HIGH ENERGY DENSITY BATTERY DEVELOPMENT STATUS REPORT

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NOSC

(Figure 2-1)

Looking at the Navy applications for high energy density batteries, you can see quite a range of applications, rates, and capacities; anywhere from remote sensors with the low rate, low capacity to the vehicular propulsion, which is high rates and high capacities.

(Figure 2-2)

As a net result, we have been looking or have developed a family. The largest one is a low-rate undersea implementation type of battery. Then, you see the 120-kilowatt-hour high rate for undersea propulsion. We have the 1.2-kW high rate battery for economeasures equivalent 600-watt-hour medium rate battery for a manpack for the Marine Corps.

In the middle of the illustration there are various cell technologies including the prismatic, the D sizes, and other assortment of button assortments and discs.

The film I have is what we did almost a year ago in the development, testing the first developmental cells of a large 17-inch thionyl chloride cells.

May I have the film, please?

(Film)

I defy any of the other cells you have to come through this test equally well. The interesting thing, the cell that went bad in reverse voltage gave this characteristic.

(Figure 2-3)

The important thing, of course, is this point right here. We have done a considerable amount of investigation, and we find that there is a critical point here in the neighborhood of -0.9 volts. Every cell that has ruptured in reverse voltage has gone to this point just prior to rupture.

So, it is important if you don't have an internal means of protecting or preventing that voltage appearing in the reverse direction on any of the lithium cells, you should have a Shockey diode to parallel it and prevent that voltage.

(Figure 2-4)

As a result of this test which was a 500-ampere hour, 17-inch cell, we decided on an improvement effort to obtain full capacity which means from 1/2- to 1-3/8-inch thick cell, from 500 ampere-hours to 1500 ampere-hours ambient temperature.

Obviously, we needed some work done on the vent relief device. We need a higher current feedthrough. And we had to improve the reverse voltage technique and to reduce the case weight.

(Figure 2-5)

A review of the safety problems indicates that three things can occur. Explosion occurs when the lithium melts, and the resolution of this, of course, is to prevent the lithium from melting. Release reactive materials from the cell before the lithium melts or control the lithium when it melts.

Explosion can occur when the cells are deeply discharged, and you have to provide some electrical controls either internally or externally to prevent voltage reversal. Hazardous materials are expelled from the cells during adverse conditions. We can contain, dilute, or minimize the quantity of hazardous materials and increase the tolerance for adverse conditions.

(Figure 2-6)

We said we were going to do some additional tests in the fall of 1978. Well, this is fall of 1979, so 1 year later and $1 million later we now have a new set of cells.

This is a typical and desirable set of curve that we are looking for. This particular curve was on one of the smaller cells, a 2 1/2-inch diameter cell performing at 0°C.

Thus, you will notice here that we started the open circuit voltage, and it drops down to the 3 volts, a fairly high rate. That is a 2-ampere rate on the 5-ampere hour cell. Now down to about 3 volts, it stays here and falls off rapidly. Passes through 0 to about -0.1 at which time it locks up an internal switching device and holds it constant for as long as you want to go.

Interesting, we took temperature at the same time and the normal heating during discharge, as it came to the point where there is no more lithium, the internal resistance went up. And being a constant current drive, the temperature was increased until the lockup took place, and then the normal cooling curve resulted.

(Figure 2-7)

We had four more cells of the large configuration just this month – let's see, about the latter of September. This is a 17-inch cell under the same conditions of 12-ampere rate at 0°C. Again, it gave pretty near the flat configuration we have looking at this curve in here as to why that dropped off.

It fell off rapidly at a predetermined time. It dropped momentarily to the last – the neighborhood to 0.1 to 0.3, then locked up and stayed constant for the rest of its life. This is about 150 to 180 percent of the ampere-hour rating of this cell, and that is a safe discharge reverse voltage condition.

(Figure 2-8)

We are now really looking at the future, and we see a sort of family of applications or a amily of cells. This should meet most of our applications ranging from low rate, medium rate, high ate, and the very high rate which is usually the reserve cell, the small, medium, and large capacity. 'his is sort of a family of cells that we think are immediate to the Navy applications.

DISCUSSION

OTZINGER: Will you describe how you achieve lockup?

WILLIS: This is essentially proprietary information with ALTUS.

OTZINGER: I see.

LEAR: When you did the discharges after storage or whatever, did you notice any of the lag n the voltage coming up through the potential?

WILLIS: Every cell that we discharge we do a depolarization curve to measure that time lement, and the most severe that we have seen has been 12 seconds between the time the load was ıp high and the voltage was up above 3 volts. Normally it is in the order of 1 second.

LEAR: I have one other question. These were 150-, 120-ampere hour cells?

WILLIS: 1500-ampere hour cells.

LEAR: Why did you go so long in reverse direction with the voltage continuing on?

WILLIS: When a cell is in a battery configuration, it can see 100-percent ampere-hour capacity.

Assuming a cell is dead due to long period of storage and internal leakage of some sort, when you put the battery in service, the maximum it will be able to see is 100-percent rated capacity.

We take it into 150, maybe 200 percent just as a safety factor, just to prove that the thing is not really working.

ANGRES: Have you had any accidents lately with cells in reversal? And question number two is, is there any significant physical data of the reproducible Altus technology? I have not seen anything.

WILLIS: As I said, we received four more of the experimental cells in the larger configuration at 1500 ampere-hours. We put all four of them on discharge and reverse voltage. One did rupture, but it was predictable.

(Figure 2-9)

In the early physical measurements of the cell, which is cell No. 94 there, you can see it was lightweight, about half a pound lightweight. And then we put that one on discharge and reverse voltage with this result.

(Figure 2-10)

You will notice that there was number one, a discontinuity during the discharge which, again, flagged that one as a bad cell, I will say. Went down into reverse voltage and got very erratic here.

Not it lasted in excess of 150 percent of its capacity. But in order to obtain data as to what causes reversals – I mean explosions – and how long it would go before it would happen, we let the thing continue. And again, as soon as we hit -0.9 volts, it went.

So, it was predictable. We watched it, we knew it was going to happen, and that is it.

LEAR: Is the discharge rate the same after you go into reversal?

WILLIS: It is 12 amperes constant current.

LEAR: Totally? In other words, you took out more than 2400-ampere hours capacity out of that cell?

WILLIS: Yes. Well, we did not take it out. It was driven at 12 amperes. After reversal it is driven at 12 amperes.

LEAR: You took out roughtly 1100 ampere-hours of capacity, 96 hours.

WILLIS: Say this was the cutoff point . . .

LEAR: 95 hours. About 1100 ampere-hours of that cell.

WILLIS: Actually to the cutoff point. Now I don't have the discharge capacity there.

(Figure 2-11)

This is the setup we used in which we take a power supply and actually drive it at a constant controlled 12 amperes during the whole cycle. It is 12 amperes because this particular cell is rated at 1200 ampere-hours at 0°C. 1500 ampere-hours at ambient temperature.

BENNETT: Have you got any shelf-life data on these at all at any temperature conditions? Have you noticed any ceramic seal problems or GTM problems?

WILLIS: We do not have any shelf-life data on the large cells. It is the same ceramic that is sed in small cells. We have had them around for a maximum of 2 years with no deterioration 'hatsoever as far as the seals are concerned.

BENNETT: Can you tell me what orientation they were in?

WILLIS: Usually they are just horizontal, flat.

BENNETT: With the seal upright?

WILLIS: With the seal upright.

BENNETT: Have you ever done any inverted?

WILLIS: Not specifically.

SLIWA: Have you prepared any, or are you preparing any information on the safe way in /hich you dispose of these batteries once they are developed? Also, what would be the storage equirements?

WILLIS: On storage, the primary purpose, of course, is to prevent short circuit. It is to ›rotect the terminal.

Secondly, this particular chemistry, as I understand it, is damaged with continued storage in xcess of 130°F. As far as disposal is concerned, we find that they dispose very readily at sea.

We have done experiments by submerging the cells in salt water in barrels where we can ›bserve it. In answer to this morning's question about using water to extinguish fires in relationship o the unit, apparently what happens is that the water will percolate or go into whatever opening is ›n the cell. In our case, it actually generated its own opening through electrolytic action on the :ase, and then it percolates. A little water goes in, and as soon as it hits the lithium or whatever :lements are inside, it generates a gas and blows the water back out again. A little water goes in and hen percolates back out, and it keeps that up over a long period of time.

And at no time is there any thermal runaway or major reaction. So, at sea disposal, seems a 'ery convenient way for us, anyhow.

SLIWA: For shore disposal we would still have to consider this hazardous waste, just as the Navy considers all lithium sulfur dioxide, and any other lithium battery is considered hazardous vaste under any conditions.

WILLIS: Not really. They are not a pressure vessel. If they had been discharged all the way lown, there would be little or no toxic material in it and no pressure in it. So, while I would 'ecommend handling them with reasonable amount of care, I see no reason why they cannot be lisposed of as industrial waste.

SLIWA: We will have to pass this through the EPA.

WILLIS: Yes.

There is no toxic materials in the sense that it is injurious to the health, long leaching problems, or anything like that. No sign of that.

SLIWA: Concerning your tests, do you expect to continually add more tests as your test series goes on? Or, do you feel that the tests that you are now conducting will be complete life-cycle type testing that is required?

WILLIS: We have to obviously test more cells to get a statistical base. We are going on to additional testing using multiple cells in a battery configuration. The first one will be a three-celled battery configuration which is scheduled to go on at Wiley Laboratories.

(Figure 2-12)

This is the sort of matrix that we normally use; discharge rates at primarily 0°C, which is our underwater application. Then, we have vibration and shock, trying to get statistical information on reverse voltage and some of the hazard evaluation. And the last three cells on this test have a battery configuration.

SLIWA: How does this compare with the technical standard that we have to have and some other test requirements?

WILLIS: I think although it does not address specific shipping containers and things like that, it does take us far in excess of anything they are requesting. Our vibration and shock, for instance, is far in excess of any of those specific applications I have seen.

Dry battery specification Mil B-18 takes the low frequency and high frequency vibrations. It also takes the drop, as you saw it, of 250 gs.

NAVAL APPLICATIONS OF HIGH ENERGY DENSITY BATTERIES

Rate \ Size	Small (~ 10 AH)	Medium (~ 100 AH)	Large (~ 1000 AH)
Low (100 hr)	Experimental Equipment Remote sensors		Remote sensors Mines Aids to navigation Standby power
Medium (10 hr)			Submersibles
High (1 hr)	Sonobuoys, Portable communications	Countermeasures Decoys	
Very high, reserve (0.1 hr)	Missiles Countermeasures	Torpedoes Targets	

Figure 2-1


NOSC
LITHIUM THIONYL CHLORIDE BATTERY DEVELOPMENT PROGRAMS
200 kW-hr LOW RATE BATTERY FOR UNDERSEA INSTRUMENTATION
120 kW VERY HIGH RATE BATTERY FOR UNDERSEA WEAPON PROPULSION
1.2 kW-hr HIGH RATE BATTERY FOR ELECTRONIC COUNTERMEASURES
LiSOCl2 CELL TECHNOLOGIES
600 W-hr MEDIUM RATE BATTERY PACK FOR FIELD TRANSCEIVER

Figure 2-2

TEST CELL DISCHARGE/REVERSE VOLTAGE PROFILE (OVERALL)

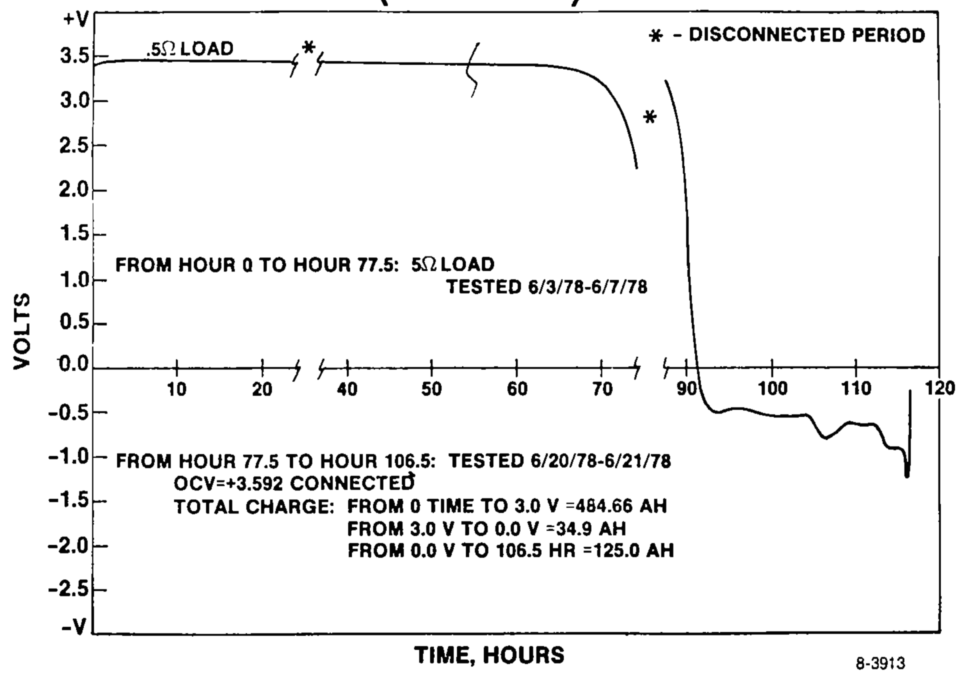


Figure 2-3

HEDB PROGRAM
CELL IMPROVEMENT EFFORTS

1. Obtain full capacity
2. Develop reliable pressure relief vents
3. Develop high current electrical feed-through
4. Develop anti-reverse voltage technique
5. Reduce case weight

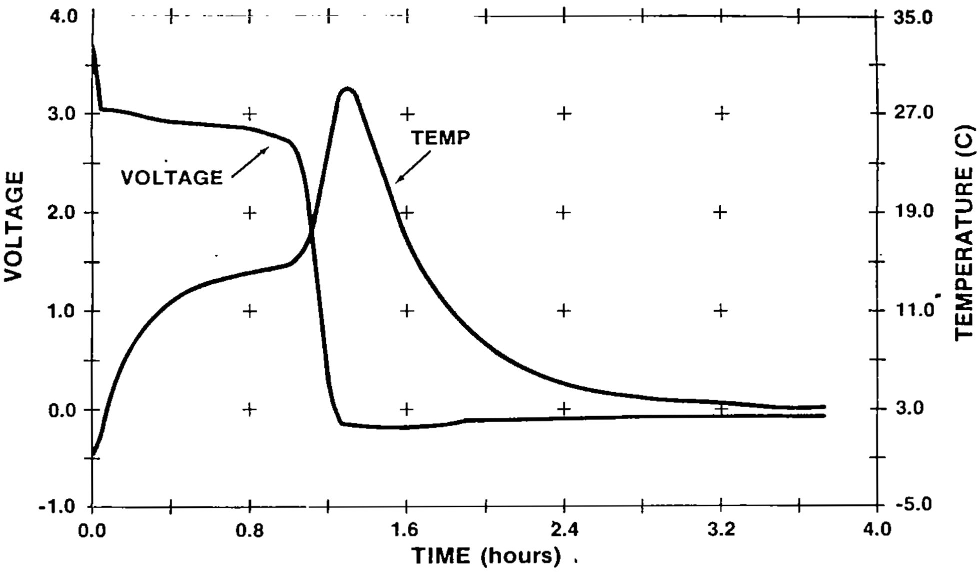
Figure 2-4

SAFETY SITUATION

PROBLEM	SOLUTION
• Explosions occur when lithium melts	• Prevent lithium from melting • Release reactive materials from cell before lithium melts • Control the lithium when it melts
• Explosions occur when cells are deeply discharged	• Provide electrical controls to prevent voltage reversal
• Hazardous materials are expelled from cells during adverse conditions	• Contain or dilute expelled products • Minimize quantity of hazardous materials • Increase the tolerance of cells to adverse conditions

Figure 2-5

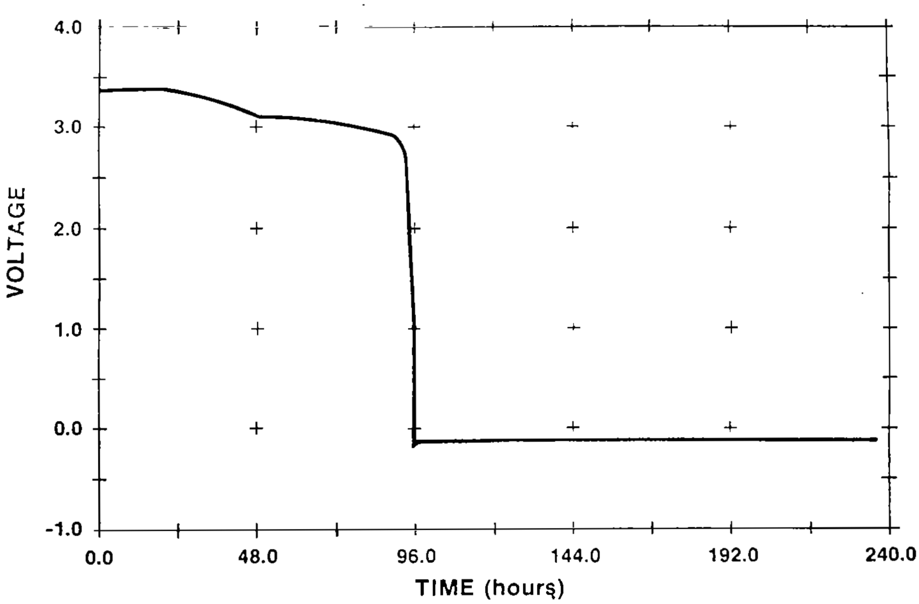
TYPICAL DISCHARGE CURVE WITH TEMPERATURE



0 degree PERFORMANCE TEST, 22 AUG 79, 2 amp RATE
ALTUS AL-250, LITHIUM THIONYL CHLORIDE, SERIAL #187

Figure 2-6

TYPICAL DISCHARGE PROFILE



0 degree PERFORMANCE TEST, 12 amp RATE, 3 OCT 79
ALTUS 17 inch CELL, LISOCL2, SERIAL #91 (3)

Figure 2-7

TYPICAL APPLICATIONS OF LITHIUM PRIMARY CELLS

Application	Rates	Capacity (AH)
Remote sensors	Low	10-100
Countermeasures & decoys	High	10-100
Portable communications equipment	Medium	20
Vehicle propulsion	High	1000-3000
Sonobuoys	High	10
Targets	High	1000
Torpedoes	Very high	50-300
Mines	Low	500
Missiles	Very High	10
Ordnance fuzing	Very High	1
Data links	Low	100
Tactical data terminals	Medium	10
Standby power	Low	10-10k
Portable lighting equipment	Medium	20

Figure 2-8

TABLE 2. ACCEPTANCE INSPECTIONS & TESTS SUMMARY

CELL NO.	DIMENSIONS (IN.) DIA. O.D.	DIA. I.D.	THICK-EDGE	THICK-BULGE	WEIGHT (LBS.)	OPEN-CIRCUIT VOLTAGE	SURFACE PH LEVEL (ppm)	WORKMANSHIP	COMMENTS
89	17.0	2.658	1.40	1.65	29.55	3.636	5	OK	Leakage from Vent. Reject
91	17.0	2.655	1.409	1.629	29.175	3.644	5	OK	Passed
94	17.0	2.658	1.40	1.625	28.89	3.632	5	OK	Passed
95	17.0	2.658	1.398	1.637	29.23	3.625	5	OK	Passed
100	17.06	2.660	1.410	1.672	29.41	3.621	5	OK	Passed

Figure 2-9

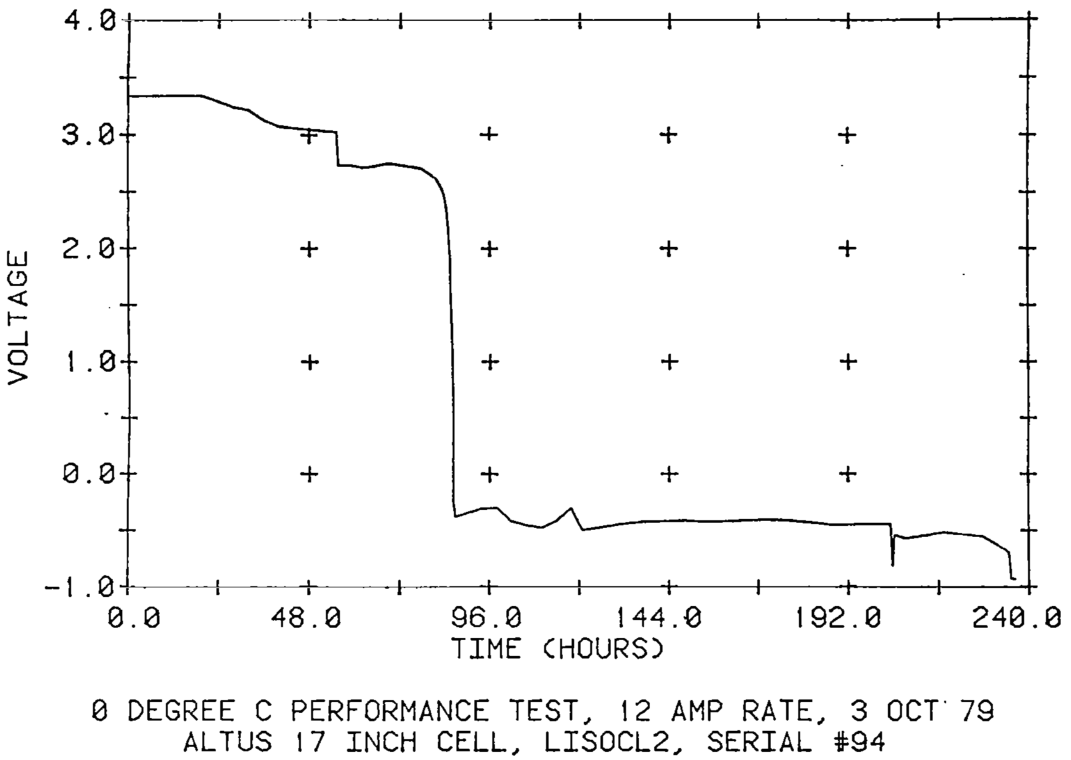


Figure 2-10

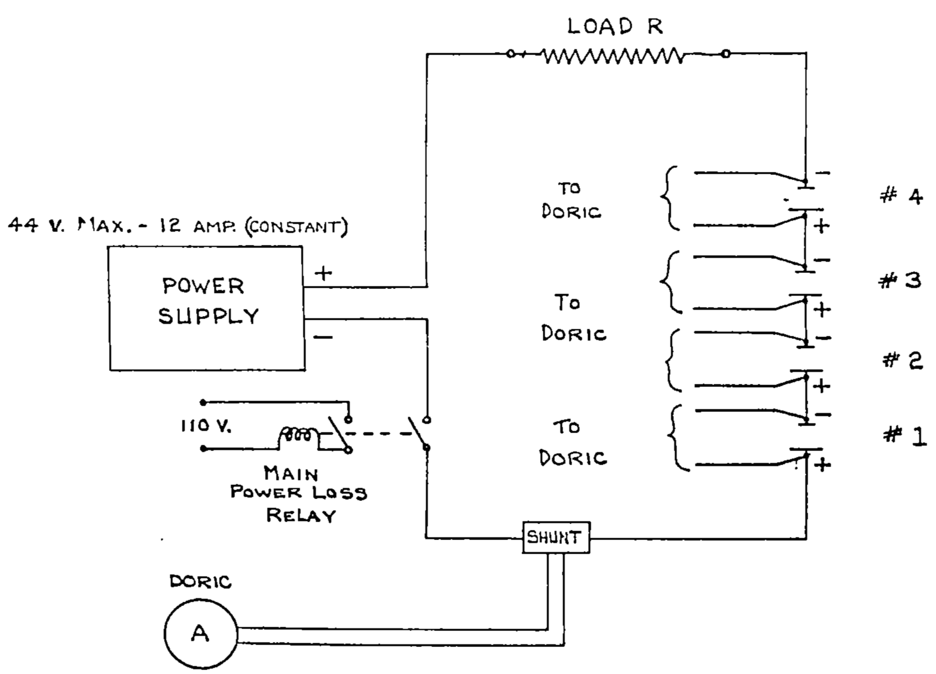


Figure 2-11

TABLE 1.

HEDB ALTUS 17", 13-CELL TEST PROGRAM MATRIX

TESTS	1	2	3	4	5	6	7	8	9	10	11	12	13
	CELL NUMBER												
ACCEPTANCE INSPECTIONS	①	①	①	①	①	①	①	①	①	①	①	①	①
PERFORMANCE													
Capacity @ 0°C. (12 Amp. Rate) Ver.	②	②								SPARE			
Capacity @ 0°C. (12 Amp. Rate) Horiz.			②	②									
Capacity @ Ambient (12 Amp. Rate)						③	③		②		②		
1/2 Discharge @ Ambient (12 Amp. Rate)					②							②	
ENVIRONMENTAL													
Vibration											③	③	②
Shock											④	④	③
Altitude											⑤	⑤	④
Hydrostatic & Discharge (to 2V)											⑥	⑥	⑤
Reverse Voltage	③	③	③	③		④	④				⑦	⑦	⑥
Post Reverse Voltage Shock											⑧	⑧	⑦
Overcurrent (100 Amp.-30 sec.)							②						
Drop - 5'						②							
HAZARD EVALUATION													
External Heat									③				
Penetration					③			③					
Drop - 6'	④	④	④	④		⑤	⑤	④					
Short Circuit								②					
DISPOSAL	⑤	⑤	⑤	⑤	④	⑥	⑥	⑤	④		⑨	⑨	⑧
	MORRIS DAM										WYLE LABS.		

(#)- DENOTES TEST SEQUENCE FOR EACH CELL.

Figure 2-12