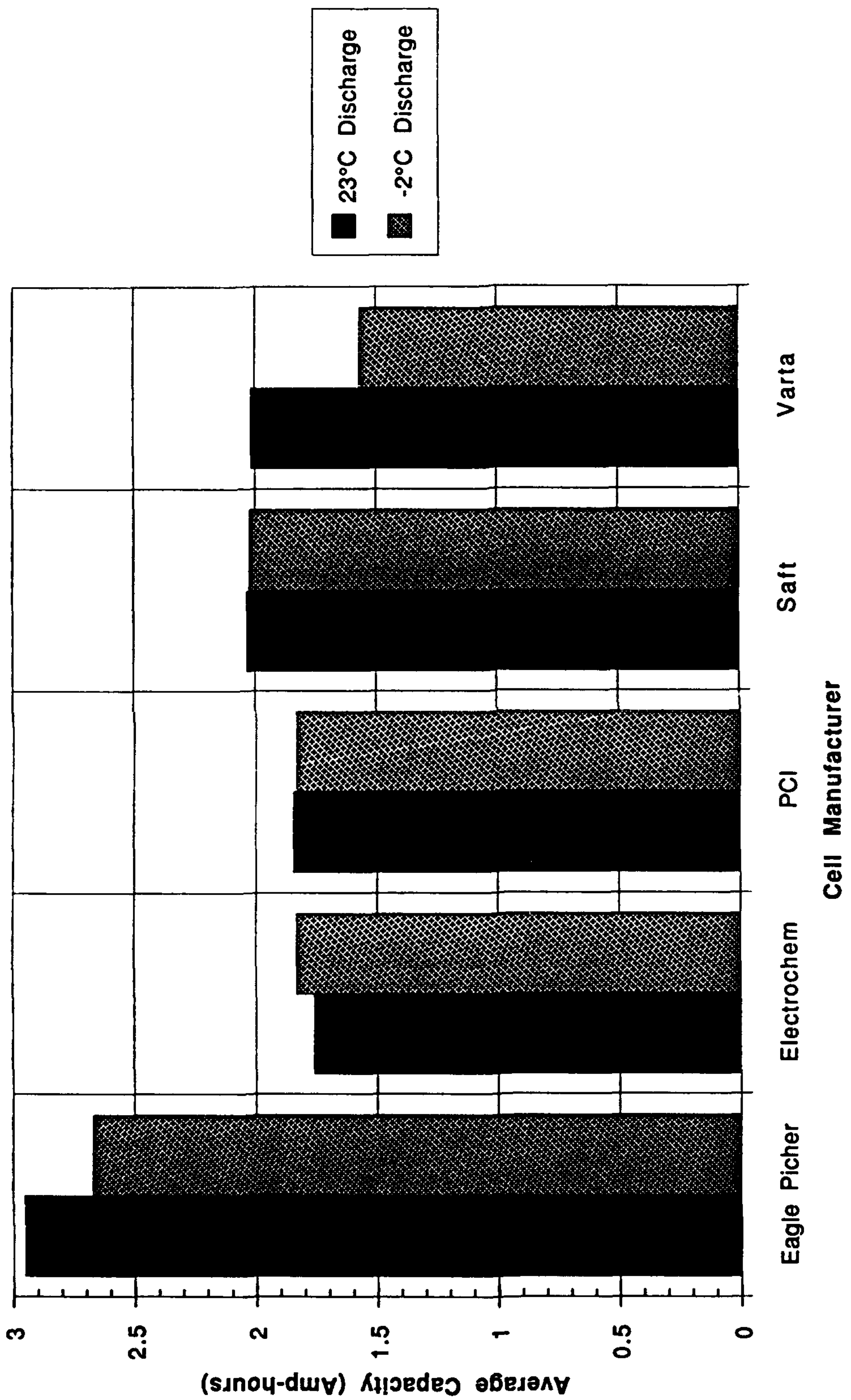

FIGURE 8. COMPARISON OF THE CAPACITY OF AA CELLS DISCHARGED AT 23°C AND -2°C AT 3 mA

The average capacity recorded to 2.0V was as follows: PCI (1.61 Ah); SAFT (1.39 Ah); E.I. (1.38 Ah); Eagle-Picher (0.51 Ah); and Varta (0.11 Ah). The low capacity of the Eagle-Picher cells was due to the failure of three of the cells to discharge above 2.0V. The AC resistances measured prior to the cell discharges provide some insight into this behavior. The three cells with the low voltage profiles had high internal impedances, whereas the cells with high voltage profiles displayed low internal impedances. This voltage behavior was not previously observed when Eagle-Picher cells were discharged at 20 mA at -2°C, even after high temperature storage as discussed below.

Only the cells from PCI, SAFT, and E.I. were able to provide consistent current pulses of about 65 mA for the required time.

<u>3 mA Discharge</u>. Cells maintained under controlled temperature at 10°C for one year were discharged at ~3 mA at -2°C for 48 hours and then subjected to a 5-second pulse with a 27-ohm load. The PCI, SAFT, E.I., Varta, and Eagle-Picher cells provided pulse currents of approximately 110, 110, 100, 75, and 45 mA, respectively. Based on the poor performance of the Eagle-Picher cells in these two pulse tests, it is believed that the cells' age, prismatic design, or a combination of these two factors severely limited their current carrying capability.

<u>Stored Cells Discharged At High Rates</u>

One of the most stringent performance requirements for mine batteries is to provide relatively high currents from stored cells at low discharge temperatures - the "old/cold" syndrome. The test plan required cells to provide 0.2 Ah capacity at a 50 mA rate after storage at 41°C.

Groups of three cells were removed at periodic intervals for evaluation. After exposure to 45 day storage at 41°C, the E.I., Eagle-Picher, and Varta cells could not be discharged above 2.0V at -2°C at 50 mA. Only the SAFT and PCI cells were capable of this performance. Thus, all the cells were not compared at 50 mA at -2°C. In subsequent tests, the SAFT and PCI cells were discharged at 50 mA and the other cells were discharged at 20 mA.

<u>Discharge at 50 mA</u> Figure 9 compares the individual cell capacities to 2.0V for the SAFT and PCI cells, respectively.

At the 50 mA rate, the SAFT cells performed very consistently at -2°C. The average cell capacity (0.94 Ah) after 45 or 100 days storage was essentially unchanged compared with the fresh cell capacity (0.93 Ah). The "fresh" cells were maintained at 10°C prior to equilibration at -2°C. The average capacity of cells stored at 41°C for periods of 135 and 180 days declined approximately 10 percent relative to the fresh cells. This magnitude of loss would be expected as a result of long term, high temperature storage based on the cell design and chemistry. The performance is well above the 0.2 Ah requirement cited above.

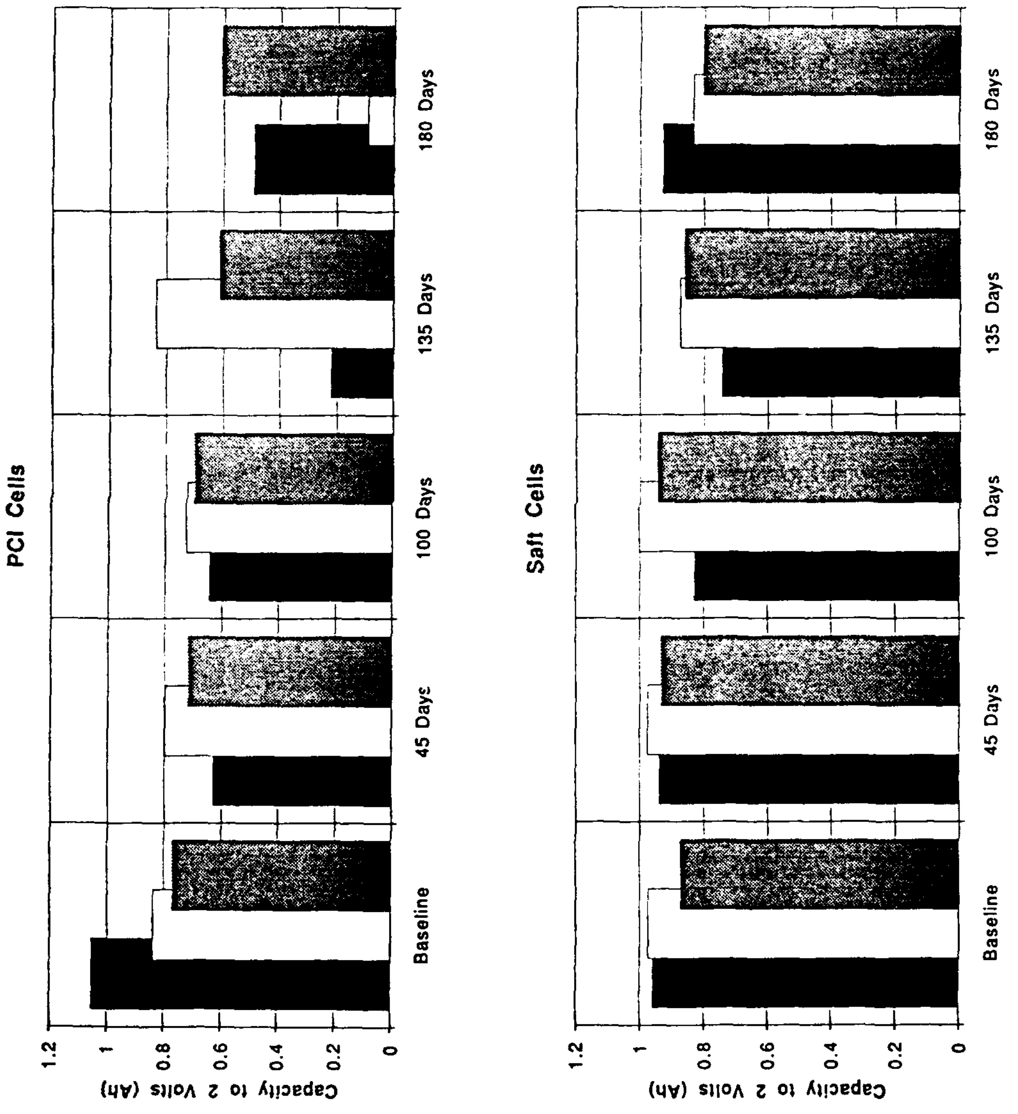

FIGURE 9. EFFECT OF 41°C STORAGE ON THE CAPACITY OF AA CELLS DISCHARGED AT 50 mA AT -2°C TO 2.0 VOLTS

The average capacity of the PCI cells at 50 mA degraded from 0.89 Ah for the fresh cells to 0.72, 0.69, 0.56, and 0.40 Ah with increasing time of storage. After extended periods of storage at 41°C, the reliability of the cells to deliver the required 0.2 Ah capacity was poor -- one-third of the tested PCI cells either failed or were marginal.

Discharge at 20 mA. The low temperature performance of the E.I., Eagle-Picher, and Varta cells at the 20 mA rate are compared as a function of storage time in Figure 10.

E.I. cells stored for 135 or 180 days at 41°C declined in consistent discharge behavior at -2°C and exhibited a significant loss (>50 percent) in average capacity relative to fresh cells.

The average capacity of the Eagle-Picher "Keeper" cells declined approximately 9 percent after 135 or 180 day storage relative to the fresh cell capacity.

The Li/MnO_2 cells from Varta failed to deliver the required 0.2-Ah capacity when discharged at 20 mA at -2°C, regardless of storage conditions. However, after storage at 41°C, a small improvement in cell capacity was observed relative to fresh cells.

50 mA Discharge Followed by a High Current Pulse. Some mine batteries are required to provide a pulse discharge, i.e., deliver a sufficiently high current for a brief period, in order to blow a fuse. In this test regime, the pulse current was to be applied approximately four hours after discharging the cell at 50 mA.

As noted above, the Eagle-Picher, E.I., and Varta cells discharged below 2V at the 50 mA rate - all three failed to provide a high current pulse. The Eagle-Picher cells failed to exceed 25 mA; the Varta cells peaked for a few seconds at 35 mA with the voltage falling to 0.5V; the E.I. cells reached 42 mA for a few seconds as the voltage fell from 1.7V to 0.8V.

Only the SAFT and PCI cells were capable of sustained, high pulse currents. The SAFT cells delivered more than 100 mA for four hours at about 3.0V. The PCI cells delivered 100 mA for two hours at 2.8V.

Stored Cells Discharged at Low Rate

Five cells from each manufacturer were placed in controlled storage at 10°C for six months followed by 45 days storage at 66°C. The cells were discharged at ~3 mA at -2°C. The discharge behavior of the best performing cells from each manufacturer are compared in Figure 11. As shown in Figure 11, voltage spiking near the end of cell life was characteristic of the PCI cells. The SAFT cells were extremely consistent; all five cells displayed nearly identical discharge behavior.

The capacity of cells discharged at 3 mA are compared as a function of storage temperature and discharge temperature in Table 2.

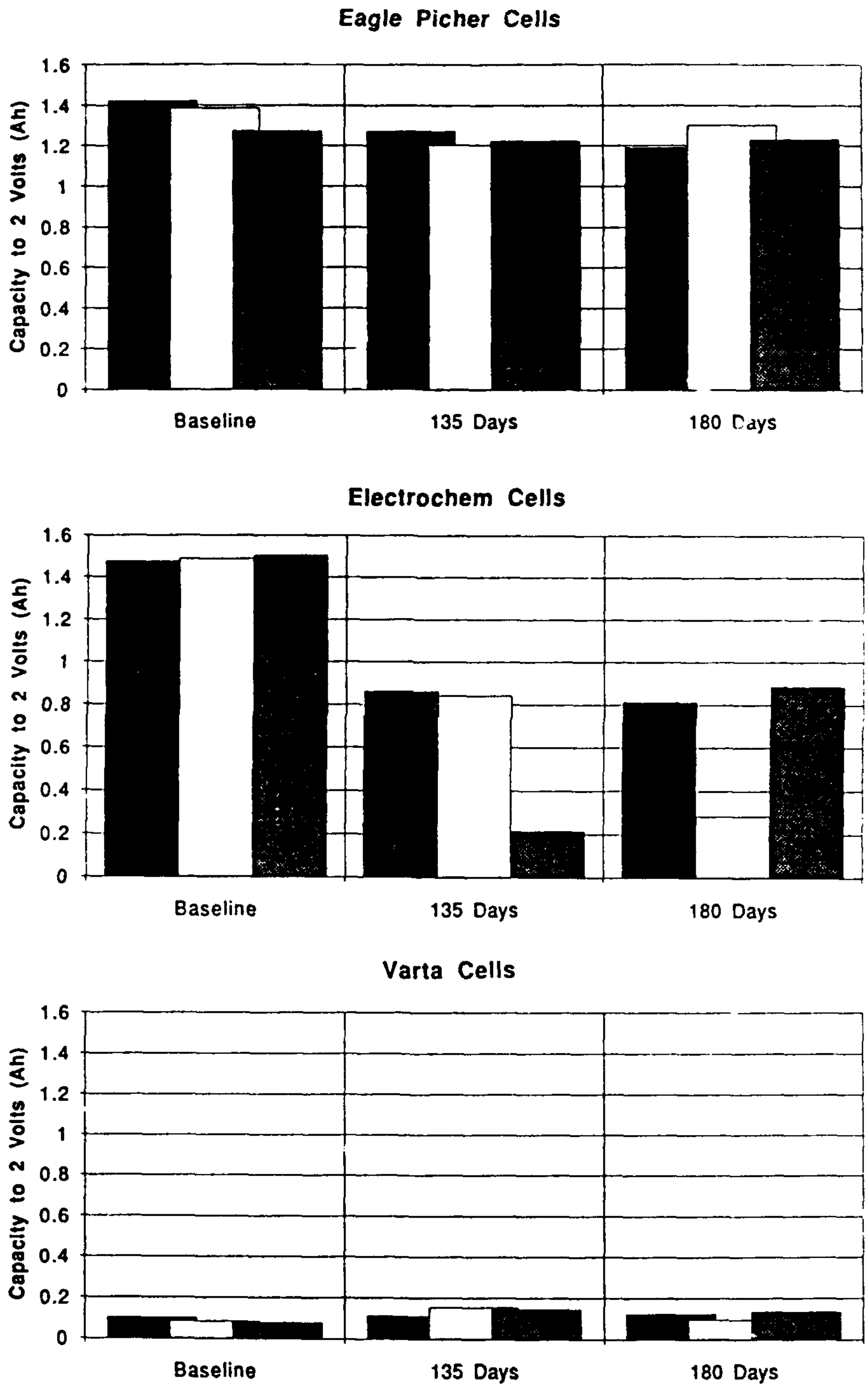

FIGURE 10. EFFECT OF 41°C STORAGE ON THE CAPACITY OF AA CELLS DISCHARGED AT 20 mA AT -2°C TO 2.0 VOLTS

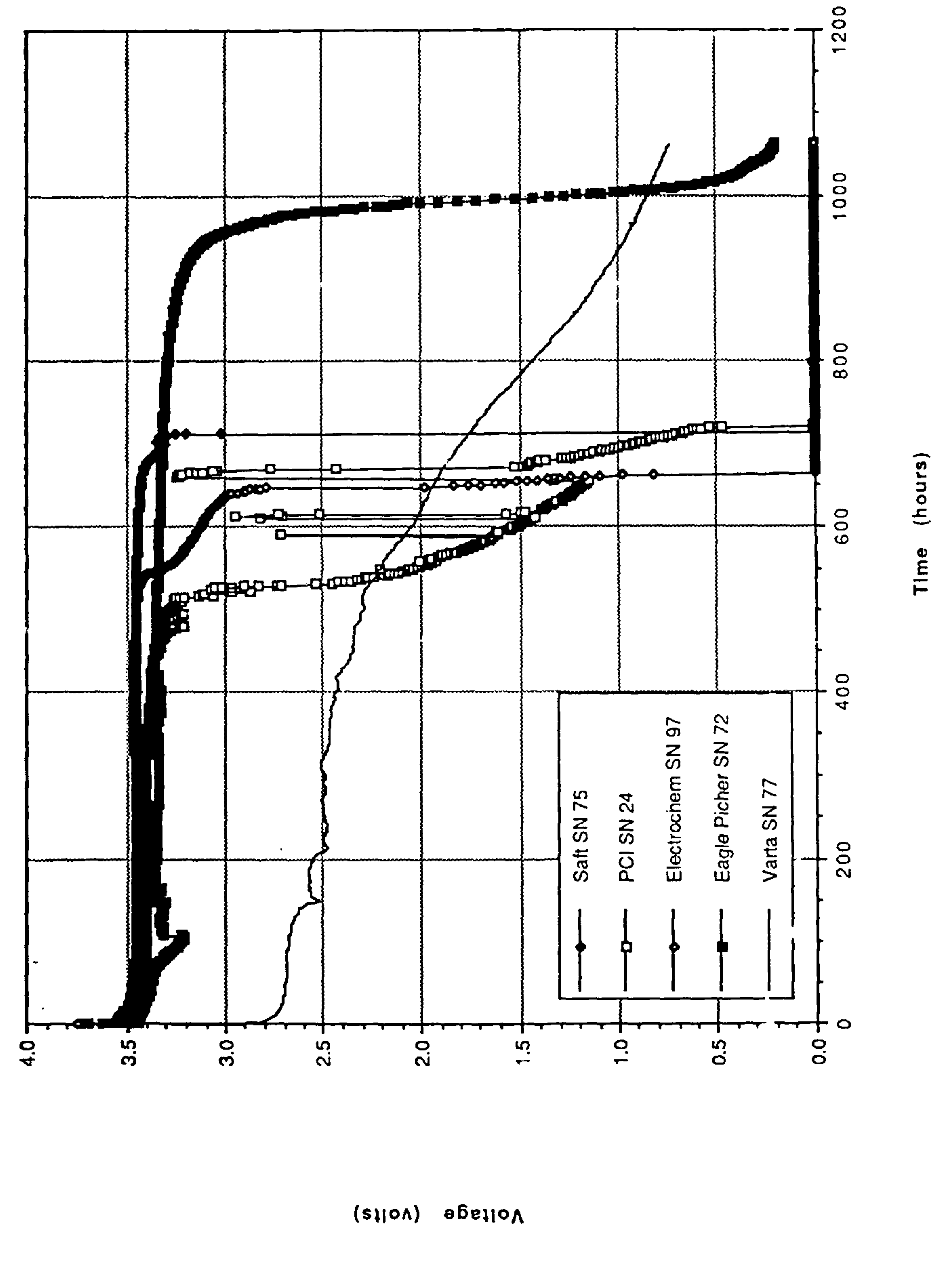

FIGURE 11. COMPARISON OF THE BEST PERFORMING CELLS DISCHARGED AT 3 mA AT -2°C AFTER 45 DAYS STORAGE AT 66°C

TABLE 2. CAPACITY OF CELLS DISCHARGED AT 3 mA AS A FUNCTION OF STORAGE AND DISCHARGE TEMPERATURE

Manufacturer	-2°C Discharge	-2°C Discharge	23°C Discharge	23°C Discharge
	Fresh Cells	45 Days/66°C Storage	Fresh Cells	45 Days/66°C Storage
Eagle-Picher	2.67 Ah	2.65 Ah	2.96 Ah	2.91 Ah
Electrochem Industries	1.84 Ah	1.82 Ah	1.76 Ah	1.76 Ah
PCI	1.83 Ah	1.62 Ah	1.85 Ah	1.63 Ah
SAFT	2.03 Ah	2.02 Ah	2.04 Ah	2.02 Ah
VARTA	1.57 Ah	1.44 Ah	2.02 Ah	1.94 Ah

High temperature storage for 45 days and low temperature discharge had little effect on the capacity of the SAFT and E.I. cells.

Eagle-Picher and PCI cells displayed contrasting capacity behavior. The capacity of Eagle-Picher cells discharged at either 23°C or -2°C was not affected by high temperature storage, whereas the PCI cells lost about 10 percent of their capacity under similar conditions. Conversely, the capacity of PCI cells was not affected by discharging at -2°C relative to 23°C, whereas the Eagle-Picher cells had 10 percent lower capacity at -2°C than at 23°C, regardless of storage conditions.

Irrespective of the discharge temperature, the capacity of the Varta Li/MnO_2 cells was about 7 percent lower after the high temperature storage for 45 days. The capacity of these cells was ~23 percent lower when discharged at -2°C relative to discharge at 23°C regardless of storage conditions.

CHAPTER 4

SUMMARY

The discharge performance of $Li/SOCl_2$ AA-size cells from four manufacturers was evaluated under a test plan designed to meet existing and future Naval mine applications. A Li/MnO_2 cell from Varta was also evaluated to compare the two chemistries.

At low rate, ambient temperature discharge, the fresh PCI cells failed to deliver the 2.2 Ah advertized capacity. Both the PCI and E.I. cells failed to deliver consistent capacity after storage. The Eagle-Picher cells displayed voltage delay after storage.

The $Li/SOCl_2$ cell technology has an inherent advantage over that of the Li/MnO_2 system, i.e., better voltage regulation, with a 0.7V higher mid-discharge voltage. However, under high temperature discharge, the Varta Li/MnO_2 cell showed better capacity retention than the $Li/SOCl_2$ cells. SAFT had the best capacity retention of the $Li/SOCl_2$ cells.

The Li/MnO_2 cells failed to deliver sufficient capacity at low temperature (-2°C) and high rates (20 mA). The Varta, E.I., and Eagle-Picher cells would not discharge at the 50 mA rate. SAFT and PCI cells performed at this rate and also provided pulse (100 mA) capability. However, the PCI cells appeared to lose capacity after elevated temperature storage as a result of inconsistent performance. Upon activation at 3 mA and -2°C, the Eagle-Picher cells were the only fresh cells to display a voltage delay to zero volt, albeit briefly.

After considering all the evaluation testing, the SAFT France series LS6BA cell technology was judged to have the best overall performance to meet the mine requirements. Although consistency of performance was an issue identified during testing, the Power Conversion Inc. (PCI) series T06/41 was identified as a second choice.

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The discharge performance of five commercial AA-size lithium cells has been evaluated to determine the feasibility of incorporating them into various battery packages for future Naval mine applications.

Fresh cells and cells stored for varying durations at high temperature were discharged at (1) ambient room temperature at low rates (3 mA) and, (2) low temperatures (-2°C) at low and high rates (3, 20, and 50 mA) including some with pulse applications.

The $Li/SOCl_2$ cells generally met all of the stringent performance requirements for mine operations. Specific test results often varied from manufacturer to manufacturer. The $Li/MnO2$ technology failed to provide sufficient capacity when discharged at -2°C at 20mA after high temperature storage and was also unable to provide high current pulses at -2°C.

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lithium battery

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